NITROGEN IN COMMERCIAL GLASSHOUSE PRACTICE*

By O. OWEN

Pollards Nurseries Ltd., Cheshunt, Herts.

FOR most crops under glass the most important considerations for applications of nitrogen are the timing of the dressings and the amounts of the materials actually used each time. It is probable that the materials themselves are of secondary importance. One of the reasons why timing is so important is that under commercial conditions most plants grow very quickly—particularly during the early part of the season. Cucumbers provide an extreme example: young plants are placed in the borders when they are 21 to 24 inches high. It is not uncommon to cut marketable cucumbers from such plants within a month. Not so spectacular are tomatoes which may be planted when the first truss of buds is just discernible and shows no sign of petal colour. These will produce marketably ripe tomatoes within 8 to 10 weeks. Clearly when growth is so rapid it is essential to maintain an adequate level of nitrogen, and indeed of all nutrients in the medium in which the crop is grown.

Many who are familiar with agricultural practice appear to hold the view that those engaged in intensive horticulture apply fertilizers far too liberally. It may therefore be useful to recall how much nitrogen is used by some of our crops. The quantities for three common glasshouse crops are shown in Table I. Chrysanthemums under glass utilize much less nitrogen than the above crops and the amount is probably less than 100 lb. per acre. The amount of nitrogen taken up by winter lettuce is to all intents and purposes negligible when compared with that of the other crops.

Table I

Rate of use of nitrogen in glasshouse practice

Crop	Observers	lb. of nitrogen used per acre per annum
Tomatoes	Lewis & Marmoy[1]	300
,,	Owen[2]	350
,,	van der Kloes[3]	400
Carnations	Davidson[4]	570
Roses	Davidson[4]	360

The quantities shown in Table I are of necessity only approximate. Values given by Lewis & Marmoy[1] are calculated from a limited number of plants grown in pots, but their marketable crop corresponded to 80 tons of tomatoes per acre. Owen's value[2] was obtained from plants grown in borders and corresponds to only 40 tons per acre which at that time (1925–26) was regarded as a satisfactory level of production. The value given by van der Kloes[3] has been calculated for 50 tons per acre. In actual commercial practice today crops of 50 to 55 tons per acre are quite common, and this level of production is noteworthy when it is remembered that it is made in soils cropped as long as 60 years with little or no rotation, and the only fallowing is that which occurs in the winter between two successive crops. It should be added that crops even higher than 55 tons per acre are not uncommon.

The values for roses and carnations have been calculated from Davidson's results quoted by Post.[4] High though the figure for carnations may seem, it is almost certain that under English conditions uptake of nitrogen is actually even higher. Again reference to crop production may be helpful. Prolific varieties of carnations will produce an average of a million blooms per acre per annum. Roses produce about half this quantity.

* Read before Agriculture Group, 19 April, 1955

It is clear therefore that, however it is done, these amounts of nitrogen have to be provided for these crops. Some of it will come from the reserves in the soil and the balance must be provided by organic manures and fertilizers.

In addition some regard must be paid to losses of nitrogen in drainage. The amounts so lost must depend on a number of factors, chief of which would appear to be the type of soil and the methods of husbandry employed. Working on a light loam overlying gravel at Cheshunt, it has been found that the loss from tomatoes amounted to 34 lb. of nitrogen per acre per annum, which corresponded to about 10% of consumption by the crop.[5] The amount of nitrogen fixed by the soil is difficult to assess. Presumably the nitrogen that is fixed is liable to become available at a different time of the season. In addition, partial sterilization of the soil by heat or chemicals is regular practice and these processes cause mineralization of organic nitrogen.

The materials actually used and their application are most easily considered in connexion with the three different stages of growth. First is the propagating stage, where probably none of the plants requires much nitrogen. A wide variety of sowing and potting mixtures is used, a suitable mixture being one in which the nitrogen is provided by the soil itself and the stable manure which should be mixed with it, although other mixtures are also advocated. It should be added that for rose propagation by grafting no additional nitrogen is added. For most crops it is essential that the soil be partially sterilized and this process, of course, makes available some of the reserve nitrogen in the soil used. In this connexion mention should be made of starter solutions. With the propagating mixture mentioned above and with the treatment of borders which follows, starter solutions are without effect, although in Scandinavia application of calcium nitrate to young carnations while still in small pots is considered to be of value.

The second stage concerns the borders in which the plants are to grow during their cropping life. The sources of nitrogen traditionally favoured are stable manure and hoof and horn, which are incorporated some time before planting the crop. Where a new crop of rose trees is being planted, a coarse hoof and horn meal of up to $\frac{3}{4}$ inch grist is used, the underlying belief being that the nitrogen will be available over a long period. In addition, heavy dressings of stable manure or, in the case of roses, of farmyard manure are also used. For tomatoes, carnations and cucumbers, hoof and horn meal of up to $\frac{1}{8}$ inch grist is used. The quantities used are frequently applied in accordance with established practice on a particular nursery, but these should be based on a knowledge of the previous crop and on a soil analysis. For a cultivated soil producing satisfactory crops, the C/N ratio is about 8 (carbon determined by the Walkley & Black method and nitrogen by the Kjeldahl method). Nitrogen to be applied should be related to the actual potassium level in the soil and the amounts likely to be used later. The carbon content can then be adjusted to the C/N ratio of 8.

Here another consideration intrudes: that of partial sterilization. The usual method to effect this is to pass live steam into the soil, one of the effects of which is to mineralize soil nitrogen. The amount so made available will vary from soil to soil and the route is via ammonia to nitrate. Periodically it is suggested that the ammonia so produced predisposes tomato plants to attacks by the fungus *Botrytis cinerea*. In fact it is rare that one finds more than a trace of ammonia in glasshouse borders under ordinary conditions. Under controlled conditions Davies & Owen[6] found that, where a soil is left completely undisturbed after steaming, ammonia concentrations rise to a high level. Where, however, a soil is used and handled in the ordinary processes of potting and planting, no build-up of ammonia occurs and nitrification takes place normally. It is important to note, however, that the type of growth in tomatoes growing in sterilized soil is different from that in unsterilized soil. Consequently different management is called for and it is possible that any apparent association between sterilization and the incidence of *Botrytis* can be attributed to faulty husbandry.

The third stage in nitrogen nutrition is in the top dressings. Emphasis has already been laid on the importance of timing. On many occasions tomato yields have been appreciably reduced because the first top dressing has been delayed or because the interval between two consecutive top dressings has been too long. This may be related to the operation of watering. Up to about 20 years ago, the traditional method was to water-in young plants when planted and, apart from an occasional light watering on the ball of soil in which the plant was raised, to give them no more water for some 6 or 8 weeks. Then water would be applied on a generous

scale, anything up to an inch of water within the week. This naturally leached nitrate away from the roots. Accordingly, if no nitrogen were added at this stage a deficiency developed and if it persisted, as it often did, loss of fruit was inevitable. For many years loss of fruit in this way in the ' middle ' of a tomato plant was accepted as normal. Observation will usually detect the onset of this deficiency before it is acute. This type still occurs but it is by no means general.

In recent years a different system of watering has been developed mainly because of a change of tomato varieties. It is now common to water the ball more frequently and a little more water is applied at each ball watering, so that in 3 or 4 weeks after planting generous amounts are being applied. Here again there is the likelihood of washing nitrates away from the roots. This is counteracted by the practice of applying top dressings at a much earlier date than formerly.

For top dressings, most growers use compound fertilizers and all contain nitrogen, but on old glasshouse soils such a practice is at best wasteful and at worst harmful. Most of these old soils contain adequate amounts of phosphorus for all crops and, while it is almost always necessary to apply potassium and nitrogen, very rarely is there a need for phosphorus. Sources of nitrogen in such mixtures are nitrates, fish, bone, blood, meat, urea, ammonium sulphate. Where growers do use ' straight ' materials, the most favoured is certainly dried blood because it is ' safe '. Fish meal and meat meal come next and a long way behind is ammonium sulphate. The belief has long been firmly held that hoof and horn is slow-acting while dried blood is quick-acting. This was examined at Cheshunt,[7, 8] and it was found that when hoof and horn, and dried blood are used at equal particle size there is little to choose between their respective rates of decomposition in soil, and they are both comparatively slow acting. Other results of interest which emerged from this work concerned guano and bone meal. A sample of reputedly genuine Peruvian guano was found to decompose very quickly in that about 70% of its nitrogen was converted into nitrate in a matter of 6 days. Acknowledgment is made to Mr. George Taylor (private communication) for the information that when guanos of this type were generally available it was the custom to analyse them for urea content, and the rapid nitrification of the guano in the experiments mentioned was no doubt due to urea. A sample of bone meal nitrified very rapidly. On examination it was found that decomposition had already started in the bag in which it had been stored. Such a sample used on plants would have produced a quick response which would probably outweigh any effects which the phosphate would produce. This probably explains why generations of gardeners have commended the use of bone meal irrespective of the subject under consideration. Another supply of bone meal fresh from the producers scarcely provided any nitrate under similar conditions.

One result of the work just described is that finely ground hoof and horn has found a place as a nitrogenous top dressing and has to a limited extent replaced dried blood.

Where compounds are used, the dressing is usually of the order of 5 cwt. per acre and this is repeated every 12 to 14 days. There are however growers who exceed this amount and apply a good deal more, and this is where the safety factor applies. Where the nitrogen is in an organic form, complete mineralization never occurs and the rate of decomposition is rarely sufficiently high to produce enough nitrate to cause root injury. Where, however, excessive amounts of completely soluble materials, such as nitrates or ammonium sulphate, are used, root injury is inevitable. This can happen with ' safe ' dried blood. In one case, tomato plants had received as sole source of nitrogen dried blood ; they showed reluctance to grow and were undoubtedly suffering from nitrogen toxicity, as the soil showed 600 p.p.m. of nitrate-N. Heavy flooding of water eventually restored the plants to normal growth.

There appears to be no reason why ammonium sulphate used rationally should not be used for all crops, e.g., at the rate of 4 or 5 cwt. per acre when the soil is moist and at such times as the crops are likely to require it. It cannot be gainsaid that, by using ammonium sulphate of the degree of purity to which we are now accustomed, trace elements contained in the organics will be missed, but it is probable that while stable manure and hoof and horn are used at the pre-planting stage plants will not suffer on this account.

There now arises the question of the detection of the need for nitrogen. Some growers are able to do this from the appearance of the plant whatever the subject happens to be, but it is extremely difficult to describe such a condition. In general, need for nitrogen is associated with loss of colour. Unfortunately it is usually the case that when this is obvious, it is too late to

correct it, and it is the preceding stage that one should recognize. The main features of an incipient deficiency in the tomato are the loss of brightness in the growing point and a greyish appearance of the younger leaves. In the case of the carnation, incipient deficiency is first shown by loss of ' bloom ' in the foliage, later the leaves tend to be erect and a serious deficiency is associated with greyness of the plant generally. These signs are much milder than those usually induced under purely artificial conditions.

From the analytical point of view there is no reason why periodical determinations of nitrate levels should not be carried out. In this way levels of nutrients could be maintained as desired. This is being done in the United States and Scandinavia on extensive scales. This procedure will have to take into account the other nutrients, which leads to consideration of the interactions of nitrogen with other elements. In general, the effects of nitrogen and potassium are opposed. Nitrogen tends to produce fleshy dark green leaves and thick stems, whilst potassium produces pale foliage and thin hard stems. In young tomato plants, excess of phosphorus in relation to nitrogen gives a bright but pale green foliage. Increase in nitrogen supply darkens the foliage. In young carnations, low nitrogen and high phosphorus concentrations produce a grey plant with little or no ' bloom ' on the leaves, and again increasing the nitrogen supply produces a darker plant. The relations between nitrogen and iron and magnesium respectively are interesting. In tomato plants, mild magnesium deficiency can be corrected by nitrogenous top dressings. This is probably a dual effect: the added nitrogen increases the uptake of magnesium and at the same time counteracts the effects of potassium. Mild iron deficiency in tomatoes is equally interesting. At one time it was sound practice to treat iron-deficient tomatoes with dried blood and this usually corrected the disorder. It was not certain whether the blood provided the necessary iron or whether the effect was an indirect one. Some simplification of the matter developed when it was found that ammonium sulphate was just as effective as dried blood.

Finally, one must mention the application of nitrogen to different varieties of the same subjects. In the case of tomato, varieties such as Ailsa Craig derived from the Sunrise type have a vigorous habit of growth and may require feeding less frequently than the weaker-growing but heavier-cropping varieties such as Potentate or Baby Lea. In the case of carnations, the variety Puritan requires far higher levels of nitrogen for satisfactory growth than does the variety Aase Thor. Similar variations occur in roses and chrysanthemums provide an extreme case.[9] Effects of nitrogen deficiency in the latter are almost as numerous as the groups of varieties, with the further complication that the effects of a deficiency are profoundly affected by the time in the life of the plant when the deficiency begins to operate.

References

[1] Lewis, A. H., & Marmoy, F. B., *J. hort. Sci.*, 1939, **17**, 275

[2] Owen, O., *J. agric. Sci.*, 1929, **29**, 413

[3] van der Kloes, L. J. J., 13th Int. hort. Congr., London, 1952, Vol. II, 871

[4] Post, K., ' Florist Crop Production and Marketing ', 1952, pp. 464, 779 (New York: Orange Judd Publishing Co. Inc.)

[5] Owen, O., *Rep. exp. Res. Sta. Cheshunt*, 1931, **17**, 56

[6] Davies, J. N., & Owen, O., *J. Sci. Fd Agric.*, 1954, **5**, 146

[7] Owen, O., Rogers, D. W., & Winsor, G. W., *J. agric. Sci.*, 1950, **40**, 185

[8] Owen, C., Winsor, G. W., & Long, M. I. E., *J. Sci. Fd Agric.*, 1951, **2**, 125

[9] Messing, J. H. L., & Owen, O., *Plant & Soil*, 1954, **5**, 101

THE FATE OF LABELLED INSECTICIDE RESIDUES IN FOOD PRODUCTS. V.*—The Nature and Significance of Ethylene Dibromide Residues in Fumigated Wheat

By R. G. BRIDGES

Ethylene dibromide labelled with bromine-82 has been used to study the absorption and decomposition of ethylene dibromide in wheat under the conditions of fumigation and on subsequent airing and heating. In spite of the high physical sorption of the fumigant and its slow rate of airing, the amount of chemical reaction between it and the wheat is small at room temperature. On heating imperfectly aired, fumigated wheat some decomposition of the ethylene dibromide to ethylene glycol occurs. There is some evidence that the glycol so formed reacts with the $-SCH_3$ of the methionine residues of the wheat protein. The hydrogen bromide liberated when ethylene dibromide is decomposed on heating appears to cause some splitting of the starch-granule sheaths. A brief appraisal of the possible nutritional and toxicological significance of the residues occurring as a result of ethylene dibromide fumigation has been made.

Introduction

The importance of studying the chemical fate of insecticide residues contaminating foodstuffs so that their possible nutritional and toxicological significance can be assessed, has been discussed in Part IV of this series.[1] The advantages of using labelled insecticides for this purpose enabling the study to be made at concentration-levels likely to occur in practice have also been discussed.[2]

Ethylene dibromide has been used for trial fumigations of bulk grain in this country[3] and has been recommended as a fumigant alone or mixed with methyl bromide in the United States and Israel.[4, 5] This paper describes the use of ^{82}Br-labelled ethylene dibromide (1 : 2-dibromoethane) to determine the probable nature of ethylene dibromide residues found in fumigated wheat.

Heuser & Freeman[6] have shown that both whole and milled wheat sorb considerable amounts of ethylene dibromide and this airs off only slowly but almost completely in the case of milled wheat. A small amount which cannot be removed by aeration appears to react with the wheat and can be determined by the increase in water-soluble bromide. The more important aspects of contamination by ethylene dibromide fumigation are the retention of ethylene dibromide due to insufficient aeration and its fate during processing such as baking.

Experimental

Preparation of ethylene dibromide labelled with bromine-82

500 mg. of pile-irradiated potassium bromide supplied by the Isotope Division, Harwell, and equivalent to approx. 100 mc. of bromine-82 at the commencement of the preparation was intimately mixed with 400 mg. of A.R. potassium dichromate. This was introduced into A (Fig. 1) on top of 1·5 ml. of A.R. concentrated sulphuric acid which had been frozen in liquid nitrogen. The stopper was immediately replaced and the whole apparatus evacuated through tap E which was then turned off. Flask C was then cooled in liquid nitrogen and the contents of A allowed to warm up. Bromine distilled over and was trapped in C. During the later stages of the reaction, A was warmed occasionally with a hot-air blower. The reaction was complete in 1 h. Condenser D was cooled with ice-cold water and the contents of C allowed to warm up to room temperature at the same time as ethylene was admitted through B from a cylinder. A slight positive pressure of ethylene was maintained and C slightly warmed until the colour of bromine was discharged. Flask C was removed and connected to an ampoule via two tubes containing soda-lime and A.R. phosphorus pentoxide respectively. ^{82}Br-labelled ethylene dibromide was distilled under vacuum into the ampoule immersed in liquid nitrogen and the ampoule sealed. The percentage yield varied between 60–70% based on weight of bromide taken. (Boiling point 131·1°.) The specific activity of the ethylene dibromide at the conclusion

* Part IV: *J. Sci. Fd Agric.*, 1955, **6**, 269

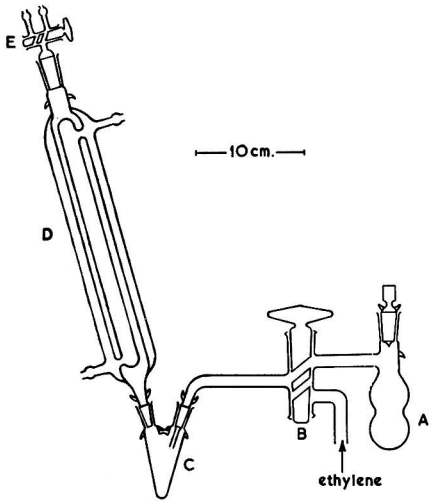


FIG. 1.—*Apparatus for the preparation of bromine-82 labelled ethylene dibromide*

of the preparation was approx. 200 μc./mg. As the radiation dose received from an unscreened 100 mc. source of bromine-82 would be approx. 600 mr./h. at a distance of 50 cm., the whole preparation and subsequent handling were carried out behind a 4-in. lead wall.

Materials

Whole English wheat, moisture content 12·3%.
Milled English wheat, moisture content 12·9%.
Wheat gluten (Hopkin and Williams), moisture content 9·2%.
Wheat starch (Hopkin and Williams), moisture content 14·3%.
Alumina.
Decolorizing charcoal.

Exposure of materials to bromine-82 labelled ethylene dibromide

The ampoule of ^{82}Br-labelled ethylene dibromide was broken in a large glass reservoir and allowed to equilibrate overnight. The materials were exposed in a two-chamber sorption apparatus[7] for 48-h. periods to samples of the labelled gas drawn from the reservoir by a technique previously described.[8]

Radio and chemical assay of the labelled fumigant

The bromine-82 content of samples was measured by counting in a liquid-sample, Geiger–Müller counter, sensitive to about 0·5% of the total disintegrations.[9] Corrections were made for probe-unit quench-time and radioactive decay, in the usual manner. The half-life of bromine-82 was taken as 35·1 h.[10]

Samples of gaseous ethylene dibromide were absorbed in 10 ml. of a 1 : 1 mixture of redistilled monoethanolamine and dioxan and left, before assay, for 48 h. at 25°, after which time decomposition to inorganic bromide is complete.[11] The bromide content of a sample of labelled gas drawn from the reservoir in an evacuated, all-glass flask was determined by Volhard's method and its radioactivity measured. This enabled the radioactivity in counts per minute per μg. of ethylene dibromide to be calculated for an arbitrarily fixed zero-time, to which all other counts were corrected.

Airing and heating of materials exposed to bromine-82 labelled ethylene dibromide

The materials exposed to ^{82}Br-labelled ethylene dibromide were aired either spread out in thin layers in a current of air or merely in open flasks. In one experiment the lower chamber of

the sorption apparatus was fitted with inlet and outlet tubes, enabling air to be drawn through two bubblers containing a 1 : 1 mixture of monoethanolamine and dioxan, after the completion of the exposure period. By changing the bubblers at intervals and determining their bromine-82 content the rate of airing was followed.

Samples of materials exposed to ^{82}Br-labelled ethylene dibromide, after various periods of airing, were heated in open test-tubes in an oil bath for ½ h. at 180–200°, roughly to simulate the thermal conditions of baking, etc.

Estimation of the total bromine-82 residues in the materials

Attempts to extract the physically-held labelled fumigant from the exposed materials with ether or non-radioactive ethylene dibromide were unsuccessful. If, however, the sample was suspended in water containing a few drops of ' Teepol ' and the suspension counted in the liquid-sample counter, then the results agreed with those obtained in the continuous airing experiment where the residue was known from the amounts of ethylene dibromide that had aired off. This method was therefore adopted as the standard procedure. Whole wheat, before suspension, was broken up in a pestle and mortar under a 1 : 1 mixture of monoethanolamine and dioxan which trapped any ethylene dibromide released during the disintegration of the grains.

Estimation of water-soluable bromine-82 in materials

The exposed material was stirred continuously with 10 ml. of 1% aqueous sodium bromide, as inactive carrier, for 1 h. The solid material was centrifuged down and the supernatant liquid extracted overnight with ether to remove any ethylene dibromide. The residual material was extracted once more with aqueous bromide, as above. The greater part of the water-soluble bromide was obtained in the first extract, the bromine-82 content of the second being usually less than 15% of the first. Whole wheat was broken up in a pestle and mortar before extraction. Estimation of the water-soluble bromine-82 was made on both the unheated and heated materials.

Examination of materials for organically-bound bromine-82

A hydrolysate of starch which had been exposed to the labelled fumigant, aired for 24 hr. and heated, was prepared by refluxing for 5 h. with N-sulphuric acid. The excess sulphate was precipitated with solid barium carbonate. Paper-partition chromatograms were run on aliquots of the hydrolysate using the following solvents for sugar chromatography:

Phenol saturated with water,[12]
2 : 1 : 2-*n*-Butanol : water : acetic acid,[13]
2 : 1 : 1-Ethyl acetate : water : pyridine, upper layer.[14]

A hydrolysate of similarly treated gluten was prepared by refluxing for 8 h. with 5N-sulphuric acid and precipitating the excess sulphate with solid barium carbonate. Paper-partition chromatograms were run on aliquots using the following solvents for amino-acid chromatography:

Phenol saturated with water,[15]
Phenol saturated with a buffer solution of pH2,[16]
25 : 25 : 6-*n*-Butanol : water : acetic acid, upper layer.[17]

The chromatograms were examined for zones of radioactivity using an automatic, radiometric scanning device.[18]

Estimation of ethylene glycol and glycol derivatives in materials exposed to ethylene dibromide and heated

In order to determine the fate of the ethylene moiety of the ethylene dibromide molecule, some experiments were made with the unlabelled fumigant. Materials were exposed to a saturated concentration of ethylene dibromide for 2–3 weeks and without airing heated for ½ h. at 180° together with unexposed materials as controls. Glycol determinations were made by treatment with hydriodic acid and estimation of the liberated ethyl iodide and ethylene.[19]

Control determinations were made with unfumigated material, as any protein containing methionine would liberate methyl iodide which would be determined with the ethyl iodide.[20] Determinations were made before and after the materials had been twice extracted with 10 ml. of water by constant stirring for 1 hr. Bromide determinations were carried out by Volhard's method on the water-extracts. Glycol determinations were also made on materials not containing starch, after they had been treated for 1 h. with an excess of 5% aqueous periodic acid, the excess acid removed with 60% hydrazine hydrate and the material heated in an oven for ½ h. at 100° to remove the excess moisture. This enabled a distinction to be made between glycol derivatives and ethylene glycol (which gives formaldehyde and so is not determined).

Investigation of possible chemical reactions between ethylene glycol and wheat constituents

Results from the glycol determinations suggested that a reaction occurred between the ethylene glycol and the wheat. The following experiments were carried out to investigate this possibility.

A sample of wheat starch was refluxed with ethylene dibromide and water or with ethylene glycol, hydrolysed, after removal of the excess reagent, by refluxing for 5 h. with N-sulphuric acid and precipitating the sulphate with solid barium carbonate. Aliquot portions of the hydrolysate were applied to filter-paper strips and partition chromatograms run with solvents for sugar chromatography. Strips were dipped in benzidine solution,[21] heated for 5 min. at 100° and compared with controls.

A sample of gluten was refluxed for ½ h. with ethylene dibromide and the excess reagent allowed to air off. It was then heated under an air condenser with 10 ml. of 1N-sodium hydroxide and nitrogen passed through two bubblers, the first containing a saturated solution of mercuric cyanide and the second a saturated solution of mercuric chloride.[22] A precipitate was formed in the mercuric chloride bubbler but not in the mercuric cyanide bubbler even after the sodium hydroxide had been strongly acidified with concentrated hydrochloric acid and heating continued. A control sample gave no precipitate in either bubbler until the sodium hydroxide was acidified, when a precipitate formed in the mercuric cyanide bubbler.*

Methionine and glutamic acid were refluxed with ethylene dibromide and water or with ethylene glycol. After removal of the excess reagent, the residues were taken up in water and filter-paper chromatograms run on aliquots using phenol saturated with water as solvent. The strips were dipped in ninhydrin solution,[23] heated at 90°, and compared with controls.

Results

Rate of airing

After exposure of milled wheat for 48 h., the initial concentration of 39 mg. of ^{82}Br-labelled ethylene dibromide/l. fell to 6 mg./l. The rate of airing was studied by continuously drawing air through the lower chamber. The initial residue was 846 p.p.m. of ethylene dibromide in the wet weight of the material, which fell rapidly in the first 24 h. to 337 p.p.m.; during the remaining 336-h. airing the fall was very gradual, the residue at the end of the airing period being 332 p.p.m. This dropped to 131 p.p.m. when the milled wheat was removed from the aeration flask and spread out as a thin layer in a current of air for a further 48 h.

Samples of gluten, starch and milled wheat were exposed simultaneously in a modified sorption apparatus[22] to an initial concentration of 36 mg. of ^{82}Br-labelled ethylene dibromide/l. which fell to 5 mg./l. after the 48-h. exposure. Whole wheat was exposed separately, the concentration falling from 29·5 mg./l. to 14 mg./l. during the 48-h. exposure. The samples were aired by spreading out in thin layers in a current of air. The total bromine-82 residue was determined after various periods of airing and the results are expressed graphically in Fig. 2. The whole wheat still contained an appreciable residue after 288 h. airing, but on milling and airing for a further 48 h., all residual ^{82}Br-labelled ethylene dibromide had aired off.

* The reaction product of ethylene dibromide and methionine —SCH_3 groups yields, on treatment with alkali, a sulphide which precipitates with $HgCl_2$. Unchanged —SCH_3 groups and the reaction product of ethylene dibromide and cysteine —SH groups are stable in alkaline solution, but on acidification give a mercaptan which precipitates with mercuric cyanide.

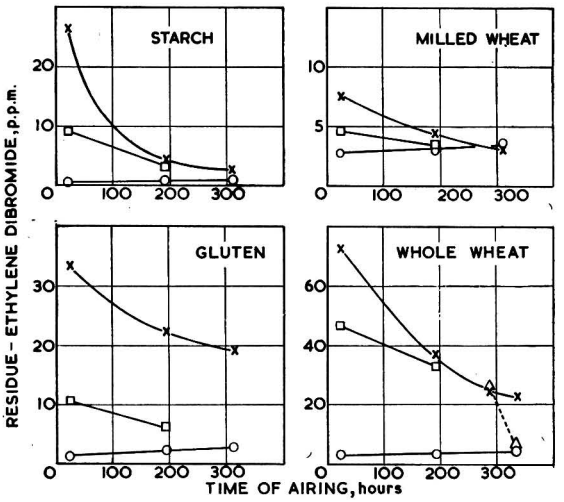


FIG. 2.—*Total ethylene dibromide residues before heating and water-soluble bromide residues both before and after heating occurring in materials exposed to ^{82}Br-labelled ethylene dibromide and aired for various periods*

—×— Total residue before heating
—○— Water-soluble residue before heating
—□— Water-soluble residue after heating
---△--- Total residue in whole wheat after milling

Fate of ethylene dibromide sorbed on wheat at room temperatures

The water-soluble bromine-82 content of milled wheat which contained an initial residue of 846 p.p.m. of ^{82}Br-labelled ethylene dibromide in the wet weight of the material was only 8 p.p.m. expressed as the equivalent of ethylene dibromide. Similar values for gluten, starch and milled and whole wheat, exposed to ^{82}Br-labelled ethylene dibromide (see *Rate of airing*), after various periods of airing are shown in Fig. 2. All samples showed a slight increase in water-soluble bromine-82 activity with increased periods of airing. The amounts of this water-soluble activity extractable from gluten and milled wheat are greater than those extracted from starch (Fig. 2 and Table I) which suggests that a chemical reaction may occur between the ethylene dibromide and some constituent of the protein.

Fate of ethylene dibromide sorbed on wheat at elevated temperatures

Values for the water-soluble bromine-82 activity, extractable from samples of gluten, starch, milled and whole wheat, exposed to ^{82}Br-labelled ethylene dibromide (see *Rate of airing*) and aired for various periods before heating are shown graphically in Fig. 2. The results are expressed as the equivalent, in p.p.m., of ethylene dibromide in the wet weight of the material. In all cases an increase in water-soluble bromine-82 activity occurred during heating, which suggested that at elevated temperatures either the ethylene dibromide decomposed or else it reacted with some constituent of the wheat. Ether extracts of the aqueous sodium bromide extracts contained no significant amount of bromine-82 activity. All bromine-82 activity was precipitated on treating the aqueous sodium bromide extracts with acidified silver nitrate. Thus only inorganic bromide was being extracted from the heated materials. Examination of the materials after two extractions with sodium bromide solution showed that only small amounts of radioactivity remained (Table I).

Any ^{82}Br-labelled ethylene dibromide which aired off during the heating was determined by passing nitrogen over the heated materials into two bubblers containing a 1 : 1 mixture of monoethanolamine and dioxan. The bromine-82 activity in the materials was determined before and after heating and also in the bubbler solution. Results are given in Table II.

The results show that during heating most of the residual ethylene dibromide is either volatilized or debrominated. Confirmation was obtained from the examination of chromatograms

Table I

Water-soluble bromine-82 residues found both before and after heating in materials exposed to ^{82}Br-labelled ethylene dibromide. (Results expressed as p.p.m. ethylene dibromide in the wet weight of the material)

Material	Total residue before heating	Water-soluble residue before heating	Water-soluble residue after heating		Total residue in heated material, after two extractions
			1st extract	2nd extract	
Milled wheat	231	9	70	11	2
Gluten	277	16	71	14	4
Starch	394	1	134	15	5
Alumina	319	5	146	23	17
Charcoal	1395	nil	85	92	768

Table II

Volatile bromine-82 lost during the heating of wheat samples after exposure to ^{82}Br-labelled ethylene dibromide. (Results expressed as p.p.m. ethylene dibromide in the wet weight of the material)

Material	Initial residue (before heating)	Final residue (after heating)	Volatile bromide trapped	Volatile bromide + final residue	% of initial residue accounted for
Milled wheat	72	27	40	67	93·0
Gluten	100	54	38	92	92·0
Starch	49	12	33	45	91·8

run on hydrolysates of gluten and starch exposed to ^{82}Br-labelled ethylene dibromide and then heated. Only one radioactive zone could be detected which corresponded in R_F value to inorganic bromide, in all the solvent systems that were used.

When alumina and charcoal were exposed to ^{82}Br-labelled ethylene dibromide and heated, a similar breakdown to inorganic bromide occurred, although in the case of charcoal difficulty was experienced in extracting the bromide (Table I). As an increase in inorganic bromide occurred on heating irrespective of the nature of the sorbent, it seems probable that the ethylene dibromide does not react chemically with the sorbent but undergoes a simple decomposition to a completely debrominated compound and inorganic bromide.

Nature of the decomposition product formed during heating ethylene dibromide sorbed on wheat

Alumina and charcoal, which had been exposed to a saturated concentration of non-radioactive ethylene dibromide for several days and then heated, were extracted with water. The extracts gave strong positive tests for 1 : 2-glycols when treated with the periodic acid–Schiff's reagent.[24] Considerable amounts of acetaldehyde were also formed when the alumina was heated, due to the dehydration of the ethylene glycol. Similar tests on gluten, starch and milled wheat were inconclusive, as controls gave a colour reaction due to water-soluble starch.

The results of a series of glycol determinations made on materials exposed to a saturated concentration of ethylene dibromide and heated, without previous airing, are given in Table III. The estimated glycol residues from volumetric bromide determinations are also given. The

Table III

Glycol determinations on materials heated after exposure to a saturated concentration of ethylene dibromide. (Results expressed as p.p.m. ethylene glycol in the heated material)

Material	Total residue by bromide determination on water extract	Total residue by hydriodic acid digestion	Residue after water extraction, by hydriodic acid digestion	Residue after periodic acid treatment, by hydriodic acid digestion
Milled wheat	1600	1900	500	—
Gluten	2200	2900	1400	2000
Starch	200	600	—	—
Alumina	—	21,300	—	nil
Charcoal	—	58,000	—	6400

accuracy of the glycol determinations was limited by the high control values of the protein-containing materials. Trial determinations on samples of commercial ethylene glycol and tetra-ethylene glycol gave recoveries of 92·8 and 90·5% respectively.

The results show that the sorbed ethylene dibromide is hydrolysed to ethylene glycol on heating. Part of the glycol residue is not extractable by water and, in the case of gluten, not affected by periodic acid treatment, which suggests a possible glycolic ether or ester formation between the ethylene glycol and constituents of the gluten. A possible reaction between ethylene glycol and the —SCH_3 group of methionine was demonstrated by the formation of a sulphide which precipitated a mercuric chloride complex when ethylene-dibromide-treated gluten was heated with alkali. Paper chromatograms of a solution of methionine treated with ethylene dibromide and water or with ethylene glycol showed, in addition to methionine, a ninhydrin-detectable compound of R_F 0·94 (phenol saturated with water solvent). The free carboxyl group of glutamic acid has been shown to be esterified in the presence of propylene glycol and hydrochloric acid[25] and a similar reaction with ethylene glycol might be expected to occur. However, examination of paper chromatograms of glutamic acid treated with ethylene dibromide and water or ethylene glycol failed to show any ninhydrin-reactive compounds other than the glutamic acid. The glycol residues in the heated, ethylene-dibromide-treated materials are entirely labile on treatment with hydriodic acid (cf. the first two columns of Table III), so that reaction between the ethylene glycol and nitrogen-containing groups of the gluten, the products of which would be stable to hydriodic acid, does not take place to any appreciable extent.

No reaction products could be detected on chromatographic examination of hydrolysates of starch treated with ethylene dibromide and water or with ethylene glycol. Some physical degradation of starch was apparent after it had been exposed to heavy concentrations of ethylene dibromide and heated. Microscopical examination showed a considerable breakdown of starch-granule sheaths. Some of the starch became water soluble and could be precipitated by adding alcohol. A similar effect was noted when starch was exposed to hydrogen bromide vapour for a short period and then heated, which suggests that the degradation is caused by the hydrogen bromide liberated during the hydrolysis of the ethylene dibromide.

Discussion

Nature of ethylene dibromide residues in wheat

When wheat is fumigated with ethylene dibromide, several types of residual contamination, depending on the subsequent treatment of the wheat, must be considered.

(i) Contamination by the ethylene dibromide due to insufficient airing. Compared with methyl bromide,[26] the rate of airing is considerably slower and the ethylene dibromide can be retained unchanged for a considerable period. Whole wheat still contained an appreciable amount of residual bromide after twelve days' airing under ideal conditions, but when once milled, the residual bromide concentration fell to zero in 48 h.

(ii) Contamination by the product of reaction between ethylene dibromide and the wheat. At normal fumigation temperatures, the amount of such reaction is small, much less than that between methyl bromide and wheat.[22] The reaction appears to occur mainly with the protein of the wheat and increases slightly with the time of airing. No attempt has been made to determine its precise nature.

(iii) Contamination, after heating, by ethylene glycol resulting from the decomposition of unaired ethylene dibromide. About $\frac{1}{3}$–$\frac{1}{2}$ of the unaired ethylene dibromide residue breaks down to glycol during heating for $\frac{1}{2}$ h. at 180°, and the remainder volatilizes.

(iv) Contamination, after heating, by the reaction products of the ethylene glycol and wheat protein. A possible site of such reaction is with the —SCH_3 group of the methionine constituent of the protein.

Nutritional significance of residues resulting from ethylene dibromide fumigation

Any reduction of the content of essential amino-acids due to reaction between the ethylene dibromide and the wheat protein during fumigation and airing would be extremely small. The largest water-soluble bromide residue recorded in the case of fumigated milled wheat was 9 p.p.m.

as ethylene dibromide (Table I). Assuming that a simple bimolecular reaction occurs with the methionine only, then such a residue would represent a reduction of less than 0·4% of the total methionine content as given for a typical wheat flour.[27] The figures for the chemically bound glycol after heating (Table III) show that, again assuming that only the methionine constituent of the protein is involved in the reaction, a residue of 500 p.p.m. represents a reduction of 60% of the total methionine content. As the glycol determinations were made in this case on milled wheat exposed to ethylene dibromide under extreme conditions, such a reduction is most unlikely to occur in practice. Reaction with amino-acid constituents of the protein other than methionine also may be possible.

The possible effect of ethylene dibromide fumigation on vitamins contained in the wheat has not been investigated. However, as there is no evidence lost of vitamin-B under conditions of methyl bromide fumigation,[28] it would seem unlikely that any loss would occur with the less reactive ethylene dibromide.

Toxicological significance of residues resulting from ethylene dibromide fumigation

Rowe *et al.*[29] have found that ethylene dibromide is a fairly toxic material when administered orally as a single dose to mammals. Glaser & Frisch[30] found that when ethylene dibromide was injected subcutaneously into mice, it was about one-half as toxic as methyl bromide. No details concerning its chronic toxicity by oral administration are available, but results obtained by examining mammals exposed to ethylene dibromide vapour for repeated periods suggest that it does not have a high degree of chronicity.[29] It is unlikely that humans would consume any appreciable quantity of wheat prior to its being heated in some process such as baking, so that the toxic hazard from fumigated wheat containing unaired ethylene dibromide is small. Farm animals, however, may be fed on unheated wheat. The acute oral LD_{50} for three-week-old chicks was found to be 0·079 g. of ethylene dibromide per kg. body weight.[29] This would be attained if a chick weighing 100 g. consumed 25 g. of wheat containing a residue of 316 p.p.m. of ethylene dibromide. Such a residue is probably higher than would normally be encountered but cannot be excluded as impossible. The detrimental effect of incompletely aired ethylene dibromide residues in grain when fed to laying hens has been observed by Professor Bondi and his colleagues.[31] A significant diminution in egg size was noted and, in extreme cases, a complete cessation of laying occurred.

Ethylene glycol is a very much less toxic substance than ethylene dibromide. The acute oral LD_{50} for ethylene glycol fed to mice is 14·6 g./kg. body weight[32] compared with 0·42 g./kg. body weight for ethylene dibromide.[29] When administered in large doses to animals, ethylene glycol is a depressant of the central nervous system and has severe toxic action on the kidneys.[32] Much larger amounts of ethylene glycol than would occur in wheat heated after fumigation with ethylene dibromide have been consumed by man without apparent harmful effects.[33] Little is known however about its chronic toxicity, but Laug *et al.*[32] regard it as not negligible and advise that it should be omitted entirely from food and drug preparations. A man, in consuming $1\frac{3}{4}$ kg. of flour products per week,[34] made exclusively from flour that has been heated after fumigation with ethylene dibromide containing a residue of 1900 p.p.m. of ethylene glycol (Table III) would ingest about 3·4 g. of ethylene glycol per week. It is extremely unlikely that such a residue could occur under normal fumigation and airing conditions and that any one person would consume continually fumigated flour products which had not been diluted with unfumigated material. The toxic hazard of ethylene glycol contamination is therefore apparently negligible.

The toxicological significance of any reaction product between the ethylene glycol and the protein constituents cannot be assessed, as the nature of the reaction products has not been fully determined. Simple ethers and esters of ethylene glycol have similar toxic action to ethylene glycol, although the toxicity of the ethers to mammals is greater.[33]

Conclusions

1. The high sorption of ethylene dibromide by wheat and its slow rate of airing present the greatest toxic hazard in its use as an insecticide. This hazard may be minimized by efficient airing both before and after milling.

2. Very small amounts of an unidentified chemical reaction occur between ethylene dibromide and the wheat protein at ordinary fumigation temperatures.

3. Part of the ethylene dibromide sorbed on wheat undergoes decomposition to ethylene glycol and inorganic bromide on heating, the remainder being lost by volatization. As ethylene glycol is a less toxic material, heating provides a safeguard against the possible toxic effect of any residual ethylene dibromide.

4. Some reaction occurs between the ethylene glycol and the wheat protein, the $-SCH_3$ group of methionine being a likely site.

5. Hydrogen bromide liberated during heating very heavily fumigated starch appears to be responsible for the splitting of starch-granule sheaths.

6. No significant changes are likely in the nutritive value of wheat as a result of ethylene dibromide fumigation.

Acknowledgments

The author wishes to acknowledge helpful discussion with Mr. F. P. W. Winteringham during the course of this work. The paper is published by permission of the Department of Scientific and Industrial Research.

Pest Infestation Laboratory
London Road
Slough
Bucks

Received 30 September, 1955

References

[1] Winteringham, F. P. W., *J. Sci. Fd Agric.*, 1955, **6**, 269

[2] Winteringham, F. P. W., Harrison, A., Jones, C. R., McGirr, J. L., & Templeton, W. H., *J. Sci. Fd Agric.*, 1950, **1**, 214

[3] Heuser, S. G., & Thomas, C. E., Pest Infestation Research, 1953, p. 28 (London : H.M.S.O.)

[4] Dawson, J. C., U.S.P. 2,606,857

[5] Aman, J., Farkas, L., & Ben-Shamai, M. H., *Ann. appl. Biol.*, 1946, **33**, 389

[6] Heuser, S. C., & Freeman, C. E., Pest Infestation Research, 1954, p. 29 (London : H.M.S.O.)

[7] Winteringham, F. P. W., *J. Soc. chem. Ind., Lond.*, 1944, **63**, 144

[8] Winteringham, F. P. W., *J. Soc. chem. Ind., Lond.*, 1946, **65**, 48

[9] Winteringham, F. P. W., *Lab. Pract.*, 1955, **4**, 196

[10] Winteringham, F. P. W., *Nature, Lond.*, 1951, **167**, 155

[11] Heseltine, H. K., private communication

[12] Partridge, S. M., *Biochem. J.*, 1948, **42**, 238

[13] Isherwood, F. A., & Jermyn, M. A., *Biochem. J.*, 1951, **48**, 515

[14] Whiting, G. C., *Nature, Lond.*, 1951, **168**, 833

[15] Consden, R., Gordon, A. H., & Martin, A. J. P., *Biochem. J.*, 1944, **38**, 226

[16] McFarren, E. F., *Analyt. Chem.*, 1951, **23**, 168

[17] Woiwod, A. J., *J. gen. Microbiol.*, 1949, **3**, 312

[18] Winteringham, F. P. W., Harrison, A., & Bridges, R. G., *Analyst*, 1952, **77**, 19

[19] Morgan, P. W., *Industr. Engng Chem. (Anal.)*, 1946, **18**, 500

[20] Baernstein, H. D., *J. biol. Chem.*, 1932, **97**, 663

[21] Horrocks, R. H., *Nature, Lond.*, 1949, **164**, 444

[22] Winteringham, F. P. W., Harrison, A., Bridges, R. G., & Bridges, P. M., *J. Sci. Fd Agric.*, 1955, **6**, 251

[23] Toennies, G., & Kolb, J. J., *Analyt. Chem.*, 1951, **23**, 823

[24] Feigl, F., ' Spot Tests ', Vol. II, 1954, p. 130 (Amsterdam : Elsevier Publishing Co.)

[25] Fraenkel-Conrat, H., & Olcott, H. S., *J. biol. Chem.*, 1945, **161**, 259

[26] Lubatti, O. F., & Harrison, A., *J. Soc. chem. Ind., Lond.*, 1944, **63**, 353

[27] Geddes, W. F., ' Food and Food Products ' (Ed. : Jacobs, M. B.), 1951, Vol. II, p. 1057 (New York : Interscience Publishers Inc.)

[28] Clegg, K. M., & Lewis, S. E., *J. Sci. Fd Agric.*, 1953, **4**, 548

[29] Rowe, V. R., Spencer, H. C., McCollister, D. D., Hollingsworth, R. L., & Adams, E. M., *A.M.A. Arch. industr. Hyg.*, 1952, **6**, 158

[30] Glaser, E., & Frisch, S., *Arch. Hyg., Berl.*, 1929, **101**, 48

[31] Bondi, A., Olomucki, E., & Calderon, M., *J. Sci. Fd Agric.*, 1955, **6**, 600

[32] Laug, E. P., Calvery, H. O., Morris, H. J., & Woodward, G., *J. industr. Hyg.*, 1939, **21**, 173

[33] Browning, E., ' Toxicity of Industrial Organic Solvents ', 1953, p. 340 (London : H.M.S.O.)

[34] Kent-Jones, D. W., & Amos, A. J., ' Modern Cereal Chemistry ', 1947, p. 317 (Liverpool : Northern Publishing Co.)

DETERMINATION OF EXCHANGEABLE CALCIUM IN SOILS CONTAINING CALCIUM CARBONATE

By S. K. TOBIA and N. E. MILAD

Previously reported methods for determination of exchangeable calcium in soil, involving extraction with solutions of sodium, potassium or ammonium chloride or shaking with a carbonate solution, are critically reviewed and their sources of error discussed.

A new procedure is recommended in which the exchangeable calcium is extracted with a 0·2N-KCl solution previously brought into equilibrium with solid calcium carbonate.

Introduction

The amount of exchangeable calcium in soil is a very important feature as it indicates, in some measure, both the physical and chemical properties of the soil. It has been shown that the fixation of the phosphate ion, either native or added in the form of a phosphate fertilizer, is due mainly to the adsorbed calcium in the soil and therefore a knowledge of its amount is necessary to assess the extent of phosphate fixation likely to take place if a soluble phosphate is added to the soil.[1]

Exchangeable cations are usually determined by leaching the soil with solutions of ammonium salts or with dilute acids. The determination of exchangeable calcium in soils containing free calcium carbonate is complicated by the solubility of calcium carbonate in the leaching solutions. Several methods, however, have been devised to overcome this difficulty. These methods can be classified into two main groups:

A. Methods based on exhaustive leaching,
B. Precipitation methods.

A. The following are examples of methods based on exhaustive leaching:

(1) The Hissink method,[2] where 10 g. of soil are leached with normal sodium chloride (in which calcium carbonate is much less soluble than in ammonium chloride), two successive litres of leachates being collected. All the exchangeable calcium and the calcium derived from the dissolution of calcium carbonate are present in the first litre. The calcium in the second litre is derived from the dissolution of calcium carbonate only and it is assumed to be equal in amount to that dissolved during the leaching of the first litre. The difference between the amount of calcium in the first and second litres thus represents the amount of exchangeable calcium.

(2) The Kelley & Brown method[3] in which the amounts of exchangeable calcium and magnesium are determined by difference. After the soil has been leached with ammonium acetate solution, the amounts of exchangeable potassium and sodium thus removed are subtracted from the total base-exchange capacity of the soil.

(3) Methods involving leaching the soil with alcoholic salt solutions. Tucker,[4] for example, used a normal ammonium chloride solution in 60% ethanol, adjusted to pH 8·5 with ammonia. He found that the solubilities of calcium and magnesium from calcium carbonate, dolomite, and magnesite in this solution are comparable with those in air-free water.

B. In methods based on precipitation, the soil is shaken with a solution containing a soluble carbonate or oxalate + carbonate to precipitate the calcium and the decrease in the concentration of the carbonate or oxalate is taken as equivalent to exchangeable calcium. The carbonate is added to restrict the solubility of calcium carbonate. These methods were devised by Puri.[5]

Experimental

(a) *Preparation of a reference soil*

Results obtained by the above methods showed great differences. It was necessary therefore to find a criterion for the validity of the method used. As a reference soil, one free from calcium carbonate and sulphate was converted into a Ca-soil by leaching with normal calcium chloride solution. The excess of calcium chloride was removed by washing with 70% alcohol until the filtrate was chloride-free, and finally the soil was dried at 100–110° for 24 hours. The exchangeable calcium was then determined by leaching with N-ammonium acetate solution

adjusted to pH 7 as proposed by Schoellenberger.[6] It was found to be equal to 42·8 milliequiv./100 g. The method to be tested was then used with the reference soil after adding 10% of powdered A.R. calcium carbonate.

(b) *Determination of exchangeable calcium by leaching with sodium or potassium chloride solutions*

Although Hissink[2] originally used N-solutions, it was found that 0·2N-solutions produced the same results as those found by using N-ammonium acetate solution. The use of such a dilute solution is desirable since a large amount of KCl or NaCl in the residue tends to interfere in the determination of calcium as oxalate.

In the determination, therefore, 10 g. of the reference soil were mixed with 1 g. of calcium carbonate and then leached with one litre of 0·2N-NaCl or -KCl followed by another litre of solution and the calcium was determined in the two separate leachates, the difference being equivalent to the exchangeable calcium. The following results were obtained:

Leaching solution concn. 0·2N	Exchangeable calcium milliequiv./100 g.
NaCl	36·6
KCl	31·4

The two solutions gave low results for the reference soil (actual, 42·8 milliequiv./100 g.), potassium chloride giving the lower value. In both cases the low result may be explained as being due to the partial conversion, during leaching, of calcium carbonate to the soluble bicarbonate by atmospheric carbon dioxide. The amount of calcium dissolved in the second litre of solution was 17·6 milliequiv. when sodium chloride was used, and 34·7 milliequiv. when potassium chloride was used, whereas the solubility of Ca from calcium carbonate in 0·2N-KCl solution, at the same temperature, was only 1·12 milliequiv./litre. The extra amount dissolved in the second litre seems to be due to the change of calcium carbonate to bicarbonate. The change of carbonate to bicarbonate was less pronounced in the leaching with sodium chloride because of the high dispersion of the sodium soil, thus restricting the passage of carbon dioxide into the soil.

It is obvious therefore, that such methods, in addition to requiring considerable time, give low results.

(c) *Leaching with alcoholic solution of ammonium chloride adjusted to pH 8·5*

Ten g. of the reference soil were mixed with 1 g. of calcium carbonate and then leached with 500 ml. of N-ammonium chloride solution in 60% ethanol, adjusted to pH 8·5 by ammonium hydroxide. The calcium was determined in an aliquot portion of the leachate and the exchangeable calcium was found to be equal to 40·2 milliequiv./100 g., which is very close to the correct value (42·8). The difference (2·6 milliequiv.) was outside the limits of experimental error which did not exceed $\pm$ 0·4 milliequiv./100 g. The low result may be explained as being due to incomplete replacement of the adsorbed calcium by the leaching solution; the ionization of ammonium chloride and of Ca-soil may be appreciably suppressed in presence of such a concentration of alcohol.

(d) *Precipitation methods*

(i) *Precipitation as calcium carbonate.*—In this method the adsorbed calcium is precipitated as carbonate by shaking the soil with a solution containing 0·1N-sodium carbonate in N-NaCl or 0·1N-potassium carbonate in N-KCl and then determining the loss in the carbonate ion in the solution. This method was used with the reference soil in the presence and in the absence of calcium carbonate, and the following results were obtained:

$CaCO_3$ added %	Exchangeable calcium (milliequiv./100 g.)	
	Na_2CO_3–NaCl	K_2CO_3–KCl
0	61·4	68
10	61·2	68·2

These results show that the amount of exchangeable calcium observed was about one and a half times the correct value. The increase cannot be due to the solubility of calcium carbonate

in the solution used, since nearly the same results were obtained in the presence and the absence of calcium carbonate in the soil. The increase may, however, be explained by the adsorption of the carbonate ion by the sodium or potassium soils. If this is true, adsorption should be proportional to the clay content, and also to the concentration of the carbonate ion in the solution. To find the effect of clay content on the adsorption of carbonate ion, a heavy soil free from calcium carbonate was diluted with different amounts of sand and the exchangeable calcium was determined by leaching with ammonium acetate and by precipitation as carbonate. The results obtained are shown in Table I.

Table I

Exchangeable calcium leached with ammonium acetate solution and precipitated as carbonate

Clay content %	Exchangeable calcium (milliequiv./100 g.)		
	Ammonium acetate (a)	K_2CO_3–KCl (b)	difference ($b-a$)
75	30	43	13
63	26	36	10
51	23	30·5	7·5
39	18·4	24·5	6·1
27	17	20·5	3·5
15	14·3	15·3	1·0

With sodium carbonate–sodium chloride solution the same general results were obtained, but the deviation from the expected results was smaller than in the case of the potassium carbonate–potassium chloride solution. The observed increase in the amount of exchangeable calcium over that determined by ammonium acetate leaching in both cases is shown in Table II.

Table II

Increase in exchangeable calcium values as compared with ammonium acetate leaching

Clay content %	% increase in exchangeable calcium	
	K_2CO_3–KCl	Na_2CO_3–NaCl
75	43·2	35
63	38·4	32·6
51	32·6	21·7
39	29	18
27	20·5	7·7
15	7	8

These figures suggest that a K-soil is more effective than a Na-soil in the adsorption of the carbonate ion, and are compatible with results on phosphate adsorption. A potassium soil was found to be more effective than the corresponding sodium soil in adsorbing the phosphate ion, potassium being less hydrated than sodium.[1]

To find the effect of concentration on the adsorption of carbonate ion, 10-g. portions of the reference soil were used with solutions containing different concentrations of potassium carbonate, the concentration of potassium chloride being kept constant. The observed increase in exchangeable calcium over the figure (42·8 milliequiv./100 g.) for the reference soil is shown in Table III.

Table III

Effect of concentration of K_2CO_3 solution on exchangeable calcium values

Normality of K_2CO_3 solution	% increase in exchangeable calcium
0·06	39·6
0·08	48·8
0·10	59·3
0·12	67·0
0·14	71·8

These results show that the observed increase in exchangeable calcium is approximately proportional to the concentration of potassium carbonate. This suggests that the higher values obtained by this method are due mainly to the adsorption of the carbonate ion by the soil.

It should also be mentioned that the method is difficult to use when the soil is rich in organic matter. The alkaline reagent dissolves an appreciable amount of humus which colours the filtrate dark brown and thus obscures the colour of the indicator used in the titration of the carbonate.

(ii) *Precipitation as calcium oxalate.*—In this method the adsorbed calcium is precipitated as oxalate by shaking the soil with a reagent containing a soluble oxalate. The decrease in the concentration of the oxalate is taken as being equivalent to the exchangeable calcium. In this determination one of the following solutions is usually used:

(*a*) A solution containing N-KCl, 0·1N-potassium oxalate and 0·015N-potassium carbonate.

(*b*) The same as (*a*) except that potassium acetate is used instead of potassium chloride.

(*c*) A solution containing 0·5N-ammonium acetate, 0·1N-ammonium oxalate and 0·25N-ammonium carbonate.

It is suggested that in these methods, the carbonate is added to restrict the solubility of calcium carbonate, especially at a temperature of not more than 10°. These reagents were used with the reference soil in the presence and in the absence of calcium carbonate and the following results were obtained:

$CaCO_3$ added %	Exchangeable calcium (milliequiv./100 g.)		
	Solution (*a*)	Solution (*b*)	Solution (*c*)
0	46·5	46	44
10	54	57	73

When calcium carbonate was present, high results were obtained, the highest being with solution (*c*). In the absence of calcium carbonate, the results were more or less close to the correct value (42·8 milliequiv./100 g.). This suggests that the high results were due mainly to the solubility of calcium carbonate in the reagent rather than to the adsorption of the oxalate ion. This conclusion was confirmed by the use of soils of different clay contents in the absence and in the presence of calcium carbonate. The exchangeable calcium in the carbonate-free soils was first determined by the usual ammonium acetate method and then with the ammonium oxalate/acetate/carbonate reagent. Calcium carbonate was then added to the soils to the extent of 2 and 10% and the exchangeable calcium was determined by using solution (*c*). The results are shown in Table IV.

Table IV

Effect of clay content of soil on exchangeable calcium leached by different solutions

Clay content %	Exchangeable calcium (milliequiv./100 g.)			
	Ammonium acetate,	Ammonium oxalate/acetate/carbonate		
	0% $CaCO_3$	0% $CaCO_3$	2% $CaCO_3$	10% $CaCO_3$
75	30	31·7	39·4	45·5
63	26	27·6	34·5	43·7
51	23	24·8	29·5	40·0
39	18·4	19·6	25·2	38·3
27	17	18·2	19·7	36·3
15	14·3	15·2	15·5	35·7

These results show, that in the case of soils containing no free $CaCO_3$, the mixed reagent gave results which were a little higher than those found by the ammonium acetate method. The difference cannot be attributed to experimental error which did not exceed 0·5 milliequiv./100 g., and may be explained by the adsorption of a relatively small amount of the oxalate ion by the soils. In the case of soils containing free calcium carbonate, the results show that the deviation from the correct value was due mainly to the amount of calcium carbonate and not to the clay

content of the soils. They further suggest that the high results were due mainly to the solubility of calcium carbonate in the reagent rather than to the adsorption of the oxalate ion.

(e) *The suggested new method*

It has been shown from the previous discussion that neither exhaustive leaching methods nor precipitation methods give correct results. The new method suggested is based on the use of a displacing solution previously brought into equilibrium with solid calcium carbonate. Ammonium acetate saturated with calcium carbonate was first used. The soil was centrifuged with the reagent, instead of leaching, to save time and to ensure thorough mixing of the soil with the reagent. Barium sulphate was also added to help in settling of the suspension.

Five g. of the soil were mixed with 50 ml. of the reagent, centrifuged for two minutes and the supernatant liquid separated by filtration through No. 40 Whatman filter paper. The process was repeated until 250 ml. or 500 ml. were collected, depending on the relative heaviness of the soil, and the calcium was determined in an aliquot portion of the filtrate by precipitation as oxalate. The difference between the calcium in the filtrate and that already dissolved in the ammonium acetate solution was taken as the exchangeable calcium. The following results were obtained, using the reference soil containing 42·8 millequiv. of exchangeable Ca per 100 g.

Exchangeable calcium (milliequiv./100 g.)		
0% $CaCO_3$	5% $CaCO_3$	10% $CaCO_3$
34	34·5	30

The low values obtained may have been due to the calcium dissolved in the ammonium acetate solution preventing the complete displacement of the adsorbed calcium.

To overcome this difficulty, another solution viz. 0·2N-KCl, was chosen in which the solubility of calcium carbonate was a minimum. The solubility of calcium from calcium carbonate in N-ammonium acetate solution at 25° was found to be 11·8 milliequiv./litre, whereas the solubility in 0·2N-KCl solution was only 1·12 milliequiv./litre.

When this solution was used, with the reference soil in the presence and in the absence of calcium carbonate, the exchangeable calcium was found to be equal to 41·2 milliequiv./100 g. The error was about 3·5% which is the least among all the methods used previously. The method was also applied to the previously used soils with different clay contents. The exchangeable calcium was first determined in the carbonate-free soils by the ammonium acetate method. Calcium carbonate was then added and the exchangeable calcium determined by the new method. The results obtained are seen in Table V.

Table V

Exchangeable calcium determined in presence of various amounts of clay

Clay content %	Exchangeable calcium (milliequiv./100 g.)		
	Ammonium acetate 0% $CaCO_3$	KCl saturated with $CaCO_3$	
		2% $CaCO_3$	10% $CaCO_3$
75	30	29·2	29·3
63	26	25·3	25·3
51	23	22·5	22·4
39	18·4	18	17·9
27	17	16·8	16·7
15	14·3	14·3	14·2

Other soils from different localities were also converted into calcium soils and the exchangeable calcium was determined by the ammonium acetate method in the absence of free calcium carbonate and by the new method after the addition of 10% $CaCO_3$. The following results were obtained (Table VI).

The results obtained show that the suggested method was affected neither by the relative heaviness of the soil nor by the calcium carbonate content. Compared with the ammonium acetate method the maximum difference was 1·6 milliequiv./100 g. In addition, the method is not time-consuming and when a suitable centrifuge is used, four samples can be treated at the same time. Moreover, it was found that the calcium dissolved from calcium carbonate by 0·2N-KCl solution did not vary over a temperature range 20–30° and was equal to 1·12 milliequiv./litre, so that only one calcium determination was necessary.

Table VI

Exchangeable calcium determined in various soils by the two methods

Soil No.	Exchangeable calcium (milliequiv./100 g.)		
	Ammonium acetate method	New method	Difference
1	42·8	41·2	− 1·6
2	39	38·1	− 0·9
3	27·3	26·4	− 0·9
4	21·0	20·7	− 0·3
5	42·2	42·2	0

Summary and conclusions

1. Methods based on leaching with sodium chloride or potassium chloride solutions, and corrected for the solubility of calcium carbonate, give low results presumably owing to the conversion of calcium carbonate into bicarbonate during leaching. The change is greater with potassium chloride solution. The percentage error may be as much as 25%.

2. Leaching with ammonium chloride dissolved in 60% ethanol, the pH being adjusted to 8·5 with ammonia, gives a much better result than the previous methods. The results were only about 6% low. However, results obtained by this method may be affected by change in pH and alcohol concentration due to evaporation during the extraction of the soil.

3. Methods based on the precipitation of exchangeable calcium as carbonate give high results owing to the adsorption of the carbonate ion by the soil complexes. The error may range from 40 to 60% depending on whether sodium or potassium carbonate was used.

4. Methods based on precipitation as oxalate also give high results mainly due to the solubility of calcium carbonate in the reagent and the subsequent precipitation of the dissolved calcium as oxalate. In a solution containing oxalate and carbonate ions, the latter were preferentially adsorbed even when the concentration was less than that of the oxalate. The percentage error increased with the calcium carbonate content of the soil.

5. Ammonium acetate solution saturated with calcium carbonate contains a relatively high concentration of dissolved calcium which probably prevents the complete displacement of the adsorbed calcium from soil and thus gives a low result.

6. A 0·2N-KCl solution previously brought into equilibrium with calcium carbonate permitted almost complete displacement of adsorbed calcium. The error was the least among those for all the methods used and did not exceed 3·5%.

Faculty of Science
Ein-Shams University
Cairo
Egypt

Received 12 October, 1955

References

[1] Tobia, S. K., & Milad, N. E., *J. Sci. Fd Agric.*, 1954, **5**, 156
[2] Hissink, D. J., *Soil Sci.*, 1923, **15**, 269
[3] Kelley, W. P., *J. agric. Sci.*, 1934, **24**, 72
[4] Tucker, B. M., *Aust. J. agric. Res.*, 1954, **5**, 706
[5] Puri, A. N., *Soil Sci.*, 1936, **42**, 47
[6] Schoellenberger, C. J., & Dreibelbis, F. R., *Soil Sci.*, 1930, **30**, 161

PLANT-GROWTH SUBSTANCES: ω-ARYL- AND ω-ARYLOXY-ALKYLCARBOXYLIC ACIDS

By K. GAIMSTER

A number of carboxylic acids of the type R·[CH_2]·CO_2H have been synthesized in connexion with studies of plant-growth activity. They include the first six or seven members of five homologous series of ω-substituted alkylcarboxylic acids, namely *o*-methoxyphenoxy-, *p*-chlorophenoxy-, 2 : 4-dichlorophenoxy-, 2 : 4 : 5-trichlorophenoxy- and 1-naphthyl-alkylcarboxylic acids; and five 1-naphthyl-alkylcarboxylic acids in which the alkyl chain is branched or otherwise modified.

The phenoxy-acids were prepared by classical methods but, for many of the 1-naphthyl acids, methods involving the use of organo-cadmium compounds were employed.

Introduction

Recent studies[1] concerning the fate in the plant of compounds having plant-growth activity have been based on the possibility that these compounds are degraded by a mechanism involving β-oxidation. Evidence for the latter has recently been reviewed by Wain.[2] A continuation of such studies led to the need for information on the plant-growth activity of a number of homologous series of ω-substituted alkylcarboxylic acids, especially of those series the first members of which were known to possess pronounced plant-growth activity.

The synthesis of the first six or seven members of five such series was thus undertaken, namely *o*-methoxyphenoxy-, *p*-chlorophenoxy-, 2 : 4-dichlorophenoxy-, 2 : 4 : 5-trichlorophenoxy- and 1-naphthyl-alkylcarboxylic acids, together with five 1-naphthyl-alkylcarboxylic acids in which the alkyl chain was branched or otherwise modified. The biological results relating to these acids have been reported and their significance discussed elsewhere.[3] The results are in full accordance with the thesis that these acids are degraded by a mechanism which involves β-oxidation.

ω-Phenoxyalkylcarboxylic acids

In the *o*-methoxyphenoxy series, the acetic[4] and propionic[5] acids have been previously prepared. In the *p*-chlorophenoxy series, the acetic,[6] propionic[7] and butyric[8] acids are known. The first seven members of the 2 : 4-dichlorophenoxy series were prepared by Synerholm & Zimmerman.[9] In the 2 : 4 : 5-trichlorophenoxy series, the acetic[10] and butyric[9] acids are known. All the acids of this type were prepared by classical methods from the appropriate phenol, using chloroacetic acid or β-bromopropionic acid respectively for the first and second members of each series. The key intermediate for higher members of each series was the appropriate ω-phenoxyalkyl bromide, which was prepared by treating the phenol with a polymethylene dibromide. From each ω-phenoxyalkyl bromide so formed, two ω-phenoxyalkylcarboxylic acids could be prepared, via the corresponding nitrile or by the malonic ester synthesis.

Of the ω-phenoxyalkyl bromides and cyanides used, the following have already been described: 1-bromo-2-*o*-methoxyphenoxyethane,[11] 1-bromo-3-*o*-methoxyphenoxypropane,[12] 1-bromo-5-*o*-methoxyphenoxypentane,[12, 13] 1-bromo-2-*p*-chlorophenoxyethane,[14] 1-bromo-3-*p*-chlorophenoxypropane,[14] 1-bromo-3-(2 : 4-dichlorophenoxy)propane,[15] 1-bromo-3-(2 : 4 : 5-trichlorophenoxy)propane,[15] and 1-cyano-3-(2 : 4-dichlorophenoxy)propane.[16] In general the intermediate ω-phenoxyalkylmalonic esters were used for the next stage without isolation in the pure state. It was noted that the chlorinated phenoxyalkylmalonic acids were more resistant to decarboxylation than were the *o*-methoxyphenoxyalkylmalonic acids. The treatment of phenoxyalkyl bromides with sodium cyanide in aqueous ethanol gave in most cases a good yield of the appropriate cyanide. It is, however, of interest from a theoretical point of view that in certain cases this reaction failed to give the expected product.

The reactions which were attempted are summarized in Table I.

In the reactions described as anomalous, none of the desired nitrile was isolated; instead, the main product was the corresponding bis-phenoxyalkane, together with some of the appropriate phenol. This suggests that a fission of the ether linkage in the phenoxy compound has

taken place. For example, treatment with sodium cyanide in 90% ethanol appears to cleave the ether linkage of 1-bromo-2-*p*-chlorophenoxyethane to form *p*-chlorophenol which, presumably, reacts with unchanged 1-bromo-2-*p*-chlorophenoxyethane to form 1 : 2-bis-(*p*-chlorophenoxy)-ethane, thus :

$$Cl{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_2{\cdot}Br \rightarrow Cl{\cdot}C_6H_4{\cdot}OH$$
$$Cl{\cdot}C_6H_4{\cdot}OH + Cl{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_2{\cdot}Br \rightarrow Cl{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_2{\cdot}O{\cdot}C_6H_4{\cdot}Cl$$

In the case of 1-cyano-3-(2 : 4 : 5-trichlorophenoxy)propane, we have an intermediate example, since, although the reaction of 1-bromo-3-(2 : 4 : 5-trichlorophenoxy)propane with sodium cyanide gave a 66% yield of a product which was very largely 1-cyano-3-(2 : 4 : 5-trichlorophenoxy)propane, analysis of the latter compound gave results which were slightly low for nitrogen and slightly high for chlorine. Alkaline hydrolysis of this nitrile resulted in a 61% yield of pure 3-(2 : 4 : 5-trichlorophenoxy)propane-1-carboxylic acid, together with about 5% of 1 : 3-bis-(2 : 4 : 5-trichlorophenoxy)propane, which was, presumably, the contaminant in the nitrile.

It is of interest in this connexion to note that in the conversion of 2 : 4-dichlorophenoxymethyl chloride to the corresponding cyanide[17] some bis-(2 : 4-dichlorophenoxy)methane was always obtained even under the best conditions evolved. Under less favourable conditions for the reaction, as much as 30% of the bis-compound could be isolated.

Further work is required on this reaction before a mechanism can be suggested, but it seems that the combined electron-attracting effect of a chlorine atom or atoms in the benzene ring and of a bromine atom not further away than the γ-carbon atom is necessary before the ether linkage becomes susceptible to attack by the reagent.

ω-1-Naphthyl-alkylcarboxylic acids

In this series, the well-known substituted acetic acid is usually prepared by some modification of the method of Boessneck[18] but a variety of other methods have been used. Although a number of ways have been used for the preparation of the propionic acid, perhaps the most convenient method is that of Mayer & Sieglitz.[19] The preparation of the corresponding butyric acid has been described by a number of workers.[20, 21]

No attempt has been recorded to devise a method which would be of general application to the series except that of Manske & Ledingham,[22] who attempted to carry out a stepwise ascent of this series by reducing an acid to the corresponding alcohol by the use of sodium in ethanol followed by conversion of this alcohol to the corresponding bromide and a malonic ester synthesis to give the next higher homologue but one. Thus, by starting from the second and third members of this series, the fourth and fifth members were prepared. The analytical figures given[22] for the fourth and fifth members of the series were not, however, in very good agreement with theoretical values and the authors admitted that such a method was not suitable for making any of the succeeding members. An attempt was therefore made to devise a preparative method which would be generally applicable to the series. The method finally adopted was one based on that described for the preparation of ethyl 2-1′-naphthoylethane-1-carboxylate.[23, 24] The method is essentially the conversion of 1-naphthylmagnesium bromide to the corresponding organo-cadmium compound, which is treated with the ω-ester-acid chloride of a dibasic acid.

Table I

Reaction of ω-phenoxyalkyl bromides, $RO{\cdot}[CH_2]_n{\cdot}Br$, *with sodium cyanide*

R	*n* = 2	3	5
o-Methoxyphenyl *	—	N	N
p-Chlorophenyl	A	A	N
2 : 4-Dichlorophenyl	A	N	N
2 : 4 : 5-Trichlorophenyl	—	N*	N

N = normal reaction
A = anomalous reaction

* A small amount of the anomalous product was isolated.

The keto-ester thus produced is reduced and hydrolysed to the appropriate ω-1-naphthyl-alkylcarboxylic acid. The method of choice for this hydrolysis and reduction was found to be the modification of the Wolff–Kishner reduction described by Huang-Minlon,[25] although Clemmensen reduction, preceded or followed by hydrolysis, was also used in some cases.

These steps may be represented by the following scheme:

$$C_{10}H_7\cdot[CH_2]_n\cdot MgBr \xrightarrow{CdCl_2} C_{10}H_7\cdot[CH_2]_n\cdot Cd_{\frac{1}{2}} \xrightarrow{Cl\cdot CO\cdot[CH_2]_m\cdot CO_2R} C_{10}H_7\cdot[CH_2]_n\cdot CO\cdot[CH_2]_m\cdot CO_2R \rightarrow C_{10}H_7\cdot[CH_2]_{n+m+1}\cdot CO_2H.$$

R = Me or Et

This method was successfully applied to the third, fourth, fifth and sixth members of the series. The method failed, however, when 1-naphthylmethylmagnesium chloride was used; in attempts to prepare higher homologues than the sixth member of the series, pure samples of the keto-esters could not be obtained; neither was it possible to purify the crude 1-naphthyl-alkylcarboxylic acids prepared by hydrolysis and reduction of these impure keto-esters. The ω-ester-acid chlorides were prepared by the action of thionyl chloride on the corresponding mono-ester which was itself prepared either, in the case of succinic and glutaric acids, by the action of methanol on the anhydride, or, for higher homologues, by the semi-esterification of the appropriate dicarboxylic acid. In this latter connexion, the method of working up using a chemical separation[26] was found more convenient than the method[27] based simply on fractional distillation under reduced pressure of the resulting mixture of diester, mono-ester and unchanged acid. The third member of the series of ω-1-naphthyl-alkylcarboxylic acids, namely, 3-1′-naphthylpropane-1-carboxylic acid, was also prepared by the 'ketonic' hydrolysis of the condensation product of the sodium derivative of ethyl acetoacetate with 1-bromo-2-1′-naphthylethane.

1-Naphthyl-alkylcarboxylic acids with branched or modified chain

1-1′-Naphthylpropane-2-carboxylic acid, $C_{10}H_7\cdot CH_2\cdot CHMe\cdot CO_2H$, was prepared by a method[28, 29] involving the methylation of diethyl 2-1′-naphthylethane-1 : 1-dicarboxylate; and the resulting malonic ester was hydrolysed and decarboxylated. In the author's hands, this decarboxylation showed a reluctance to go to completeness, and a pure sample of the required acid was only obtained by converting the incompletely decarboxylated material to its acid chloride, which, after purification, was converted to the acid. 3-1′-Naphthyl-2-methylpropane-1-carboxylic acid, $C_{10}H_7\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$, has previously been prepared[30] by a malonic ester synthesis from 2-bromo-1-1′-naphthylpropane. However, since 1-1′-naphthylpropane-2-carbonyl chloride was available from the previous synthesis, this material was successfully converted by means of the Arndt–Eistert synthesis to the required higher homologue. 2-1′-Naphthylpropane-1-carboxylic acid, $C_{10}H_7\cdot CHMe\cdot CH_2\cdot CO_2H$, was prepared by a method[31] involving a Reformatsky reaction between methyl 1-naphthyl ketone and ethyl bromoacetate. 6-1′-Naphthyl-4-ketohexane-1-carboxylic acid, $C_{10}H_7\cdot[CH_2]_2\cdot CO\cdot[CH_2]_3\cdot CO_2H$, was prepared by hydrolysis of the corresponding ethyl ester which was an intermediate in the syntheses of the straight chain acids. 2-1′-Naphthylmethylbenzene-1-carboxylic acid, $C_{10}H_7\cdot CH_2\cdot C_6H_4\cdot CO_2H$, was prepared by Clemmensen reduction of 2-1′-naphthoylbenzene-1-carboxylic acid obtained[32] from dinaphthylcadmium and phthalic anhydride.

An attempt was made to extend to branched-chain acids the method applied to the straight-chain acids, namely, the reaction of an ester-acid chloride with an organo-cadmium compound. To this end, 2-methoxycarbonyl-2-methylpropane-1-carbonyl chloride, one of the ester-acid chlorides corresponding to *as*-dimethylsuccinic acid, was prepared. The latter acid[33] was converted via its anhydride to the monomethyl ester and thence to the ester-acid chloride. Reaction between the latter and dinaphthylcadmium took place smoothly, but the resulting keto-ester could not be obtained analytically pure. From attempts to reduce and hydrolyse this ester, no crystalline acid was obtained.

Experimental

ω-Phenoxyalkyl bromides

These were prepared by the same general method, an example of which is given below. The physical constants of the new ω-phenoxyalkyl bromides are given in Table II.

Table II

ω-Phenoxyalkyl bromides

	M.p.	B.p.	Found Ag halide %	Formula	Required Ag halide %
1-Bromo-6-*o*-methoxyphenoxyhexane	—	154–160°/0·04 mm.	*—	$C_{13}H_{19}O_2Br$	—
1-Bromo-5-*p*-chlorophenoxypentane	—	130–138°/0·4 mm.	120	$C_{11}H_{14}OClBr$	119·5
1-Bromo-6-*p*-chlorophenoxyhexane	32°	185–195°/10 mm.	109	$C_{12}H_{16}OClBr$	113
1-Bromo-5-(2 : 4-dichlorophenoxy)pentane	39–40°	135–150°/0·15 mm.	154	$C_{11}H_{13}OCl_2Br$	152
1-Bromo-5-(2 : 4 : 5-trichlorophenoxy)pentane	34–36°	211–220°/15 mm.	175	$C_{11}H_{12}OCl_3Br$	178
1-Bromo-6-(2 : 4 : 5-trichlorophenoxy)hexane	39–41°	181–200°/0·09 mm.	170	$C_{12}H_{14}OCl_3Br$	171

* Found : Br, 27·2 ; $C_{13}H_{19}O_2Br$ requires Br, 27·9%

1-*Bromo*-6-(2 : 4 : 5-*trichlorophenoxy)hexane.*—2 : 4 : 5-Trichlorophenol (79 g., 0·4 mole) was dissolved in a solution of potassium hydroxide (25 g.) in methanol (100 ml.), and the solution added to a stirred solution of 1 : 6-dibromohexane (390 g., 1·6 mole) in methanol. After refluxing with stirring for four hours, the suspension was filtered and the bulk of the methanol removed by distillation on the steam-bath. The residue was poured into water, the heavy oil separated, and the aqueous layer extracted with ether. The ethereal extracts and oil were combined, dried, and the ether removed. The residue was distilled to give, firstly, 306 g. of crude 1 : 6-dibromohexane as a pale yellow oil, b.p. 108–120°/10 mm., and then 100 g. (69%) of the required *bromide* as a practically colourless oil, b.p. 181–200°/0·09 mm., which solidified on cooling to colourless needles, m.p. 39–41°.

ω-Phenoxyalkyl cyanides

These nitriles were all prepared by the same general method, an example of which is given below. The physical constants of the ω-phenoxyalkyl cyanides are listed in Table III.

Table III.

ω-Phenoxyalkyl cyanides

	M.p.	B.p.	Found N %	Found Cl %	Formula	Required N %	Required Cl %
1-Cyano-3-*o*-methoxyphenoxypropane	—	170–175°/10 mm.	7·25	—	$C_{11}H_{13}O_2N$	7·33	—
1-Cyano-5-*o*-methoxyphenoxypentane	—	136–145°/1 mm.	5·97	—	$C_{13}H_{17}O_2N$	6·4	—
1-Cyano-5-*p*-chlorophenoxypentane	47–48°	—	6·27	15·5	$C_{12}H_{14}ONCl$	6·28	15·9
1-Cyano-5-(2 : 4-dichlorophenoxy)-pentane	34–35°	183–187°/0·1 mm.	5·27	—	$C_{12}H_{13}ONCl_2$	5·4	—
1-Cyano-3-(2 : 4 : 5-trichlorophenoxy)-propane*	94–95°	—	4·6	40·8	$C_{10}H_8ONCl_3$	5·3	40·2
1-Cyano-5-(2 : 4 : 5-trichlorophenoxy)-pentane	47–48°	—	4·5	36·1	$C_{12}H_{12}ONCl_3$	4·78	36·4

* This material was shown to be contaminated with 1 : 3-bis-(2 : 4 : 5-trichlorophenoxy)propane ; the latter was recovered during the subsequent hydrolysis of this nitrile to the corresponding acid.

1-*Cyano*-5-(2 : 4-*dichlorophenoxy)pentane.*—Sodium cyanide (6 g.) in water (6 ml.) was added to 1-bromo-5-(2 : 4-dichlorophenoxy)pentane (15·6 g., 0·05 mole) in ethanol (40 ml.). The solution was refluxed overnight, the bulk of the ethanol was removed by distillation, the residue poured into water (100 ml.) and the oil which separated was extracted with ether. The ethereal solution was dried, the ether removed and the residue distilled. The required nitrile (11·3 g., 87%) was obtained as a colourless oil, b.p. 183–187°/0·09 mm., which solidified on standing to a colourless solid, m.p. 34–35°.

Anomalous reaction of ω-phenoxyalkyl bromides

(a) *Attempted preparation of* 1-*cyano*-2-*p*-*chlorophenoxyethane.*—1-Bromo-2-*p*-chlorophenoxyethane (23·6 g., 0·1 mole) in ethanol (40 ml.) was added over 1 hour to a stirred refluxing

solution of sodium cyanide (6 g.) in water (8 ml.). The resulting solution was refluxed with stirring for 8 hours, the bulk of the ethanol was removed by distillation and the residue was poured into water.

The pale brown granular solid which separated was filtered off, washed with water, dried at 35°, and recrystallized from benzene–light petroleum (b.p. 40–60°) to give 7·4 g. of colourless prisms, m.p. 133–134°. Recrystallization of this material from ethanol gave 6·0 g. of colourless blunt needles, m.p. 133–134°. Qualitative elementary analysis showed the absence of nitrogen and the presence of chlorine [Found: C, 59·1; H, 4·3; Cl, 24·5%; molecular weight, 280. Calc. for $C_{14}H_{12}O_2Cl_2$ (1 : 2-bis-*p*-chlorophenoxyethane): C, 59·3; H, 4·24; Cl, 25·1%; molecular weight, 283].

(b) *Attempted preparation of* 1-*cyano*-3-p-*chlorophenoxypropane.*—Sodium cyanide (6 g.) in water (8 ml.) was added over 20 minutes to a stirred refluxing solution of 1-bromo-3-*p*-chlorophenoxypropane (25 g., 0·1 mole) in ethanol (40 ml.). The resulting solution was refluxed with stirring for a further 2 hours, the bulk of the ethanol was removed by distillation and the residue was poured into water (250 ml.). The oil which separated was extracted with chloroform; evaporation of the chloroform solution left a dark brown oil which partially crystallized on standing. The crystals were filtered off, washed with light petroleum (b.p. 40–60°), and dried at 35° to give pale brown, long needles (2·9 g.), m.p. 117°. Further dilution of the filtrate with light petroleum (b.p. 40–60°) caused separation of 9·6 g. of alkali-soluble brown solid with a phenolic odour (probably largely *p*-chlorophenol).

Recrystallization of the 2·9 g. of needles from chloroform–light petroleum (b.p. 40–60°) gave colourless needles, m.p. 119°. Qualitative elementary analysis showed the presence of chlorine and a trace of nitrogen [Found: N, less than 0·4; Cl, 24·6. Calc. for $C_{15}H_{14}O_2Cl_2$ (1 : 3-bis-*p*-chlorophenoxypropane): Cl, 23·9%].

ω-Phenoxyalkylcarboxylic acids

The physical properties and methods of preparation are given in Table IV. Representative examples of the methods of preparation are given below.

5-o-*Methoxyphenoxypentane*-1-*carboxylic acid.* — 1 - Cyano - 5 - *o* - methoxyphenoxypentane (21·9 g., 0·1 mole) was refluxed for 8 hours with a solution of sodium hydroxide (15 g.) in water (18 ml.) and ethanol (50 ml.). Distillation to dryness on the steam-bath under reduced pressure gave a colourless residue which was dissolved in hot water (100 ml.). The resulting solution, after filtration, was acidified to Congo red with hydrochloric acid and cooled in ice. The pale cream solid which separated was filtered off, washed with water and recrystallized from aqueous ethanol to give 16·8 g. (77%) of the required *acid*, as colourless plates, m.p. 101–102°.

Diethyl 6-o-*methoxyphenoxyhexane*-1 : 1-*dicarboxylate.*—To a stirred refluxing solution of sodium (9 g.) in dry ethanol (200 ml.), was added diethyl malonate (90 g.) over 5 minutes, followed by 1-bromo-5-*o*-methoxyphenoxypentane (54·6 g., 0·2 mole) over 10 minutes. The solution was refluxed for a further 4 hours, the bulk of the ethanol was removed by distillation and the residue was poured into water (1 litre). The orange-coloured oil which separated was extracted with ether, the solvent removed and the residue distilled. After a forerun of diethyl malonate, 45·5 g. (66%) of the required *ester* was obtained as a colourless oil, b.p. 171–199°/0·2 mm. (Found: C, 65·6; H, 8·1. $C_{19}H_{28}O_6$ requires C, 64·8; H, 7·9%).

6-o-*Methoxyphenoxyhexane*-1-*carboxylic acid.*—Diethyl 6-*o*-methoxyphenoxyhexane-1 : 1-dicarboxylate (35·2 g., 0·1 mole) was added over 30 minutes to a boiling stirred solution of potassium hydroxide (20 g.) in water (20 ml.) and the solution was refluxed with stirring for a further 4 hours. Water (20 ml.) was added and the solution was concentrated by the removal of 25 ml. of distillate. To the boiling stirred residue was added dropwise over one hour a mixture of sulphuric acid (18 ml.) and water (50 ml.). Refluxing with stirring was continued for a further 6 hours. After being cooled in ice, the solution was extracted with ether, and the ethereal extract was washed with water and dried. Removal of the ether gave a red oil which solidified on keeping; the solid was recrystallized from aqueous ethanol to give 18 g. (72%) of a faintly grey microcrystalline powder, m.p. 55–56°; recrystallization of this material from benzene–light petroleum (b.p. 40–60°) gave 13·5 g. (54%) of the required *acid*, as colourless prisms, m.p. 61–62°.

Table IV

ω-Phenoxyalkylcarboxylic acids $RO\cdot[CH_2]_n\cdot CO_2H$

Acid	R	*n*	Synthetic route	M.p.	Crystalline form	Solvent	Found C %	Found H %	Found Cl %	Formula	Required C %	Required H %	Required Cl %
3-*o*-Methoxyphenoxypropane-1-carboxylic acid	*o*-methoxyphenyl	3	B	84–85°	prisms	(*a*)	62·8	6·9	—	$C_{11}H_{14}O_4$	62·9	6·5	—
4-*o*-Methoxyphenoxybutane-1-carboxylic acid	,,	4	C	79–80°	,,	(*a*)	63·6	7·18	—	$C_{12}H_{16}O_4$*	64·4	7·15	—
5-*o*-Methoxyphenoxypentane-1-carboxylic acid	,,	5	B	101–102°	plates	(*b*)	65·6	7·5	—	$C_{13}H_{18}O_4$	65·5	7·6	—
6-*o*-Methoxyphenoxyhexane-1-carboxylic acid	,,	6	C	61–62°	prisms	(*a*)	66·4	7·7	—	$C_{14}H_{20}O_4$	66·7	7·9	—
4-*p*-Chlorophenoxybutane-1-carboxylic acid	*p*-chlorophenyl	4	C	71°	,,	(*a*)	—	—	15·6	$C_{11}H_{13}O_3Cl$	—	—	15·5
5-*p*-Chlorophenoxypentane-1-carboxylic acid	,,	5	B	77–78°	needles	(*a*)	—	—	14·9	$C_{12}H_{15}O_3Cl$	—	—	14·7
6-*p*-Chlorophenoxyhexane-1-carboxylic acid	,,	6	C	74–75°	prisms	(*b*)	—	—	14·1	$C_{13}H_{17}O_3Cl$	—	—	13·9
7-*p*-Chlorophenoxyheptane-1-carboxylic acid	,,	7	C	110–112°	,,	(*c*)	—	—	12·8	$C_{14}H_{19}O_3Cl$	—	—	13·1
2-(2 : 4 : 5-Trichlorophenoxy)ethane-1-carboxylic acid	2 : 4 : 5-trichlorophenyl	2	A	142–144°	plates	(*a*)	—	—	39·6	$C_9H_7O_3Cl_3$	—	—	39·6
4-(2 : 4 : 5-Trichlorophenoxy)butane-1-carboxylic acid	,,	4	C	96–97°	micro-prisms	(*a*)	—	—	35·3	$C_{11}H_{11}O_3Cl_3$	—	—	35·8
5-(2 : 4 : 5-Trichlorophenoxy)pentane-1-carboxylic acid	,,	5	B	73–74°	,,	(*a*)	—	—	34·1	$C_{12}H_{13}O_3Cl_3$	—	—	34·2
6-(2 : 4 : 5-Trichlorophenoxy)hexane-1-carboxylic acid	,,	6	C	94–95°	,,	(*a*)	—	—	32·1	$C_{13}H_{15}O_3Cl_3$	—	—	32·7
7-(2 : 4 : 5-Trichlorophenoxy)heptane-1-carboxylic acid	,,	7	C	55°	,,	(*a*)	—	—	30·4	$C_{14}H_{17}O_3Cl_3$	—	—	31·3

Synthetic routes

(A) $R\cdot OH \xrightarrow{Br\cdot[CH_2]_2\cdot CO_2H} RO\cdot[CH_2]_2\cdot CO_2H$

(B) $R\cdot OH \xrightarrow{Br\cdot[CH_2]_x\cdot Br} RO\cdot[CH_2]_x\cdot Br \longrightarrow RO\cdot[CH_2]_x\cdot CN \longrightarrow RO\cdot[CH_2]_x\cdot CO_2H$

(C) $R\cdot OH \xrightarrow{Br\cdot[CH_2]_x\cdot Br} RO\cdot[CH_2]_x\cdot Br \longrightarrow RO\cdot[CH_2]_x\cdot CH[CO_2Et]_2 \longrightarrow RO\cdot[CH_2]_{x+1}\cdot CO_2H$

Solvents: (*a*) Benzene/light petroleum (b.p. 40–60°); (*b*) aqueous ethanol; (*c*) benzene

* Found: OMe, 13·6. $C_{12}H_{16}O_4$ requires OMe, 13·8.

Diethyl 4-p-*chlorophenoxybutane*-1 : 1-*dicarboxylate.* — 1-Bromo-3-*p*-chlorophenoxypropane (25 g., 0·1 mole) was treated by the method described for the preparation of diethyl 6-*o*-methoxyphenoxyhexane-1 : 1-dicarboxylate. The required *ester* (23·5 g., 61%) was obtained as a colourless oil, b.p. 132–150°/0·07 mm. (Found : Cl, 11·26. $C_{16}H_{21}O_5Cl$ requires Cl, 10·8%).

4-p-*Chlorophenoxybutane*-1-*carboxylic acid.*—Diethyl 4-*p*-chlorophenoxybutane-1 : 1-dicarboxylate (8·2 g., 0·025 mole) was treated in the manner described for the preparation of 6-*o*-methoxyphenoxyhexane-1-carboxylic acid. In this case decarboxylation did not occur. The product obtained was recrystallized from benzene–light petroleum (b.p. 40–60°), to give 4·2 g. (72%) of 4-p-*chlorophenoxybutane*-1 : 1-*dicarboxylic acid* as colourless prisms, m.p. 108–110° (Found : Cl, 13·1. $C_{12}H_{13}O_5Cl$ requires Cl, 13·0%). This acid was decarboxylated by heating for 4 hours under reduced pressure (10 mm.) in an oil-bath at 180°. On cooling, the melt solidified to a pale brown mass which was recrystallized from benzene–light petroleum (b.p. 40–60°), to give 2·3 g. (70%) of material with m.p. 65–69°. A further recrystallization from benzene–light petroleum (b.p. 40–60°) gave 1·8 g. (45%) of the required *acid* as colourless prisms, m.p. 71°.

Derivatives of ω-phenoxyalkylcarboxylic acids

p-*Bromophenacyl ester of* 3-o-*methoxyphenoxypropane*-1-*carboxylic acid.*—3-*o*-Methoxyphenoxypropane-1-carboxylic acid (1·9 g.) was suspended in water (5 ml.) and neutralized with 2N-sodium carbonate solution to which was added a further 0·2 g. (0·01 mole in all) of the acid. The resulting solution, which was acid to phenolphthalein, was added to a hot solution of *p*-bromophenacyl bromide (3·07 g., 0·011 mole) in ethanol (70 ml.) and the resulting solution was refluxed for 1 hour and allowed to cool.

The solid which separated was filtered off, and recrystallized from ethanol to give the required *ester* (0·65 g., 16%) as colourless micro-needles, m.p. 116–117° (Found : Br, 20·0. $C_{19}H_{19}O_5Br$ requires Br, 19·7%).

p-*Phenylphenacyl ester of* 3-o-*methoxyphenoxypropane*-1-*carboxylic acid.*—*p*-Phenylphenacyl bromide (3·07 g.) in ethanol (70 ml.) and 3-*o*-methoxyphenoxypropane-1-carboxylic acid (2·1 g., 0·01 mole) in sodium carbonate solution were caused to react as in the preparation of the *p*-bromophenacyl ester, to give the required *ester* (2·7 g., 67%), as colourless micro-needles (from ethanol), m.p. 135° (Found : OMe, 7·95. $C_{25}H_{24}O_5$ requires OMe, 7·7%).

ω-1-Naphthylalkylcarboxylic acids

Monoesters of dibasic acids

The monomethyl esters of succinic and glutaric acids were obtained by the action of methanol on the appropriate anhydride.[34] The monoethyl esters of adipic, pimelic and sebacic acids were obtained by semi-esterification of the appropriate acid.[26, 27]

Ester-acid chlorides

Treatment of the monoesters with thionyl chloride[34] gave the corresponding acid chlorides ; the properties of the three higher members are listed in Table V.

Halides used were 1-bromonaphthalene,[35] 1-chloromethylnaphthalene[36] and 1-bromo-2-1′-naphthylethane.[37]

Keto-esters

The keto-esters, whose properties and synthetic routes are summarized in Table VI, were prepared by essentially the same method, a typical example of which is described below.

Methyl-6-1′-*naphthyl*-4-*ketohexane*-1-*carboxylate.*—The apparatus consisted of a 1-litre, three-necked, round-bottom flask, fitted with a stainless-steel stirrer[38] driven by a powerful motor, reflux condenser (closed by drying tube) and dropping funnel.

2-1′-Naphthylethylmagnesium bromide was prepared in this flask from 1-bromo-2-1′-naphthylethane (47 g., 0·2 mole) and magnesium (4·8 g.) in dry ether (250 ml.). The Grignard solution was cooled in ice and anhydrous cadmium chloride (22 g., 0·12 mole) was added as rapidly as possible. The suspension was then refluxed with stirring for 1 hour, after which time a small sample was removed which gave a negative Gilman reaction.[39]

The bulk of the ether was removed by distillation and replaced by dry benzene (200 ml.) and

Table V

Ester-acid chlorides

$EtCO_2{\cdot}[CH_2]_n{\cdot}COCl$

	n	B.p.	Found Cl %	Formula	Required Cl %
4-Ethoxycarbonylbutane-1-carbonyl chloride	4	113–114°/15 mm.	18·6	$C_8H_{13}O_3Cl$	18·5
5-Ethoxycarbonylpentane-1-carbonyl chloride	5	134–136°/15 mm.	17·0	$C_9H_{15}O_3Cl$	17·2
8-Ethoxycarbonyloctane-1-carbonyl chloride	8	173–175°/15 mm.	14·6	$C_{12}H_{21}O_3Cl$	14·3

Table VI

Keto-esters $1\text{-}C_{10}H_7{\cdot}[CH_2]_n{\cdot}CO{\cdot}[CH_2]_m{\cdot}CO_2R$

Prepared by the reaction $1\text{-}C_{10}H_7{\cdot}[CH_2]_n{\cdot}Br \longrightarrow 1\text{-}C_{10}H_7{\cdot}[CH_2]_m{\cdot}(Cd)_{\frac{1}{2}} \xrightarrow{ClCO{\cdot}[CH_2]_m{\cdot}CO_2R} 1\text{-}C_{10}H_7{\cdot}[CH_2]_n{\cdot}CO{\cdot}[CH_2]_m{\cdot}CO_2R$

Name	n	m	R	B.p.	Found C %	Found H %	Found OR %	Formula	Required C %	Required H %	Required OR %
Methyl 2-1′-naphthoylethane-1-carboxylate	0	2	Me	169–180°/0·5 mm.	74·2	6·0	—	$C_{15}H_{14}O_3$	74·4	5·8	—
Methyl 3-1′-naphthoylpropane-1-carboxylate	0	3	Me	158–163°/0·1 mm.	—	—	12·1	$C_{16}H_{16}O_3$	—	—	12·1
Ethyl 4-1′-naphthoylbutane-1-carboxylate	0	4	Et	145–161°/0·07 mm.	76·0	7·22	—	$C_{18}H_{20}O_3$	76·1	7·05	—
Methyl 6-1′-naphthyl-4-ketohexane-1-carboxylate	2	3	Me	173–185°/0·08 mm.	—	—	10·8	$C_{18}H_{20}O_3$	—	—	10·9
Ethyl 7-1′-naphthyl-5-ketoheptane-1-carboxylate	2	4	Et	193–201°/0·1 mm.	—	—	12·55	$C_{20}H_{24}O_3$	—	—	14·4
Ethyl 8-1′-naphthyl-6-keto-octane-1-carboxylate	2	5	Et	201–207°/0·04 mm.	—	—	12·1	$C_{21}H_{26}O_3$	—	—	13·8
Ethyl 8-1′-naphthoyloctane-1-carboxylate	0	8	Et	145–152°/0·3 mm.	—	—	16·4	$C_{22}H_{28}O_3$	—	—	13·2

the reaction mixture was again cooled in ice. 3-Methoxycarbonylpropane-1-carbonyl chloride (24·8 g., 0·15 mole) in dry benzene (50 ml.) was added over 5 minutes, causing the separation of a solid complex which was at first sticky and difficult to stir, but which soon reverted to a granular solid. The reaction mixture was refluxed with stirring for 3 hours, cooled and poured into a mixture of ice (500 g.) and water (500 ml.). Sufficient 2N-sulphuric acid was added to bring the mixture acid to Congo red, and a small quantity of solid was removed by filtration through Hyflo. The benzene layer was separated from the filtrate and the aqueous layer was extracted with benzene (2 × 60 ml.). The combined benzene extracts were washed with water, dilute sodium bicarbonate solution, and again with water, and dried. The residue remaining after removal of the benzene was distilled under reduced pressure. The required *keto-ester* was obtained as a pale yellow oil, b.p. 170–185°/0·08 mm.

As can be seen from Table VI, some of the longer chain keto-esters were not obtained pure.

ω-1-Naphthyl-alkylcarboxylic acids

5-1′-*Naphthylpentane-1-carboxylic acid.*—Ethyl 4-1′-naphthoylbutane-1-carboxylate was hydrolysed by refluxing with 10% ethanolic potassium hydroxide solution. Clemmensen reduction[40] of the crude acid obtained by acidification of this reaction gave the required *acid* as colourless prisms, m.p. 70–72°, from light petroleum (b.p. 40–60°) (Found: C, 79·1; H, 7·3. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·44%).

4-1′-*Naphthylbutane-1-carboxylic acid.*—(*a*) By Clemmensen reduction.—Methyl 3-1′-naphthoylpropane-1-carboxylate was reduced[40] to give *methyl* 4-1′-*naphthylbutane-1-carboxylate* as an almost colourless oil, b.p. 164–172°/0·1 mm., which solidified on standing (Found: C, 78·6; H, 7·2. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%). Alkaline hydrolysis of this ester gave the required *acid* as colourless prisms, m.p. 87–89°, from light petroleum (b.p. 40–60°) (Found: C, 78·9; H, 7·17. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%).

(*b*) By Wolff–Kishner reduction.—Methyl 3-1′-naphthoylpropane-1-carboxylate was reduced[25] to give the required acid, m.p. 87–89° (no depression with the sample prepared by Clemmensen reduction).

6-1′-*Naphthylhexane-1-carboxylic acid.*—Methyl 6-1′-naphthyl-4-ketohexane-1-carboxylate was reduced[25] to the required *acid*, obtained as colourless microprisms, m.p. 58–60°, from light petroleum (b.p. 40–60°) (Found: C, 79·7; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·8; H, 7·7%).

3-1′-*Naphthylpropane-1-carboxylic acid.*—Freshly distilled ethyl acetoacetate (26 g.) followed by 1-bromo-2-1′-naphthylethane (23·5 g., 0·1 mole) was added to a refluxing solution of sodium (4·6 g.) in anhydrous ethanol (100 ml.). The turbid solution was refluxed for 4 hours and then filtered. The ethanol and most of the excess ethyl acetoacetate was distilled from the filtrate to leave an orange oil which was refluxed for 2 hours with a solution of potassium hydroxide (30 g.) in ethanol (100 ml.). The resulting solution was poured into water (1 litre). Alkali-insoluble material was removed by extracting this milky solution with ether. The resulting alkaline solution was boiled with charcoal, filtered and brought to pH 7 by the addition of hydrochloric acid. The brown tarry material was removed by filtration through Hyflo and the filtrate was acidified to Congo red with hydrochloric acid and set aside overnight.

The cream-coloured solid was filtered off, washed with water and recrystallized from 150 ml. of hot water to give the required acid as colourless needles, m.p. 106° (no depression with material which had been prepared by reduction of 2-1′-naphthoylethane-1-carboxylic acid and which melted at 109–110°).

1-Naphthyl-alkylcarboxylic acids with branched or modified chains

2-1′-*Naphthylmethylbenzene-1-carboxylic acid.*—2-1′-Naphthoylbenzoic acid[32] (4·5 g.) was reduced by the Clemmensen method[25] to give the required *acid* (α-1′-*naphthyl-o-toluic acid*) (1 g.) as colourless microprisms, m.p. 144–145°, from benzene (Found: C, 82·1; H, 5·4. Calc. for $C_{18}H_{14}O_2$: C, 82·4; H, 5·35%).

1-1′-*Naphthylpropane-2-carbonyl chloride.*—1-1′-Naphthylpropane-2-carboxylic acid[28] (6·4 g.) in dry benzene (20 ml.) was refluxed for 40 minutes with thionyl chloride (5 ml.). The benzene was removed by distillation and the residue distilled to give the required *acid chloride* (4·3 g.) as a colourless oil, b.p. 190–195°/15 mm. (Found: Cl, 14·95. $C_{14}H_{13}OCl$ requires Cl, 15·3%).

2-Methyl-3-1′-naphthylpropane-1-carboxylic acid

N-Methyl-*N*-nitrosourea[41] (17·5 g.) was added over 30 minutes in portions of about 1 g. to a stirred mixture of ether (250 ml.) in 40% aqueous potassium hydroxide (70 ml.) at 0–5°. The yellow ethereal diazomethane solution was separated, dried at 0° over potassium hydroxide and treated with a solution of 1-1′-naphthylpropane-2-carbonyl chloride (8·8 g., 0·038 mole) in dry ether (50 ml.) at 5–10°. The solution was set aside overnight and the ether was then removed by distillation under reduced pressure at 25–30° to give the crude diazoketone (8 g.) as a yellowish-brown, viscous oil. This diazoketone was dissolved in dry dioxan (60 ml.) and the resulting solution was added over 1 hour to a stirred mixture of silver oxide (1·3 g.), anhydrous sodium carbonate (3·3 g.), sodium thiosulphate (2 g.), and water (130 ml), maintained at 50–60°. The suspension was maintained at 60–70° for a further hour, cooled to 20° and acidified to Congo red with dilute nitric acid. To this was added ether (100 ml.) and the mixture was filtered through Hyflo. Ether extraction of the filtrate and evaporation of the dried ethereal extract gave a pale brown syrup (9·2 g.) which was distilled to give a pale yellow oil (4·1 g.), b.p. 220–226°/15 mm., which slowly solidified on standing. Recrystallization of this material from benzene–light petroleum (b.p. 40–60°) gave the required acid (2·0 g.) as a pale fawn micro-crystalline solid, m.p. 86–88°. Bachmann & Cortes,[30] using a different route, claim m.p. 89–91° (Found: C, 78·8; H, 7·0. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·0%).

Acknowledgments

The author wishes to thank Professor R. L. Wain and Dr. H. J. Barber for their advice and interest and the Directors of May & Baker Ltd. for the generous provision of facilities.

Chemical Research Laboratories
May & Baker Ltd.
Dagenham, Essex

Received 18 November, 1955

References

[1] Fawcett, C. H., Ingram, J. M. A., & Wain, R. L., *Nature, Lond.*, 1952, **170,** 887
[2] Wain, R. L., *Ann. appl. Biol.*, 1949, **36,** 558
[3] Wain, R. L., & Wightman, F., *Proc. roy. Soc.*, 1954, [B] **142,** 525
[4] Auwers, K., & Haymann, K., *Ber. dtsch. chem. Ges.*, 1894, **27,** 2804
[5] Pfeiffer, P., Oberlin, H., & Konermann, E., *Ber. dtsch. chem. Ges.*, 1925, **58,** 1955
[6] Michael, A., *Amer. chem. J.*, 1887, **9,** 216
[7] Chakravarti, D., & Dutta, N., *J. Indian chem. Soc.*, 1939, **61,** 639
[8] Nair, C. N., & Peacock, D. H., *J. Indian chem. Soc.*, 1935, **12,** 318
[9] Synerholm, M. E., & Zimmerman, P. W., *Contr. Boyce Thomson Inst.*, 1945, **14,** 369
[10] Pokorny, R., *J. Amer. chem. Soc.*, 1941, **63,** 1768
[11] Wohl, A., & Berthold, E., *Ber. dtsch. chem. Ges.*, 1910, **43,** 2180
[12] Merck, Ger. P. 184,968
[13] Leese, C. L., & Raphael, R. A., *J. chem. Soc.*, 1950, p. 2725
[14] Gagnon, P. E., Boivin, J. L., & Giguère, J., *Canad. J. Res.*, 1950, **28, B,** 352
[15] Walker, D. F., *J. Amer. pharm. Ass.*, 1950, **39,** 396
[16] Newman, M. S., Fones, W., & Renoll, M., *J. Amer. chem. Soc.*, 1947, **69,** 718
[17] Barber, H. J., Green, M. B., & Zwartouw, H. T., *J. appl. Chem.*, 1953, **3,** 419
[18] Boessneck, P., *Ber. dtsch. chem. Ges.*, 1883, **16,** 639
[19] Mayer, F., & Sieglitz, A., *Ber. dtsch. chem. Ges.*, 1922, **55,** 1835
[20] Haworth, R. D., *J. chem. Soc.*, 1932, p. 1125
[21] Schlenk, W., Bergmann, O., & Bergmann, E., *J. Soc. chem. Ind., Lond.*, 1933, **52,** 209T
[22] Manske, R. H. F., & Ledingham, A. E., *Canad. J. Res.*, 1939, **17, B,** 14
[23] Riegel, B., Burr, J. G., Kubico, M. A., & Gold, M. H., *J. Amer. chem. Soc.*, 1948, **70,** 1073
[24] Dauben, W. G., & Tilles, H., *J. org. Chem.*, 1950, **15,** 785
[25] Huang-Minlon, *J. Amer. chem. Soc.*, 1946, **68,** 2487
[26] Brown, G. B., & Baker, B. R., *J. org. Chem.*, 1947, **12,** 162
[27] Swan, S., Oehler, R., & Buswell, R. J., *Org. Synth.*, Coll. Vol. II, p. 276
[28] Blicke, F. F., & Maxwell, C. E., *J. Amer. chem. Soc.*, 1939, **61,** 1782
[29] Fieser, L. F., & Novello, F. C., *J. Amer. chem. Soc.*, 1940, **62,** 1855
[30] Bachmann, W. E., & Cortes, G. D., *J. Amer. chem. Soc.*, 1943, **65,** 1329
[31] Boekelheide, V., & Larrabee, C. E., *J. Amer. chem. Soc.*, 1950, **72,** 1240
[32] de Benneville, P. L., *J. org. Chem.*, 1941, **6,** 462
[33] Vogel, I., *J. chem. Soc.*, 1928, p. 2019
[34] Cason, J., *Org. Synth.*, **25,** 19
[35] Clarke, H. T., & Brethen, M. R., *Org. Synth.*, Coll. Vol. I, p. 121
[36] Cambron, A., *Canad., J. Res.*, 1939, **17, B,** 10
[37] Haworth, R. D. & Mavin, C. R., *J. chem. Soc.*, 1933, p. 1014
[38] Hershberg, E. B., *Industr. Engng Chem.* [*Anal.*], 1936, **8,** 313
[39] Gilman, H., & Schulze, F., *J. Amer. chem. Soc.*, 1925, **47,** 2002
[40] Martin, E. L., *J. Amer. chem. Soc.*, 1936, **58,** 1438
[41] Arndt, F., *Org. Synth.*, Coll. Vol. II, p. 461

THE DEPLETION OF INSECTICIDAL EMULSIONS IN CONTACT WITH SHEEP FLEECE

By A. F. MACHIN

The depletion and subsequent fate of insecticide and solvent from emulsions of BHC, DDT, Dieldrin and Aldrin in contact with sheep fleece under equilibrium conditions has been studied. It is shown that this depletion is essentially due to the grease associated with the fleece. There are marked differences between the depletion of BHC and Dieldrin on the one hand and DDT and Aldrin on the other; the mechanism of depletion is discussed with particular reference to these differences.

Introduction

During the last ten years, the extensive use of dips containing BHC and DDT for the control of ecto-parasites of sheep has shown that selective removal of insecticide during dipping, particularly in emulsion dips, may rapidly reduce the concentration of insecticide.[1, 2, 3] Although comparatively little attention has been paid to the mechanism of this phenomenon, it has been recognized that the type of wetting agent used in compounding emulsion dips has a marked influence on the rate of depletion; thus Heath & Mitchell,[2] who tested DDT emulsions against the sheep tick, found that deposition of the insecticide was much greater from a cationic than an anionic emulsion, while Addison & Furmidge[4–9] carried out a detailed study of the reactions of cationic wetting agents with fleece which indicated that the nature and concentration of the wetting agent had a profound effect upon the depletion of emulsions.

The present work is concerned with the reactions of emulsions of BHC, DDT, Dieldrin and Aldrin with sheep fleece, in the natural state and after removal of grease or suint, under equilibrium conditions. It is intended to be complementary to that of Addison & Furmidge in providing a basis for the formulation of insecticidal emulsions. With this object in view, non-ionic wetting agents were used to avoid reaction with wool-grease or suint and thus restrict the loss of wetting agent to that due to direct sorption. Although equilibrium is not reached during normal dipping it is believed that the conclusions to be drawn from this work can be applied in practice. It was found experimentally that the concentration of BHC in an emulsion in contact with fleece fell to its equilibrium value in about 30 minutes and that roughly one-third of this loss occurred in one minute (the usual period of dipping).

Experimental

Materials

Emulsion constituents.—The BHC was lindane containing not less than 99% γ-isomer and the DDT contained 80–85% *pp'*-isomer. Dieldrin and Aldrin contained 80% HEOD (1 : 2 : 3 : 4 : 11 : 11-hexachloro-6 : 7-epoxy-1 : 4 : 5 : 6 : 7 : 8 : 9 : 10-octahydro-1 : 4-5 : 8-di*endo*-methylenenaphthalene) and 85% HHDN (1 : 2 : 3 : 4 : 11 : 11-hexachloro-1 : 4 : 5 : 8 : 9 : 10-hexahydro-1 : 4-5 : 8-di*endo*methylenenaphthalene), respectively. The solvent was Hopkin and Williams' '*o*-xylene', containing 99% *o*-xylene, the remainder being non-aromatic. Tween 80 (polyoxyethylene sorbitan mono-oleate) and Crill No. 12 (polyoxyethylene sorbitan tri-oleate) were used as wetting agents.

Fleece.—Clippings which included both flank and back fleece from crossbred Oxford downland sheep which had not previously been dipped were thoroughly mixed. Although no attempt was made to estimate accurately the size distribution, the mean dimensions of fibres from a composite sample were found to be approximately 90 mm. long and 0·04 mm. diameter, the weight being about 0·13 mg. If it is assumed that the fibre together with its coating of grease and suint can be regarded as a solid cylinder, these figures indicate a surface area of roughly 900 sq. cm. per g.

Reagents.—These were all of 'Analar' or 'Laboratory Reagent' quality. 'Analar' ether was distilled once to remove aromatic or unsaturated impurities.

Methods

(a) *Grease and suint.*—The procedures of Addison & Furmidge[5] were followed for the extraction and determination of grease and suint. The mean grease and suint contents found were 12·3% and 16·5%, respectively.

(b) *Preparation of emulsions.*—A solution of 5% w/v of each insecticide and 10% w/v Crill No. 12 in *o*-xylene was blended in an ' Atomix ' homogenizer with 49 volumes of distilled water containing 0·2% w/v Tween 80, to give emulsions containing 0·1% w/v insecticide and approximately 1·5% w/v (1·8% v/v) solvent. The oil phase in each emulsion consisted of globules about 1 μ in diameter: after keeping for 24 hours there was no visible change, and analyses of the unstirred emulsions agreed well with those of the dip immediately after preparation.

(c) *Reaction between fleece and emulsions.*—Samples of fleece (3·3 g. of native wool, 2·75 g. of suint-free wool and 2·9 g. of degreased wool) which had been stored at fairly constant temperature (16–19°) and relative humidity (60–70%) were immersed in 300 ml. of each emulsion and shaken mechanically in glass-stoppered jars for 30 minutes. (The ratio of weight of wool to volume of emulsion is approximately twenty times that corresponding to the dipping of a single sheep in a 240-gallon bath.) After reaction, as much of the emulsion as possible was returned to the jar by squeezing and samples were withdrawn for analysis. The process was repeated until twelve samples had been successively treated in each emulsion.

(d) *Recovery of solvent and insecticides from fleece.*—The bulked fleece samples from each experiment were extracted twice by mechanical shaking with distilled water (700 ml.) for 2 hours. After draining, the fleece was rinsed briefly with ether, then extracted twice more by mechanical shaking for two-hour periods.

(e) *Estimation of solvent and insecticides.*—Emulsion samples and aqueous extracts of fleece were extracted with ether and the ethereal solutions, together with those from the ether-extraction of the treated fleece, dried with anhydrous sodium sulphate, filtered and diluted to a known volume.

The solvent was estimated by measuring the absorption at 2630 Å, using a Hilger ' Uvispek ' spectrophotometer, the apparent *o*-xylene contents being corrected for absorption due to insecticide (absorption by wetting agents was negligible at the concentrations concerned). The method is essentially that of Tunnicliff, Brattain & Zumwalt.[10]

Insecticides were estimated after evaporation of ether by a procedure differing only in minor details from that of Wichmann *et al.*,[11] involving a modified Stepanow dechlorination[12] with sodium and *iso*propanol. The liberated chloride was determined by titration with mercuric nitrate according to the method of Bohm & Stürz.[13] Insecticide contents were calculated in terms of the chlorine present in pure BHC, DDT, HEOD and HHDN.

Results

Figs. 1, 2 and 3 show the percentage of the initial concentration of insecticide remaining after reaction with successive samples of natural, suint-free and grease-free wool respectively; the depletion of *o*-xylene in contact with natural and grease-free wool is similarly plotted in Figs. 4 and 5. The broken portions of curves A and B of Fig. 1 and curve B of Fig. 2 are derived from the lower parts of these curves by extrapolation.

The recoveries of the four insecticides from natural wool are presented in Table I and the corresponding recoveries of *o*-xylene in Table II.

Discussion

Influence of grease and suint

It is evident from Figs. 1–5 that depletion of both insecticide and solvent is essentially due to the grease associated with the wool fibre. The role of the grease is confirmed by the results shown in Table I, from which it is seen that roughly three-quarters of the total weight of each insecticide deposited on the fleece was recovered by rinsing rapidly with ether, implying that little

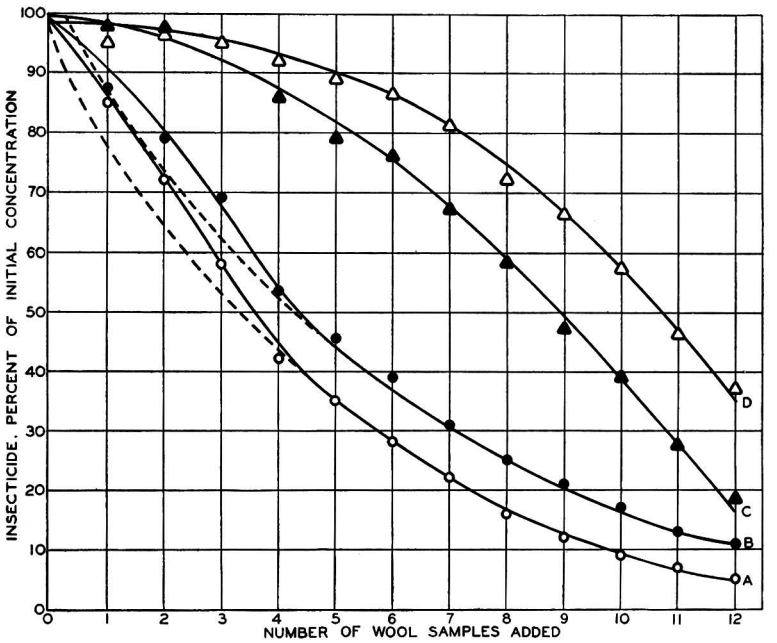


FIG. 1.—*Depletion of insecticide, natural wool*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion
Curve C: Aldrin emulsion
Curve D: DDT emulsion

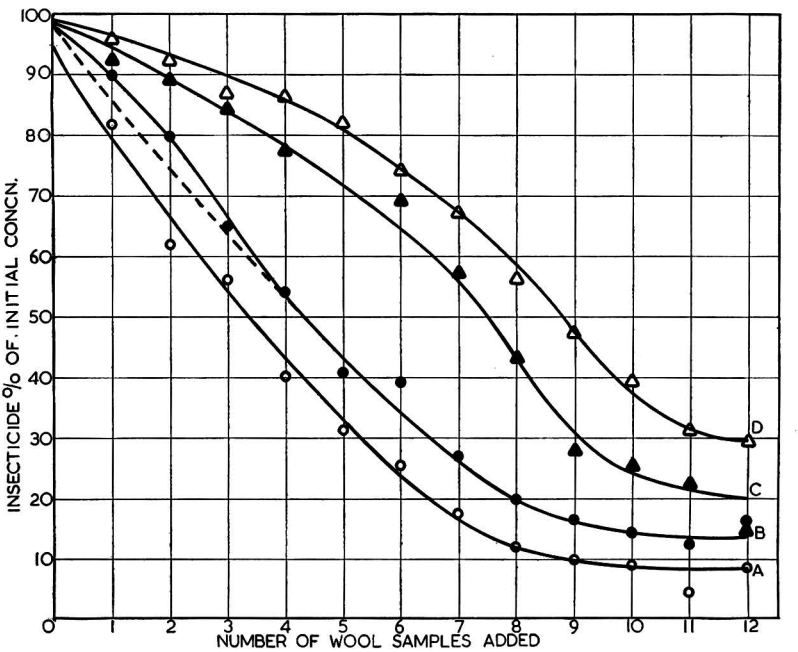


FIG. 2.—*Depletion of insecticide, suint-free wool*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion
Curve C: Aldrin emulsion
Curve D: DDT emulsion

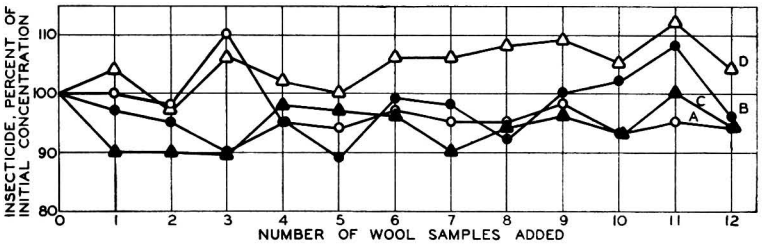


FIG. 3.—*Depletion of insecticide, grease-free wool*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion
Curve C: Aldrin emulsion
Curve D: DDT emulsion

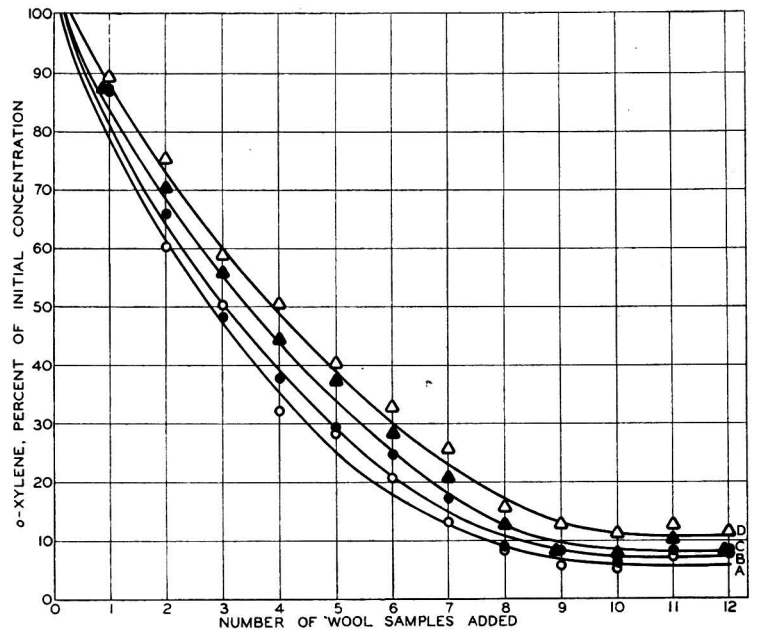


FIG. 4.—*Depletion of o-xylene, natural wool*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion
Curve C: Aldrin emulsion
Curve D: DDT emulsion

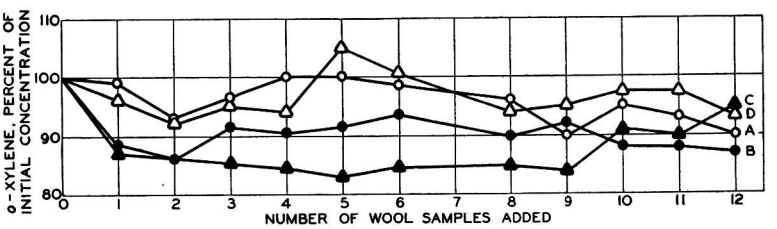


FIG. 5.—*Depletion of o-xylene, grease-free wool*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion
Curve C: Aldrin emulsion
Curve D: DDT emulsion

Table I

Recovery of insecticides from reaction with natural wool

	Emulsion			
	BHC	DDT	Dieldrin	Aldrin
Insecticide in initial emulsion, g.	0·292	0·305	0·303	0·284
Insecticide in final emulsion, g.	0·005	0·036	0·010	0·018
Withdrawn by sampling, g.	0·030	0·089	0·042	0·066
Removed mechanically by wool, g.	0·028	0·056	0·032	0·0395
Removed selectively by wool, g.	0·229	0·128	0·218	0·158
Recovered in first aqueous extract, g.	0·019	0·041	0·020	0·0315
Recovered in second aqueous extract, g.	0·006	0·003	0·0035	0·003
Recovered in ether rinse, g.	0·157	0·098	0·151	0·111
Recovered in first ether extract, g.	0·050	0·021	0·042	0·025
Recovered in second ether extract, g.	0·002	0·002	0·0035	0·003
Recovery of mechanically lost insecticide by aqueous extraction, %	89	79	73	87
Recovery of selectively lost insecticide by ether extraction, %	91	95	90	88
Overall recovery, %	92	95	90	91

Table II

Recovery of solvent from reaction with natural wool

	Emulsion			
	BHC	DDT	Dieldrin	Aldrin
Solvent in initial emulsion, g.	4·36	4·73	4·50	4·36
Solvent in final emulsion, g.	0·08	0·17	0·11	0·10
Withdrawn by sampling, g.	0·39	0·59	0·44	0·48
Removed mechanically by wool, g.	0·33	0·44	0·345	0·35
Removed selectively by wool, g.	3·63	3·56	3·67	3·47
Recovered in first aqueous extract, g.	0·22	0·30	0·26	0·23
Recovered in second aqueous extract, g.	0·08	0·10	0·095	0·09
Recovered in ether rinse, g.	2·26	2·19	2·24	2·04
Recovered in first ether extract, g.	0·66	0·47	0·46	0·43
Recovered in second ether extract, g.	0·045	0·03	0·03	0·04
Recovery of mechanically lost solvent by aqueous extraction, %	91	91	103	94
Recovery of selectively lost solvent by ether extraction, %	82	76	74	72
Overall recovery, %	86	81	81	78

or no penetration of the fibre by insecticide or solvent could have occurred. In this connexion Fiedler & Du Toit[14, 15] found that BHC, Dieldrin and Aldrin diffuse along the wool fibre although DDT, DDD and Methoxychlor do not, the evidence for this being that the three former insecticides, but not DDT or its analogues, were present in new wool grown after dipping. (It is not quite clear whether Fiedler & Du Toit envisage actual penetration of the fibre by the insecticide, followed by diffusion within it, or merely diffusion in the yolk layer. The latter view is in accord with the present findings and with the experiments of Speakman[16] who demonstrated that the capillary spaces within the wool fibre are of about the size of the *n*-propanol molecule and are therefore too small to admit the insecticides discussed here.) The behaviour of the DDT group of insecticides seems surprising, since it would be supposed that solutes in the grease would become uniformly distributed by diffusion, but an explanation may be found in the observation by Lennox[17] that yolk flows from root to tip of the wool fibre at a rate of about 8 mm. per month. The concentration of insecticide at any point on the fibre, which will depend upon the opposing effects of diffusion and grease flow, will therefore be roughly proportional to the initial concentration in the grease. Since Fiedler & Du Toit employed 0·5% insecticidal suspensions, a close correlation between their findings and the results described here is not to be expected, but the considerations just mentioned suggest that there is at least a general agreement. On the other hand, the view that solution of the insecticide in wool-grease is the essential mechanism of depletion from non-ionic emulsions appears to conflict with the conclusions of Laudani[18] who noted a selective removal of DDT from non-ionic emulsions in contact with woollen garments. It does not seem possible to explain this apparent contradiction, although the high DDT content of the emulsifiable concentrates used by Laudani (25% and 30%) in conjunction with the temperature (90° F) may have caused some mechanical deposition due to evaporation of the solvent.

The influence of suint on depletion is apparently slight: the corresponding pairs of curves in Figs. 1 and 2 are of the same general shape, but an interesting point of difference occurs in the inflexion of the curves for the depletion of DDT and Aldrin of suint-free wool (Fig. 2, C and D). This will be discussed below when the differences between the insecticides are considered in detail. A further characteristic exhibited by all the emulsions used on the suint-free wool was a tendency to break after the first three or four wool samples had been dipped, presumably owing to the lack of surface-active compounds such as the potassium salts of fatty acids present in suint,[19] so that the curves of Fig. 2 show the effects of mechanical loss of insecticide as well as depletion: they will also be subject to a greater sampling error than those of Fig. 1.

Differences between insecticides.—Comparison of the curves of Fig. 1 shows that they can be grouped into two pairs, A and B being similar in shape and showing a high rate of depletion, while C and D are of 'opposite' shape and depletion is less pronounced.

If the first three experimental points of curves A and B are ignored and the extrapolated curves considered, their shape is seen to be similar to that associated with the adsorption of a solute from solution and can be shown to agree reasonably with the 'classical adsorption isotherm':

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c$$

where x = weight of solute adsorbed, m = weight of adsorbent, c = equilibrium concentration of the solution and k and n are constants. Fig. 6, which is derived from the extrapolated curves, indicates an approximately linear relation between the logarithm of the weight of insecticide sorbed by each wool sample (x) and the logarithm of the corresponding equilibrium concentration (the weight of sorbent, m, will be approximately constant, although its value will vary slightly owing to the solution of wool-grease in xylene). The values of x have been corrected by subtraction of insecticide mechanically removed as unchanged emulsion. Fig. 4 shows that the depletion of the solvent follows the same pattern as that of BHC and Dieldrin; hence it appears that the globules of xylene containing dissolved insecticide can be regarded as being analogous to

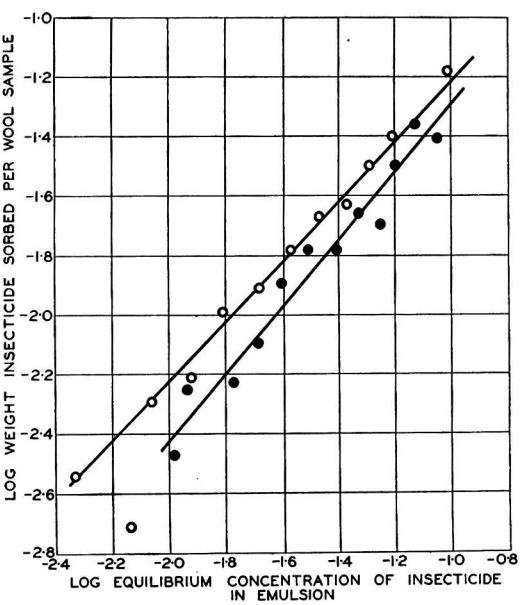


FIG. 6.—*Relation between log(weight of insecticide absorbed) and log(corresponding equilibrium concentration)*

Curve A: BHC emulsion
Curve B: Dieldrin emulsion

the molecules of solute in a solution in contact with an adsorbent, although it is apparent that the quantity of insecticide deposited on the fleece is too great to be accounted for by surface adsorption alone. It may be inferred from electron and *X*-ray diffraction measurements[20, 21] that the cross-sectional area of the γ-BHC molecule is approximately 30 sq. Å, so that a unimolecular adsorbed layer would consist of some 3×10^{17} molecules per g. of wool. The weight of BHC taken up (excluding the mechanical removal of unchanged emulsion) varied between 0·003 and 0·045 g. per sample, i.e. between about 6 and 100 times the weight of a unimolecular layer.

The behaviour of DDT and Aldrin (Fig. 1, C and D) shows no analogy with adsorption from solution. When Figs. 1 and 4 are compared, it is clear that the depletion of xylene in the DDT and Aldrin emulsions follows an entirely different course from that of the insecticides, implying that the uptake of the latter should be examined in the light of their partition between xylene and wool-grease. If the mutual solubility of xylene and grease is disregarded, the Distribution Law requires that

$$\frac{\text{equilibrium concentration of insecticide in xylene}}{\text{equilibrium concentration of insecticide in wool-grease}} = \text{constant}$$

The values found for this ratio are given in Table III. They can only be approximate since a variable, unknown, amount of grease will be dissolved from the wool at each stage, but it can be seen that those for DDT, and to a certain extent those for Aldrin, show reasonable constancy when it is borne in mind that the calculation of the ratio involves the possible summation of a number of other errors. The values of the ratio for BHC and Dieldrin on the other hand extend over a considerably wider range (the highest being some twenty times the lowest) and demonstrate that partition of these insecticides between the two phases is not a limiting factor in their depletion.

Table III

Ratio of concentration of insecticide in solvent to its concentration in wool-grease

Sample	Ratio			
	BHC	DDT	Dieldrin	Aldrin
1	0·44	4·3	0·55	4·6
2	0·65	3·6	0·94	19
3	0·59	3·8	1·0	1·9
4	0·79	4·3	0·67	1·4
5	1·2	6·0	1·5	3·2
6	1·7	9·5	2·0	8·5
7	2·7	4·9	2·3	4·2
8	3·9	5·1	4·8	5·8
9	6·9	9·2	6·4	6·3
10	6·9	5·9	10	8·1
11	11	4·8	6·0	3·5
12	7·4	6·0	8·2	5·8

The shape of the DDT and Aldrin curves can now be qualitatively explained. As the initial uptake of these insecticides is relatively lower than that of their solvent, their concentration in the xylene phase must increase, so that the immersion of fresh samples will result in a higher deposition of insecticide on the wool. As depletion proceeds, a point will be reached where the ratio of wool-grease to the xylene remaining in the emulsion will be high enough to offset the greater xylene-solubility of the insecticide; depletion will then follow a similar path to that of BHC and Dieldrin. This is thought to be the explanation of the inflexions of curves C and D, Fig. 2, referred to previously. Conversely, the departure of the experimental points from the extrapolated depletion curves of BHC and Dieldrin (Fig. 1) may be due to the limitation of depletion by the high ratio of xylene to wool-grease, although the difference between observed and extrapolated values is perhaps too slight to be regarded as significant.

Conclusions

It appears that if the effects of variation of the emulsifying agent are ignored, the depletion of insecticidal emulsions is largely governed by the solubility of the solvent in wool-grease and

the partition of the insecticide between wool-grease and solvent. It follows that the rate of depletion will also be affected by the concentration of insecticide in the solvent and of solvent in the emulsion. A suitable solvent for avoiding excessive depletion would readily dissolve the insecticide while being itself only slightly soluble in wool-grease.

Acknowledgments

The author wishes to thank the Director of the Veterinary Laboratory for permission to publish this work, Mr. M. H. Moore for his valuable technical assistance, Miss N. Smith for the preparations of Figs. 1–6 and Mr. A. R. Philpotts, of the Distillers Co. Ltd., for his analysis of the *o*-xylene used, advice on the estimation of xylene and helpful discussion.

Veterinary Laboratory
Ministry of Agriculture, Fisheries and Food
New Haw, Weybridge
Surrey

Received 5 October, 1955

References

[1] Cragg, J. B., *Nature, Lond.*, 1945, **155**, 394
[2] Heath, G. B. S., & Mitchell, J. G., *Vet. J.*, 1946, **102**, 130
[3] Jolly, D. W., Stones, L. C., Page, K. W., & Brander, G. C., *Vet. Rec.*, 1953, **65**, 131
[4] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1952, **3**, 315
[5] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1952, **3**, 320
[6] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1952, **3**, 330
[7] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1954, **5**, 139
[8] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1954, **5**, 212
[9] Addison, C. C., & Furmidge, C. G. L., *J. Sci. Fd Agric.*, 1954, **5**, 440
[10] Tunnicliff, D. D., Brattain, R. R., & Zumwalt, L. R., *Analyt. Chem.*, 1949, **21**, 890
[11] Wichmann, H. J., Patterson, W. I., Clifford, P. A., Klein, A. K., & Glaborn, H. V., *J. Ass. off. agric. Chem. Wash.*, 1946, **29**, 188
[12] Stepanow, A., *Ber. dtsch. chem. Ges.*, 1906, **39**, 4056
[13] Bohm, E., & Stürz, O., *Chemie*, 1942, **55**, 319
[14] Fiedler, O. G. H., & Du Toit, R., *Nature, Lond.*, 1951, **168**, 608
[15] Du Toit, R., & Fiedler, O. G. H., *Onderstepoort J. vet. Sci.*, 1953, **26**, 65, 405
[16] Speakman, J. B., *Trans. Faraday Soc.*, 1930, **26**, 61
[17] Lennox, F. G., *Commonw. Aust. Coun. sci. industr. Res.*, 1938, Pamphlet No. 83
[18] Laudani, H., *U.S. Dept. Agric., Bureau of Entomology and Plant Quarantine*, 1953, Pamphlet E-858
[19] Freney, R., *Bull. Coun. sci. industr. Res. Aust.*, 1940, **130**, 52
[20] Bastiansen, O., Ellefsen, Ø., & Hassel, O., *Acta chem. scand.*, 1949, **3**, 918
[21] van Vloten, G. W., Kruissink, Ch. A., Strijk, B., & Bijvoet, J. M., *Acta cryst., Camb.*, 1950, **3**, 139

THE NUTRITIVE VALUE OF FISH PROTEINS*

By D. S. MILLER

Commercial fish meals have been examined for their net protein utilization by rats and have been found to be of poorer nutritive value than laboratory fish preparations, which have a net protein utilization of about 80%. The factors responsible are chiefly the conditions of drying and consequent occurrence of the Maillard reaction. No damage was detectable in the dried product after storing for 3 months at room temperature. It is shown that water as well as sugar and protein, is an essential for the Maillard reaction, and it is suggested that anti-Maillard reagents may offer some hope for the prevention of damage during drying. For rats, methionine is the limiting amino-acid in the damaged meals and might be added with advantage to these products.

Introduction

The value of white fish meal as an animal-protein concentrate for the feeding of livestock is well recognized and suggestions have been made that it should be used to supplement human diets. During the war, fish proteins were used as a substitute for egg albumin in bakery and

* Read before the Food Group, 9 February, 1955

confectionery, and recently a trial was undertaken by F.A.O. in Chile on the acceptability of deodorized fish flour incorporated in biscuits.[1] However, deodorization is apparently not appreciated by most protein-deficient communities and further trials by F.A.O., U.N.I.C.E.F., and other organizations are being undertaken with ordinary fish meals.

A literature search yields considerable material describing growth tests on fish meals (e.g., references 1–19) but only a limited number of nitrogen balance studies appear to have been carried out.[20–27] These show a range of values for net protein utilization for oily fish from 41 to 85% and for white fish from 60 to 90%. During the 1930's a number of comparisons were made of products taken from various types of drier[16–22] and these showed that the nutritive value of vacuum-dried meals was better than those produced in steam driers, which in turn were superior to flame-dried meals. However, some recent growth-tests[2–5] have demonstrated that there is little to choose between the three standard methods of drying and, although this is still disputed by some authorities,[11, 14, 15] it may well be a reflection of improved techniques in the industry. The present work was undertaken in view of the wide variation of values reported in the literature and the lack of information regarding the nutritive value of fish meals produced at the present time.

Experimental

The classical method of determining the biological value of proteins is both long and tedious involving N-balances on the experimental animal with test and control diets, a typical procedure[28] giving three results after 7 weeks. The method employed here[29] is based on carcass analysis and is both shorter and less laborious. It gives net protein utilization (N.P.U.), the product of biological value and digestibility, which is that proportion of the intake nitrogen retained by the animal and is normally expressed as a percentage. This value can be derived from body nitrogen determinations as follows:

$$\text{N.P.U.} = [B - (B_k - I_k)]/I,$$

where B and B_k are total body-N, and I and I_k are intake-N, of the animals on test and non-protein diets, respectively.

The ideal would be a measurement of the body-N of the same rat fed both the test protein and starved of protein. This is of course impossible but the equivalent can be achieved by use of control groups. In practice four litters of eight rats are arranged in eight groups of four rats so that each group contains one rat from each litter and each group has the same total weight. Seven of these groups are fed test diets and one group a non-protein diet. At the end of ten days the animals are killed and body-N determined by Kjeldahl digestion of the whole carcass, or alternatively from a relationship between the carcass N/H_2O ratio and age which is independent of diet. This relation calculated from the examination of approximately 350 carcass analyses is:

$$\log (4{\cdot}8 - y) = 0{\cdot}437 - 0{\cdot}0123x$$

where $y = N/H_2O\%$ and x = age in days. Thus at the end of the feeding period the animals are killed, incisions are made into the skull, thoracic and body cavities and a dry weight determination is made. From the age of the rat and its body-water content, one can calculate the body-N and, by substitution in the previous equation, N.P.U. can be determined. Fuller details of the method have been published elsewhere.[29a]

Results and discussion

Methods of drying

A number of commercial fish meals have been assayed with the results shown in Table I. The British meals were obtained from a number of fish meal manufacturers and are the normal products as supplied to the farmer. The N.P.U. values for white fish meals range from 51 to 61%. The oily meal, UK 1, was bought as 'fertilizer' and although no information is available as to its production it can be presumed to have been heated strongly during manufacture. Meals obtained from other countries show substantially the same range of values. The highest the author has obtained is 68% (SA 3), and no sample has yet been examined with greater value than 70% as reported by Sure & Easterling.[27] Meal SA 2 produced by Marine Oils Ltd. of South Africa

is of interest as it was used in the now famous Chile experiment (biscuit acceptability trials with school children). This company now claim to be producing products of higher value.

Table I

% *Net protein utilization (N.P.U.) of some commercial fish meals*

Meal	Fish	Drier	N.P.U.	S.E.	*n*
UK 1	Oily	—	33·1	± 2·2	5
2	White	Steam	51·0	± 3·3	6
3	White	Steam	57·3	± 3·2	6
4	White	Steam	61·4	± 2·4	8
5	White	Steam	58·2	± 0·8	5
6	Dogfish	Steam	52·5	± 1·5	2
N 1	White	—	62·2	± 2·0	2
SA 1	Pilchard	—	33·0	± 2·0	3
2	Deodorized	—	67·0	± 1·8	4
3	White	—	68·3	± 2·4	3

In comparison with these commercial materials, carefully dried laboratory products show much higher values (Table II, Nos. 1*a–c*). Sample 1*c* was dried *in vacuo* with infra-red heating; No. 1*a* by repeated washing with acetone until the residual water was less than 5% and then spreading out in air to allow evaporation of the acetone; No. 1*b* was prepared by stirring the fish material with N-caustic soda solution for 3 hours, filtering to remove the bones and other insoluble matter, then precipitating at pH 4, washing to remove salt, and acetone drying. All these samples gave N.P.U. values approximating to 80, showing this to be the value of undamaged fish. The products so obtained are superior to casein and meat proteins but inferior to egg protein.[30]

Table II

% *Net protein utilization (N.P.U.) of some laboratory cod preparations*

No.	Treatment	N.P.U.	S.E.	*n*
1*a*	Acetone-dried	79·5	± 3·5	4
b	Extracted proteins	80·3	± 2·2	9
c	Heat-dried (50° max.)	83·0	± 1·0	2
d	Heat-dried (70° max.)	73·0	± 1·4	3
e	Heat-dried (100° max.)	66·0	± 2·9	3
f	Heat-dried (120° max.)	63·0	± 3·0	3
2*a*	Extracted proteins	78·6	± 1·9	3
b	2*a* heated for 24 h. at 50°	75		
c	2*a* ,, ,, ,, ,, 65°	71		
d	2*a* ,, ,, ,, ,, 95°	76		
e	2*a* ,, ,, ,, ,, 105°	70·0	± 1·0	3
3*a*	Extracted proteins	72·3	± 3·2	4
b	3*a* heated for 24 h. with 0% H_2O	65·0	± 2·0	3
c	3*a* ,, ,, ,, ,, 9% ,,	43·0	± 1·0	3
d	3*a* ,, ,, ,, ,, 17% ,,	40·0	± 3·0	3
4*a*	Extracted proteins	80·0	± 3·4	4
b	4*a* heated for 24 h. at 0% R.H.	70·0	± 1·0	2
c	4*a* ,, ,, ,, ,, 23% ,,	66·0	± 1·3	2
d	4*a* ,, ,, ,, ,, 69% ,,	63·5	± 0·5	2
e	4*a* ,, ,, ,, ,, 97% ,,	62·5	± 0·5	2
5*a*	Acetone-dried	68·3	± 0·6	2
b	Wet storage for 7 days, then acetone-dried	70·8	± 0·1	2
6*a*	Extracted proteins	77·0	± 4·0	3
b	,, ,, , wet storage for 4 days	78·5	± 3·5	3
c	,, ,, , ,, ,, ,, 8 ,,	81·5	± 3·5	3
7*a*	Extracted proteins	78·6	± 0·6	3
b	,, ,, , dry storage for 100 days	79·3	± 3·5	3

These laboratory-dried products were light white powders in comparison with the brown colour of commercial fish meals and the increase in their nutritive value is probably due to avoidance of the Maillard reaction.[31] This reaction—sometimes known as the browning reaction—is said to lead to the formation of complexes between amino groups and reducing sugars. These complexes are not metabolized by the animal and some amino-acids are rendered unavailable, thus lowering the nutritive value. In the case of fish the sugar could be derived free from body fluids or from loosely bound sugar in nucleo- and glyco-proteins. Recent work by Tarr[32] shows that the browning of fish is correlated with the free pentose in the original material and there is liberation of ribose from a number of compounds by an enzyme system present in the flesh of fish.[33] It has also been shown[33, 34] that pentoses are considerably more active than hexoses in the Maillard reaction: the most active compound is glucuronic acid which is freely distributed in the animal kingdom and can be presumed present in fish.

In the original paper of 1912, Maillard states that the reaction is chiefly influenced by the temperature, being violent at 150°, rapid at 100°, slow at 37° and observable after a period of some weeks at 0°. An attempt was therefore made to dry fish under conditions of controlled temperature with the results shown in Table II (Nos. 1*c–f*). The fish was spread out on metal sheets and the temperature of the metal was kept constant. The results show an increasing degradation with rise in temperature. As far as can be ascertained, a large proportion of the driers in this country rely on steam as a source of heat where maximum drying temperature will be little more than 100°, but Lovern[35] has described flame driers where the inlet temperature is approx. 1000° and such machines are said to be working efficiently if the meal is not scorched; some driers working at reduced pressure are now in use. The temperature of the material itself during drying is difficult to measure because of the evaporative changes taking place, and it is notable that even with flame driers the outlet air temperature is as low as 75°.

In view of this difficulty, further work was confined to fish proteins prepared from fish house waste and subjecting them to constant conditions which could be more easily controlled. In this way factors such as vitamin and oil content which have tended to complicate previous growth experiments (e.g., references 3–6, 17, 21) are also eliminated. The protein so prepared is not so readily degraded by heat as the whole fish (Table II, samples 2*a–e*). This is in agreement with Tarr *et al.*[14] who found no fall in nutritive value with low-temperature herring meals which had been heated after drying.

Effect of moisture

Heat treatment of the fish protein in the presence of moisture, however, resulted in more marked degradation and loss of nutritive value. The results where the protein was heated with different amounts of added water in sealed jars, are given in Table II (Nos. 3*a–d*). The work of Lea & Hannan[36] has demonstrated an interesting relationship between degree of browning and relative humidity. These authors used casein/glucose mixtures with an excess of sugar and showed that the loss of amino-groups rises to a peak at 70% relative humidity, with minimum losses at the dry and wet extremes. This phenomenon might have some bearing on the practical design of fish driers, but it was not confirmed with cod proteins (Table II, Nos. 4*a–e*). The relative humidity in these experiments was controlled by the use of saturated salt solutions; the protein was heated in closed containers in the presence of, but out of contact with the solution. If the work of Lea & Hannan were applicable, the meal treated at 69% relative humidity should show a minimum value, but this was not the case for there was a gradual decrease in N.P.U. as the relative humidity, at which the protein was heated, increased.

Effect of storage

Even with the most careful treatment, variations in dried fish preparations are apparent and even materials which have not been subjected to heat have given, though very infrequently, N.P.U. values below 70%. In view of Maillard's original statement that browning takes place slowly even at 0°, it was thought that the period of storage of the fish used in these experiments, prior to receipt, might be responsible for these variations, but this hypothesis was not confirmed by experiment (Table II, Nos. 5*a–7b*).

A batch of frozen cod fillet was purchased and divided into two (Nos. 5*a* and *b*), one half being acetone-dried at once, and the remainder after 7 days at room temperature. This was not a good quality material, but despite obvious bacterial contamination after the 7 days, the N.P.U. was unchanged. In another experiment (Nos. 6*a–c*), some frozen cod fillet was dissolved in NaOH solution, the solution filtered and the protein precipitated with HCl, and stored in the salt curd state where bacterial contamination was at a minimum. The results again showed no change in N.P.U. Several authors[5, 7, 37] have shown that no toxic effects result from feeding decomposed fish meal, and these results tend to confirm this. Finally, it has not been possible to detect damage of dry cod proteins stored at room temperature over a period of 3 months (Nos. 7*a* and *b*).

Limiting amino-acid

From the work of Lea & Hannan[38] lysine is the most susceptible amino-acid in the Maillard reaction and under their conditions $\frac{2}{3}$ of the available lysine had disappeared from casein after a period of 5 days at 37°; subsequently, feeding tests with this material by Henry & Kon[39] showed a drop in biological value from 78 to 62. Analytical work with fish products[4, 40–42] has shown that the availability of lysine as well as other amino-acids diminishes as a result of heat treatment, and in a growth test with chicks Tarr and others[14] report that the addition of lysine to an over-heated herring meal improved its nutritive value slightly. However, supplementation of five fish meals with lysine did not improve their N.P.U. (Table III).

Table III

Net protein utilization of fish meals supplemented with lysine and methionine. % Net protein utilization and standard error

Meal	No addition	+ 5% L-lysine	+ 2% DL-methionine	Methionine response
UK 1	33·1 ± 2·2	35	48·8 ± 0·8 (5)	47%
4	61·4 ± 2·4	60	69·5 ± 0·7 (3)	13%
5	58·2 ± 0·8	57	68	17%
6	52·5 ± 1·5	55	62	18%
SA 1	33·0 ± 2·0	29	52	58%

The limiting amino-acid was therefore determined biologically by supplementing the protein with triads of the nine essential amino-acids of the rat. Triads were used to minimize the number of tests required. The experimental design and results are shown in Table IV. Each row and each column represent a test in which the protein was supplemented with three amino-acids. It will be seen that the greatest response was with the second row and first column indicating methionine, which was common to both triads, as the limiting amino-acid. Subsequent supplementations confirmed this (Table III). The greatest response was shown with the

Table IV

Net protein utilization (N.P.U.) of a commercial fish meal supplemented with triads of amino-acids

Meal UK 4 alone, N.P.U. = 61·4 ± 2·4

Histidine	Lysine	Tryptophan	65
Methionine	Threonine	Leucine	69
Valine	*iso*Leucine	Phenylalanine	56
70	60	63	

poorer meals, but the nutritive value of each was improved. In no case, however, does the addition of methionine raise the N.P.U. of these commercial fish meals to the value of 80 obtained with laboratory-dried fish, so that methionine may not be the only amino-acid rendered unavailable during processing.

Good agreement was obtained between the method used here and the gross protein values obtained with chicks by Carpenter & Ellinger[43] at the Rowett Research Institute when feeding diets based on practical poultry rations.

More recently these authors[44, 45] found a correlation between chemically determined ' available lysine ' and gross protein values. This may be due to a different amino-acid requirement of the chick or the ' available lysine ' content may reflect the extent of Maillard reaction and the concomitant degree to which methionine has been rendered unavailable. The value of methionine supplementation of chick diets is shown by American workers,[45a–e] while Reed *et al.*[46] and Saxena & McGinnis[47] obtain best results with methionine and fish meal.

Inhibition of the Maillard reaction

A preliminary attempt has been made to find ' anti-Maillard ' substances which could serve a purpose similar to that of antioxidants in the oils and fats field. Two attempts made involve points of some theoretical interest. Tarr & Bissett[48] have reported that the browning of fish during drying can be minimized by first storing the fish at 0° for 2 days in the presence of the live cells of *Lactobacillus pentoaceticus*. This organism is reputed to have ribose-oxidase activity and is used in the same way that glucose oxidase is used to prevent browning in the drying of eggs.[49–51] If it is possible to remove all the free sugar, no browning should take place, but attempts in these laboratories to reproduce this effect have so far been unsuccessful.

Sulphur dioxide has been suggested as a means of preventing the browning reaction and is used in the fruit and other industries[52–54] to prevent brown coloration of the Maillard type. In an experiment where proteins and water were heated in a container through which there was a free flow of sulphur dioxide, there was an absence of brown coloration compared with the control through which nitrogen had been passed under the same conditions. However, the N.P.U. of these products showed no significant difference being, respectively, $64 \pm 1{\cdot}0$ and $61{\cdot}0 \pm 1{\cdot}0$; both were damaged in comparison with the untreated material which gave a value of $80{\cdot}0 \pm 0{\cdot}6$. Subsequent experiments showed that brown meals can be easily bleached by SO_2.

Another possibility to be investigated is the use of small quantities of amino-compounds as suggested by Bate-Smith & Hawthorn,[49] which might react with the free sugars and leave the protein undamaged. This principle in reverse has been demonstrated with fruit juices, whereby formaldehyde is added to remove small traces of amino-compounds from sugar solutions.[52] In this respect cysteine is of interest as it is said to form a colourless Maillard compound.[55]

Conclusions

It is apparent from the experiments here described that the protein quality of commercial fish meals is impaired to a variable extent during the drying process; this impairment is due to the action of heat in the presence of moisture and is the result of the Maillard reaction. Since moisture is inevitably present in the fish body, the damage during processing can only be minimized by low-temperature drying, unless some anti-Maillard substance can be found. The N.P.U. could, however, be raised by the addition of a small percentage of methionine, but the optimum amount, practicability, and economics of this must await field trials. On storage, fish meals retain their feeding value for at least 3 months.

Acknowledgments

I wish to thank the directors of The Crookes Laboratories Ltd. for permission to publish this paper, Marine Oils Ltd. (South Africa) for permission to include a result on one of their meals, and Miss J. Roberts for much of the animal work.

The Crookes Laboratories Ltd.
37–43 Gorst Road
Park Royal
London, N.W.10

Received 25 March, 1955: amended manuscript, 18 October, 1955

References

[1] F.A.O., *Memorandum*, 1954, **3**, No. 9, 4
[2] Carpenter, K. J., Ellinger, C. M., & Shrimpton, D. H., *Proc. Nutr. Soc.*, 1954, **13**, xx
[3] Clandinin, D. R., *Poult. Sci.*, 1949, **28**, 128
[4] Southcott, B. A., & Tarr, H. L. A., *J. Fish. Res. Bd Can.*, 1953, **10**, 64
[5] Lanham, W. B., & Nilson, H. W., *Comm. Fish. Rev.*, 1947, **9**, No. 8, 1
[6] Bieley, J., Tarr, H. L. A., *Progr. Rep. biol. Sta. Nanaimo & Vancouver*, 1951–54, **85**, 83; **87**, 42; **89**, 79; **90**, 11; **90**, 14; **92**, 10; **94**, 27; **99**, 12

[7] Lassen, S., Bacon, E. K., & Dunn, H. S., *Industr. Engng Chem. (Industr.)*, 1951, **43**, 2082
[8] Drummond, J. C., *J. Physiol.*, 1918, **52**, 95
[9] El Raw, I., & Geiger, E., *J. Nutr.*, 1952, **47**, 119.
[10] Evans, R. J., Carver, J. S., & Carrol, I. D., *Arch. Biochem.*, 1944, **3**, 337
[11] March, B. E., Stupich, D., & Bieley, J., *Poult. Sci.*, 1949, **28**, 718
[12] Evans, R. J., Carver, J. S., & Hamm, W. S., *Poult. Sci.*, 1944, **23**, 491
[13] Lanham, W. B., & Lemon, J. M., *Food Res.*, 1938, **3**, 549
[14] Tarr, H. L. A., Bieley, J., & March, B. E., *Poult. Sci.*, 1954, **33**, 242
[15] Rhian, M., Carver, J. S., Harrison, R. W., & Hamm, W. S., *Bull. Wash. St. agric. Exp. Sta.*, 1942, **416**, 3
[16] Daniel, E. P., & McCollum, E. V., *Rep. U.S. Bur. Fish.*, 1931, No. 2
[17] Maynard, L. A., Bender, R. C., & McCay, C. M., *J. agric. Res.*, 1932, **44**, 591
[18] Oshima, K., & Itaya, S., *Bull. agric. chem. Soc. Japan*, 1938, **14**, 512 (English summary p. 42)
[19] Wilgus, H. S., Norris, L. G., & Heuser, G. F., *Industr. Engng Chem. (Industr.)*, 1935, **27**, 419
[20] Maynard, L. A., & Tunison, A. V., *Industr. Engng Chem. (Industr.)*, 1932, **24**, 1168
[21] Schneider, B. H., *J. agric. Res.*, 1932, **44**, 723
[22] Wilder, O. H. M., *J. agric. Res.*, 1934, **49**, 715, 723
[23] Du Toit, B. A., & Smuts, D. B., *Onderstepoort J. vet. Sci.*, 1941, **16**, 191
[24] Bender, A. E., Miller, D. S., & Tunnah, E. J., *Proc. Nutr. Soc.*, 1953, **12**, ii
[25] Beveridge, J. M. R., *J. Fish. Res. Bd Can.*, 1947, **7**, 35
[26] Allison, J. B., *Advanc. Protein Chem.*, 1949, **V**, 155
[27] Sure, B., & Easterling, L., *J. Nutr.*, 1952, **48**, 401
[28] Henry, K. M., Kon, S. K., & Watson, H. B., 'Milk and Nutrition', 1937, pt. 1, p. 37 (Reading: National Institute for Research in Dairying)
[29] Bender, A. E., & Miller, D. S., *Biochem. J.*, 1953, **53**, vii
[29a] Miller, D. S., & Bender, A. E., *Brit. J. Nutr.*, 1955, **9**, 382
[30] Block, R. J., & Mitchell, H. H., *Nutr. Abstr. Rev.*, 1946, **16**, 249
[31] Maillard, L. C., *C.R. Soc. Biol., Paris*, 1912, **72**, 599
[32] Tarr, H. L. A., *Nature, Lond.*, 1953, **171**, 344
[33] Tarr, H. L. A., *Food Tech., Champaign*, 1954, **8**, 15
[34] Lewis, V. M., & Lea, C. H., *Biochim. biophys. Acta*, 1950, **4**, 532
[35] Lovern, T. A., *Fish. News, Aberd.*, 1951, 1987
[36] Lea, C. H., & Hannan, R. S., *Biochim. biophys. Acta*, 1949, **3**, 313
[37] Barrow, A. L., Garrard, E. H., & Branion, H. D., *Canad. J. comp. Med.*, 1950, **14**, 42
[38] Lea, C. H., & Hannan, R. S., *Biochim. biophys. Acta*, 1950, **5**, 433
[39] Henry, K. M., & Kon, S. K., *Biochim. biophys. Acta*, 1950, **5**, 455
[40] Bissett, H. M., & Tarr, H. L. A., *Poult. Sci.*, 1954, **33**, 250
[41] Ingvaldsen, T., *Canad. Chem. Metall.*, 1929, **13**, 97
[42] Ingalls, R. L., *et al.*, *Bull. Mich. agric. Exp. Sta.*, 1950, 219
[43] Carpenter, K. J., & Ellinger, G. M., private communication, 1955
[44] Carpenter, K. J., & Ellinger, C. A., *Poult. Sci.*, 1954, **34**, 1451
[45] Carpenter, K. J., & Ellinger, C. A., *Biochem. J.*, 1955, **61**, Proc. xi
[45a] Bird, H. R., & Mattingley, J. P., *Poult. Sci.*, 1945, **24**, 29
[45b] Gerry, R. W., Carrick, C. W., & Hauge, S. M., *Poult. Sci.*, 1948, **27**, 181
[45c] Saxena, H. C., & McGinnis, J., *Wash. agric. Exp. Sta.*, 1952, Circ. 197
[45d] Matterson, L. D., *et al.*, *Poult. Sci.*, 1953, **32**, 817
[45e] Rosenberg, H. R., *et al.*, *Poult. Sci.*, 1955, **34**, 1308
[46] Reed, J. R., Quisenberry, J. H., & Couch, J. R., *Poult. Sci.*, 1954, **33**, 41
[47] Saxena, H. C., & McGinnis, J., *Poult. Sci.*, 1952, **31**, 934
[48] Tarr, H. L. A., & Bissett, H. M., *Progr. Rep. biol. Sta. Nanaimo & Vancouver*, 1954, **98**, 3
[49] Bate-Smith, E. C., & Hawthorne, J. R., *J. Soc. chem. Ind., Lond.*, 1945, **64**, 297
[50] Stewart, G. F., Best, L. R., & Lowe, B., *Proc. Inst. Fd Tech.*, 1943, p. 77
[51] Kline, R. W., Sonoda, T. T., & Hanson, H. L., *Food Tech., Champaign*, 1954, **8**, 343
[52] Stadtman, E. R., *Advanc. Food Res.*, 1948, **1**, 325
[53] Gehman, H., & Osman, E., *Advanc. Food Res.*, 1954, **5**, 53
[54] Mackinney, G., Friar, H. F., & Balog, E., *Fruit Prod. J.*, 1943, **22**, 294, 315
[55] Kline, R. W., & Fox, S. W., *Iowa St. Coll. J. Sci.*, 1946, **20**, 265

FUMIGATION OF AGRICULTURAL PRODUCTS. XIV.*—Treatment of Peas and Beans with Methyl Bromide

By O. F. LUBATTI and R. E. BLACKITH

Peas and beans are notably resistant to damage by methyl bromide fumigation. Even when these seeds contain as much as 19% water, they may safely be fumigated at concentration–time products sufficient to control the infestation of legumes with insects usually found in stored products. Peas and beans differ from onion seed and groundnuts in that the damage done by fumigation is substantially independent of the moisture content of the seed. They will, nevertheless, deteriorate if stored at more than about 15% moisture content from the action of the moisture by itself. However, as with the other seeds, peas and beans

* Part XIII: *J. Sci. Fd Agric.*, 1956, **7**, 149

that survive damp storage or fumigation with methyl bromide give essentially the same yield as do untreated seeds. Attempts to relate the results of germination tests in sand to viability tests with tetrazolium salt have proved difficult, although damage to the seeds could be detected by this method.

Previous parts of this series have described the effects of methyl bromide fumigation on the germination and growth of oily seeds such as groundnuts and onion seeds.[1, 2] Insect infestation of the less oily legumes, such as cowpeas, is of great importance in tropical regions, and in this paper the treatment of peas and beans is described, these hardier plants being more appropriately studied under English conditions, as well as being in themselves of interest. The peas, Market Gem, and beans, Prolific Longpod, were each divided into twelve groups, severally allotted to one of four moisture contents (13, 15, 17, or 19%) and one of three fumigation treatments (concentration–time products of 1000 mg.h./l. and 400 mg.h./l. or control, unfumigated seeds). The peas and beans were found to have the initial moisture contents of 15·1 and 14·7% respectively.

The methods by which the seeds were conditioned to known moisture contents, and then fumigated, were similar to those which have recently been described.[2] The moisture contents given above are in any event a rough guide, because different parts of one seed and *a fortiori* seeds of different species are of different moisture contents when in equilibrium with a fixed relative humidity.

Experimental

Conditioning and determination of the moisture content of seeds

In order to obtain a range of seeds of different moisture content, 250-g. batches of peas and 1000-g. batches of beans were allowed to take up moisture in the humid atmosphere of a cabinet or were dried in a large desiccator over calcium chloride.

The conditioning cabinet, 41 × 34 × 29 in., made of timber is provided internally with an air-circulation system. The atmosphere is humidified by placing in the cabinet three flat glass basins 17 cm. diameter, containing water. Evaporation is facilitated by dipping wicks, consisting of narrow strips of filter paper, in the water of the basins. The internal surface of the cabinet was protected by the application of several coats of paint. The internal temperature of the cabinet was thermostatically controlled at 20°.

The progress of wetting was determined by rapidly transferring the seed from the shallow metal trays used for conditioning, to tared metal boxes, which were weighed on a suitable balance.

In the case of the dry batches the loss of weight was ascertained at intervals by withdrawing from the desiccator the seeds contained in a muslin bag and weighing them enclosed in a tared metal box.

The conditioned batches of seed were stored in air-tight jars.

The moisture content determination was similar to the two stage air-oven method specified in the Handbook of the Official Grain Standards of the U.S. Department of Agriculture.[3] Proportionally larger amounts of seed were used in the first stage of the specified procedure, viz. 100 g. for peas, 150 g. for beans.

The moisture content of the seeds used is given in Table I. This range straddles the critical levels for which sorption of methyl bromide on peas and beans is minimal.

Fumigation of the peas and beans

The glass jars containing the seeds were stored in a constant-temperature room at 20°. Two hundred g. of peas or 750 g. of beans from the jars were quickly weighed on a rough balance and transferred to the appropriate fumigation chamber, which was immediately closed.

This type of chamber has been described by Lubatti & Smith,[4] and is of cylindrical metal, 20 l. capacity, provided with a suitable ampoule breaker and sampling taps.

The chamber was left in the constant-temperature room for 48 hours. Over this period of time, the seed under test conditions the atmosphere of the chamber. A glass ampoule containing a weighed amount of methyl bromide was then fractured in the ampoule breaker. The chamber,

resting on its side, was rolled gently to and fro about 20 times so as to distribute evenly the vaporized fumigant, then kept in the constant-temperature room for the allotted time.

Determination of the concentration of the fumigant

Duplicate gas samples were collected from the chamber about 15 minutes before the end of fumigation. The details of the sampling technique and the method of determination are given by Lubatti & Blackith.[2]

As shown by Lubatti & Smith[4] the internal surface of the chamber as well as the material to be fumigated participate in the sorption of methyl bromide. In order to assess the concentration–time product it was therefore necessary to determine the rate of fall of concentration in the chambers with the load of 200 g. of peas and 750 g. of beans during the 24-h. duration of the tests.

The integrated concentration can be calculated graphically from the area under the curve showing the rate of fall of the concentration.

This was done in a series of preliminary experiments. The initial concentrations of fumigant and the load of peas and beans used were closely the same as employed in the final tests. In these tests only the final concentration of fumigant was determined and for the purpose of calculating the concentration–time product the rate of fall was assumed to be the same as that obtained in the preliminary tests. This procedure was found necessary to avoid a very large number of determinations; the nature of the experiments does not demand extreme accuracy.

The concentration–time products calculated by this method are given in Table I.

Table I

Moisture contents and fumigation treatment of peas and beans

Peas (Market Gem)		Beans (Prolific Longpod)	
Moisture content %	Concn.–time product (mg.h./l.)	Moisture content %	Concn.–time product (mg.h./l.)
13·1	440 970	13·3	400 950
15·1	390 980	14·7	360 930
16·9	400 960	17·2	390 920
19·9	390 990	19·6	380 960

Design of the experiments

The germination tests in sand

The biological responses of the seeds were tested three months after fumigation, during which period the seeds were maintained at the moisture contents to which they were initially conditioned.

With twelve rows of seeds in each replicate of the experiment, a complete replicate could be accommodated in a 4 × 4 ft. wooden seed-box, allowing 35 seeds in each row. Six such boxes, containing 3 in. of sharp sand, were sown in April 1955 immediately after other seeds were set in the open. The six boxes contained three complete replicates of the experiment on peas, and three of that on beans. These germination tests were performed in a warm glasshouse.

Daily records of emergence were kept, and after two weeks the heights of the pea seedlings were measured. The plants were then lifted, before being weighed, washed free from sand, and allowed to dry on wire netting until all superficial water had evaporated, but not until the leaves had begun to wilt. The bean seedlings were treated similarly after three weeks of growth. Seeds that had failed to germinate satisfactorily were separately recorded as ' dead '. Despite the provision of wire-netting covers for the seed-boxes, some losses unconnected with the treatments were experienced, and these have been allowed for in the covariance analysis of the data.

Viability tests with 'tetrazolium salt'

Fifty seeds of each moisture content and fumigation treatment were soaked in plain water for 17 h. and then divided between the cotyledons and along the radicle. The half-seeds were immersed for 3 h. in a freshly prepared 2% solution of 'tetrazolium salt' and then washed with plain water, and the viability of the seed judged from the extent and intensity of the staining.

The field trials

Similar trials were sown in the open in light soil, again providing three complete replicates of the experiment on each variety. Seventy seeds, set 4 in. apart, made up each of the rows, which were 20 in. apart. As in the germination tests, the 12 treatment combinations were allotted their positions in each block by a fresh randomization for each replication.

Daily emergence records were made. Trapping and extensive use of guard rows round the plots kept losses by mice and birds at an unusually low level. Conditions for growth were excellent throughout the season, and heavy yields were obtained when the crops were harvested at the end of July. The produce from each row was weighed separately in two fractions, picked a week apart, in order to simulate commercial harvesting as closely as possible.

At the end of June, an auxiliary measurement of the height of each bean plant was made, but the habit of growth of the peas precluded this measurement for this crop.

Results

Germination trials

The influence of the various treatments on the germination of peas and beans was clearly defined and is shown in Table II. A notable feature is that both plants react alike to fumigation and to storage at different moisture contents. This similarity is the more striking because these results differ from those found in earlier work with onion seed and groundnuts. Previously, a critical set of conditions was found, such that more severe treatments killed most of the seeds. In the present experiment, although the moderate treatment of 400 mg.h./l. diminished the germination of peas by 6·7%, and that of beans by 25·2%, the much more severe dosage of 1000 mg.h./l. left 77·9 and 46·0% alive respectively. These reductions are significant at the 0·1% level.

A further, unexpected, result was that no significant interaction between moisture content and fumigation damage was detected. The damage done by the fumigant was essentially the same whether the seed was dry or damp. Further, this damage to the seed is confined to those which fail to produce shoots above the ground. No significant influence of fumigation or of dampness in storage was found in the course of an analysis of covariance, in which the differences in the heights and weights of the young plants are distinguished from the differential germination capacity of the variously treated seeds.

Viability tests

Considerable difficulty was experienced in assessing the viability of the stained seeds, between 10 and 50% of the seeds in each category being indeterminate. The results of this test are set out in Table II with the germination tests for comparison. Batches of seed which had been damaged by the treatments give reasonably good agreement when tested by either method. Curiously, it is the undamaged seed for which disagreement is more pronounced. A plausible explanation is that untreated seeds contain a proportion of less virile individuals, which, whilst viable if no further hardship is imposed on them, are susceptible to treatments which the normal seeds survive. These less virile seeds might well give indeterminate staining when soaked in tetrazolium salt solutions.

Despite these difficulties of assessment, the staining test gave significant indications of the influence of fumigation damage, of damp storage, and of the slightly greater tolerance of peas than of beans to fumigation, results in accord with those from the full germination tests in sand.

Table II

% Germination of treated peas and beans

Fumigation treatment (mg.h./l.)	Peas			Beans		
	Sand (glasshouse)	Soil (open)	Tetrazolium salt	Sand (glasshouse)	Soil (open)	Tetrazolium salt
Controls	74·5	70·7	52·0	90·0	78·2	73·0
400	69·5	62·7	64·5	67·4	65·0	83·5
1000	58·1	52·9	58·5	41·4	37·5	55·6
Moisture content %						
13	78·7	68·1	79·3	71·1	65·6	78·0
15	73·7	69·0	65·3	71·1	66·7	78·7
17	73·3	66·2	49·3	69·2	61·6	69·3
19	43·8	45·2	39·3	53·7	47·1	56·7

Field trials

The heights of the bean plants reflect damage done to the seeds by fumigation. The average height of the beans given 400 mg.h./l. is slightly, though not significantly, greater than that of the controls. Plants from seeds given 1000 mg.h./l. were on an average shorter by 4·4 cm. or 5% of the heights of the controls ($P < 0{\cdot}001$). There was no evidence, from the heights of the plants, that the higher moisture contents were deleterious, except for weak evidence of an interaction between moisture content and fumigation damage ($0{\cdot}05 > P > 0{\cdot}01$).

The analysis of the heights of the plants contained two estimates of experimental error, that between plants in the same row, and that between rows treated alike, with block differences eliminated. Despite the fact that the blocks were almost square on the ground, plants within rows were highly significantly less variable than were rows treated alike. These differences reflected a marked height gradient, running across the blocks and accounting also for large mean differences between blocks. This gradient illustrates the unpredictability of field experiments, since this same piece of ground had appeared to be free from fertility gradients when sown with onions the previous year.[2]

The yields of the rows were adjusted, by means of a covariance analysis, for the number of plants in the stand. This method of analysis is preferable to one in which the yields per plant are computed because the yield per plant is to some extent influenced by the spacing, and this in turn is wider for rows in which some seeds have failed to germinate as a result of the treatments received by them.

There were no significant differences among the yields of the rows, when so analysed, according to the treatments given to the seeds.

The analysis of the number of seeds germinating in each row, which preceded the covariance analysis, confirmed the results obtained from the glasshouse experiments, as Table I shows. Of particular importance is the confirmation of the absence of any significant modification of the fumigation damage by the moisture content of the seeds. American results suggest that such an interaction may occur when kidney beans receive a nominal dose of 720 mg. h./l. of methyl bromide,[5] but this effect is still weak by comparison with that found with other types of seed.[1, 2] However, American work discloses that severe damage is induced when the beans are fumigated more than once.[5]

Discussion

The outstanding result from this work has been the disclosure of exceptional resistance to fumigation and to dampness in these less oily leguminous seeds. Unlike the onion seed, groundnuts, or potatoes previously examined, no clearly critical combination of moisture content and dosage was found for these legumes, separating lethal treatments from essentially harmless ones. The increase of responses for a given increase of fumigant dosage is but slight—in the language of biological assays the regression line is flat. We may borrow further from experience with biological assay, and divide the possible causes of this low slope into the two main sources, a wide

range of tolerances among the seeds once the methyl bromide has penetrated to the site of action, alternatively, the poor penetration of the fumigant to its site of action. Stringer[6] has shown how these two properties of a bio-assay system lead to flat regression lines. The freedom of access of fumigant to its site of action is known as its availability.

The decision between these alternatives is important for a proper understanding of the mode of action of fumigants. Two investigations are being put in hand, the one a cytological study of damage to root tips, the other a study of the moisture contents of seeds, and of parts of seeds, in equilibrium with known relative humidities. Despite their preliminary nature, we can already say that the latter investigation shows that peas of 19·9% moisture content absorb water more rapidly than those of 13% moisture. This result suggests, as Lubatti[7] has already noted, that the seed coat is rendered more permeable at higher moisture contents. However, under the favourable germination conditions of the glasshouse tests, the initially moister seeds showed no greater damage attributable to fumigation than did those which were drier. Changes of availability, therefore, do not seem to be of great importance to the magnitude of the damage done by methyl bromide, which fact suggests that the seeds have, intrinsically, a wide range of tolerances to methyl bromide. This conclusion is, however, tentative.

A close inspection of those seedlings which have obviously been damaged suggests that these legumes possess exceptional regenerative powers, and this ability of the radicle to remain alive until a destroyed root system can be grown afresh is probably the clue to the differences between these legumes and the other plants whose responses to methyl bromide have been studied. The tip of the radicle is the most sensitive part of the seed and may be discoloured and damaged as far back as the junction with the endosperm. Only if both shoot and root are severely damaged will the seeds rot in the ground. If the root alone is destroyed the seed puts out its shoot which may remain alive for many weeks, often distorted into an arc with the leaves still imprisoned within the cotyledons. The balance between restoration of the root system from the unusually restricted tissue available, or the death of the seed, probably depends substantially on the fungal attack on the individual seed, a circumstance unlikely to be connected with the fumigation treatment.

This balance is likely to depend on the cultural conditions. Perhaps this dependence is the reason why neither fumigation nor damp storage affect the growth of plants in sand, but diminish growth in soil. In unfavourable seasons this evidence of damage may become more marked, although our results suggest that the ultimate yield is less likely to be affected.

One fact which emerges from this discussion is that each type of seed needs a separate investigation. The results of experiments with fumigated groundnuts, for instance, cannot be generalized to cover the responses of legumes such as peas and beans, the different responses of which may be associated with their reduced content of oil.

Acknowledgments

This work has been supported by a grant from the Agricultural Research Council, for which we are grateful. We are glad to acknowledge the assistance of Miss M. Roberts in this work.

Imperial College Field Station
Sunninghill
Berks.

Received 7 November, 1955

References

[1] Somade, H. M. B., *J. Sci. Fd Agric.*, 1955, **6**, 799

[2] Lubatti, O. F., & Blackith, R. E., *J. Sci. Fd Agric.*, 1956, **7**, 149

[3] U.S. Dept. of Agric., 'Handbook of the Official Grain Standards'

[4] Lubatti, O. F., & Smith, B., *J. Soc. chem. Ind.*, 1948, **67**, 347

[5] California Dept. of Agric., Seed Fumigation Circular No. 8, and Suppl. No. 1, Aug. 1955

[6] Stringer, A., *Ann. appl. Biol.*, 1948, **35**, 527

[7] Lubatti, O. F., *Nature, Lond.*, 1945, **155**, 572

A STUDY OF THE STRUCTURE OF MILK CRUMB

By JAMES SAUNDERS

An indication of the structure of milk crumb has been obtained by studying its water sorption isotherm together with those of its components.

During the vacuum drying of a sucrose–milk mixture, a proportion of a material is formed with a greater affinity for water vapour. There is no evidence of complex formation between the other ingredients of milk crumb.

A preliminary examination of the mixture containing the sucrose–milk complex was made. There was no evidence of any effect on the flavour or the viscosity of milk chocolate containing such material.

It is deduced that there is no interaction involving hydrophilic groups between milk and chocolate liquor during milk crumb manufacture.

Introduction

As part of an investigation into the structure of milk chocolate, various properties of milk crumb are being studied.[1] During a preliminary examination of the water-vapour/milk-crumb equilibria,[2] it was found not possible to relate directly the amount of water adsorbed by milk crumb with its milk solids content. It was considered desirable to examine this property of milk crumb in greater detail.

Experimental

Materials used

In order to reduce the systems studied to the simplest possible, only the fat-free ingredients of milk crumb were used. When the three fat-free constituents, namely, sucrose, skimmed milk solids and fat-free chocolate liquor, are considered in the light of possible interaction, it is seen that there are three possibilities:

(1) the skimmed milk may react with defatted chocolate liquor,
(2) the sucrose may react with skimmed milk,
(3) the sucrose may react with chocolate liquor.

Eight samples were therefore made up as follows:

(1) roller-dried skimmed milk powder;
(2) finely-ground chocolate liquor rendered fat-free by repeated petrol extraction and cold-air drying;
(3) a dry mixture of samples (1) and (2) in the proportion of 79·9/20·1 parts by weight on a dry basis;
(4) mixture (3) was reconstituted with water in the proportion of 20/80 parts by weight and dried under vacuum with a shelf temperature of about 140° F;
(5) a mixture of sample (1) and sucrose in the proportion of 34·9/65·1 parts by weight on a dry basis was reconstituted and vacuum-dried as for sample (4);
(6) a mixture of sample (2) and sucrose in the proportion of 15·8/84·2 parts by weight on a dry basis was reconstituted and vacuum-dried as for sample (5);
(7) a dry mixture of samples (1) and (2) with sucrose in the proportions 31·2/10·8/58·0 parts by weight on a dry basis;
(8) mixture (7) was reconstituted with water in the proportion of 20/80 parts by weight and dried under vacuum with a shelf temperature of about 140° F.

The sucrose used was the pure commercial grade and had previously shown negligible moisture absorption at 80% R.H.

Samples (4), (6), (7) and (8) were dried in vacuum simultaneously.

The proportions of ingredients used in the various samples are approximately those expected in milk crumb.

After the samples had been prepared, they were sieved, and the − 36 + 40 fractions were conditioned at 60% R.H. for seven days in order to ensure crystallization of the sugar components.[2]

Techniques

The method and apparatus used previously[2] were again adopted with the following modifications.

The eight samples were equilibrated simultaneously within one jar by wrapping about 1 g. of each in filter paper and attaching the 'bundle' thereby formed to the wire saddle.

In addition to saturated salt solutions as a means of obtaining standard conditions of relative humidity, sulphuric acid solutions of varying concentration were used, in order to obtain a wider range.[3]

The samples were maintained at a temperature of 25° ± 0·5°C for 18 days, this period having previously been established as giving a margin of time over that required for equilibrium to be established.

After 18 days, the moisture contents of the samples were determined by a modified method which was found to be suitable for milk products. The samples were dried at a pressure of 3 mm. for 105 minutes at a shelf temperature of 80° in the presence of a calcium chloride desiccant. It was found that under these conditions the moisture was driven off with negligible browning of the samples.

Results

A series of curves was drawn (Figs. 1–4) showing the relation between weight of water sorbed and the R.H. at which the samples were stored. It should be noted that these curves represent adsorption for those relative humidities above 60% R.H. and desorption for those below.

From the graphs so obtained, the moisture contents of samples (3) to (8) at 10, 20, 30, 40, 50, 60, 70 and 75·5% R.H. were tabulated together with the theoretical moisture contents calculated from the graphs of samples (1) and (2).

The results are shown in Tables I–V, and for ease of comparison, the theoretical points are shown in Figs. 2–4.

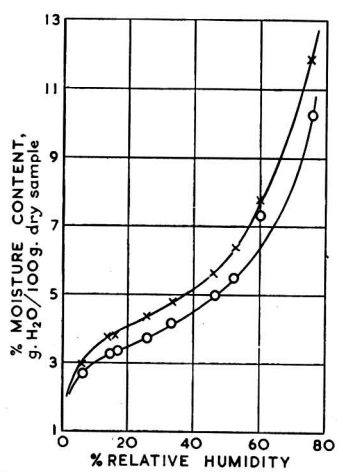


FIG. 1.—*Moisture contents of dry ingredients stored at various R.H.*

○ Skim milk powder
× Defatted chocolate liquor

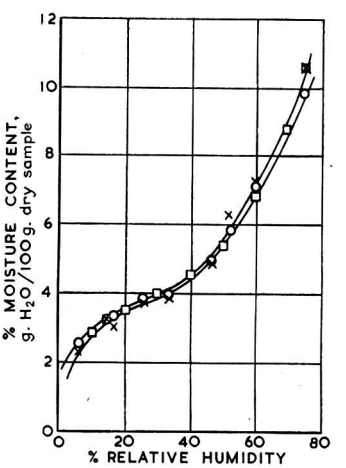


FIG. 2.—*Moisture contents of mixes of skimmed milk powder and defatted chocolate liquor stored at various R.H.*

○ Dry mix
× Reconstituted mix, vacuum dried
□ Theoretical points

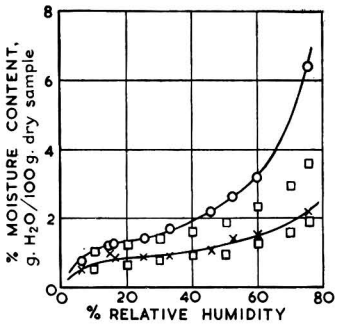


FIG. 3.—*Moisture contents of reconstituted, vacuum-dried mixes stored at various R.H.*

○ Skimmed milk powder and sucrose
× Defatted chocolate liquor and sucrose
□ Theoretical points

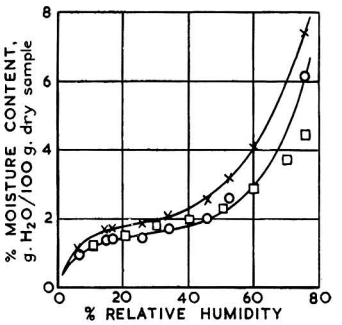


FIG. 4.—*Moisture content of skimmed milk, defatted chocolate liquor and sucrose mixture stored at various R.H.*

○ Dry mix
× Reconstituted mix, vacuum dried
□ Theoretical points

Table I

Moisture contents (g. H_2O per 100 g. of dry sample) of skimmed milk solids and defatted chocolate liquor kept at various R.H. (values taken from Fig. 1)

% R.H.	Skimmed milk solids	Defatted chocolate liquor
10	3·03	3·20
20	3·47	4·00
30	3·96	4·60
40	4·50	5·20
50	5·22	6·08
60	6·50	7·75
70	8·40	10·10
75·5	10·25	11·90

Table II

Comparison between the theoretical and actual moisture contents (g. H_2O per 100 g. of dry solids) of the reconstituted and vacuum-dried mixture of skimmed milk and defatted chocolate liquor (79·9/20·1 parts by wt.) kept at various R.H. (values taken from Fig. 2)

% R.H.	Theoretical	Dry mix	Vacuum-dried sample
10	3·06	2·98	2·80
20	3·57	3·58	3·50
30	4·08	3·92	3·82
40	4·65	4·45	4·40
50	5·39	5·45	5·45
60	6·76	6·80	7·10
70	8·73	8·60	9·16
75·5	10·58	9·81	10·60

Table III

Comparison between the theoretical moisture content (g. H_2O per 100 g. of dry material) and that of the reconstituted and vacuum-dried skimmed milk/sucrose mixture (34·9/65·1 parts by wt.) kept at various R.H. (values taken from Fig. 3)

% R.H.	Theoretical	Vacuum-dried sample
10	1·06	1·00
20	1·21	1·32
30	1·38	1·58
40	1·57	1·88
50	1·82	2·42
60	2·27	3·16
70	2·93	4·65
75·5	3·58	6·39

Table IV

Comparison between the theoretical moisture content (g. H_2O per 100 g. of dry material) and that of the reconstituted and vacuum-dried defatted chocolate liquor and sucrose mixture (15·8/84·2 parts by wt.) kept at various R.H. (values taken from Fig. 3)

% R.H.	Theoretical	Vacuum-dried sample
10	0·51	0·62
20	0·63	0·84
30	0·73	0·90
40	0·82	1·00
50	0·91	1·18
60	1·23	1·45
70	1·59	1·82
75·5	1·89	2·10

Table V

Comparison between the theoretical and actual moisture contents (g. H_2O per 100 g. of dry material) of the reconstituted and vacuum-dried mix of skimmed milk, defatted chocolate liquor and sucrose (31·2 : 10·8 : 58·0 parts by wt.) kept at various R.H. (values taken from Fig. 4)

% R.H.	Theoretical	Dry mix	Vacuum-dried sample
10	1·29	1·25	1·42
20	1·51	1·50	1·80
30	1·83	1·65	2·02
40	1·97	1·87	2·37
50	2·28	2·27	2·96
60	2·86	2·91	4·05
70	3·72	4·45	5·90
75·5	4·49	6·19	7·41

Discussion

Any reaction taking place between the ingredients of milk crumb during vacuum drying would be expected to influence the water sorption of the product since a modification of the lyophilic groups of the reactants would, in all probability, be involved.

In the examination of the results, therefore, a modification of the isotherm due to vacuum drying will indicate some type and degree of interaction of the ingredients.

Skimmed milk and fat-free chocolate liquor mixture

From the closeness of fit between the theoretical curve, the dry mix isotherm and the isotherm of the vacuum-dried product (Fig. 2), it is reasonable to state that on vacuum drying there is no interaction between these ingredients involving their lyophilic groups.

Skimmed milk and sucrose

In Fig. 3, clear indication is obtained of an alteration in sorption behaviour of the vacuum-dried product. The difference between the theoretical isotherm and the actual isotherm increases smoothly with increasing relative humidity. This aspect is examined below.

Defatted chocolate liquor and sucrose

Although the theoretical points in Fig. 3 are approximately 0·2% below the actual curve, there is no indication of a modification of the sorption behaviour. The difference between the curves is possibly due to an experimental error in determining the proportion of the water-sorbing ingredient.

Skimmed milk, defatted chocolate liquor and sucrose

In Fig. 4, further evidence is obtained of the interaction of sucrose and skimmed milk solids after vacuum drying, the pattern of the modification of sorption behaviour being similar to that already noted in Fig. 3.

A further point of interest is that, above about 60% R.H., a slight modification of the sorption behaviour of the dry mix is apparent. This would be explained if the interaction of the sucrose and skimmed milk was attributable to the protein of the latter. Lea & Hannan[4] have demonstrated that the rate of reaction between casein and reducing sugars is greatest at a relative humidity of about 65%, so it is possible that some reaction between the ingredients has taken place during equilibration of the dry mixture at the higher relative humidities.

It is clear from these results that no reaction takes place between either skimmed milk solids and defatted chocolate liquor or sucrose and defatted chocolate liquor during reconstitution with water and vacuum drying of the product, but that under these conditions, a reaction does take place between skimmed milk and sucrose.

The exact nature of the reaction will form the subject of a separate investigation, but at this stage, it is interesting to study the curve relating relative humidity and the difference in moisture content between the theoretical and actual points in the two curves concerned (see Fig. 5).

The ratio of sucrose to skimmed milk solids is the same in both cases. The points of Fig. 5 are sufficiently close, particularly in view of the manipulation of the original experimental results, to enable an indication of the sorption isotherm of the product of the reaction to be obtained. Although the number of sorption sites 'exposed' by the reaction is the same in both samples, it is not possible, at present, to calculate the amount of water sorbed by 100% of the product.

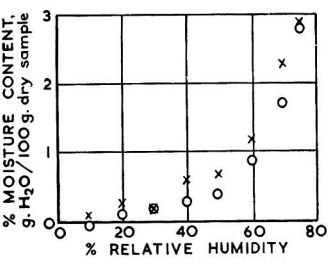


FIG. 5.—*Relation between difference in theoretical and actual moisture contents of mixtures stored at various R.H.*

○ Points from Fig. 3
× Points from Fig. 4

The shape of the curve indicates a direct adsorption of water vapour on the surface of the product, there being no evidence of the primary adsorption normally associated with protein/water isotherms.

Even at the relatively low storage relative humidity of 50%, there is an increase of 30% on the theoretical moisture content of the dry ingredients. At 70% R.H. the difference becomes nearly 60% of the theoretical and over 30% of the dry mix experimental figures.

Further consideration of the sucrose–skimmed milk complex

The sample of dried skimmed milk–sucrose mixture had no abnormal flavour.

It might be argued that the change in the dried product is due to a type of Maillard reaction between a decomposition product of sucrose and the milk protein. That this is not so is indicated by the increase in moisture sorption of the product. Supplee[5] obtains products after heating milk powders in the presence of moisture which have a lower water-sorption power than the untreated powders. Such evidence has also been obtained in this laboratory.

Other aspects of this phenomenon of immediate interest are the water sorption of milk crumb on storage and the effect of the product on the flow properties of milk chocolate.

Storage of milk crumb

On examining the figures in Table V, it can be seen that a high proportion of the rapid rise in equilibrium moisture content of milk crumb above about 60% R.H. is due to the sucrose–skim milk complex.

When these facts are borne in mind, the soundness of storing milk crumb instead of the dry ingredients would seem to bear careful consideration. The effect of moisture content of milk crumb during storage has already been considered.

The fact that, in recent years, chocolate manufacturers have tended to use milk crumb in increasing degree, as shown by the considerable extension in the trading in milk crumb as a raw material of the industry, indicates that manufacturers find in its use advantages which outweigh the potential disadvantages by its high capacity for water sorption.

Milk chocolate viscosity

The flow properties of milk chocolate are largely characterized by the properties of milk crumb, and it might be anticipated that the increased affinity for water of the vacuum-dried product will tend to increase the viscosity of fluid chocolate.

A preliminary test indicates that the likely effect on the viscosity of the product is not greater than of a ' dry ' mixture of milk and sucrose, with its normal content of adsorbed water, but this requires further investigation.

It is significant that no modification of the sorption properties of chocolate liquor occurs after drying with milk or sucrose. This indicates that there can be no compound formation in milk crumb by interaction of these materials involving the lyophilic groups of the ingredients.

Conclusions

The structure of milk crumb is basically an intimate mixture of chocolate liquor, milk solids, sucrose and adsorbed water.

The original ingredients remain unaltered during processing, except for a proportion of a complex which is formed between sucrose and non-fat milk solids.

The significance of this complex in milk chocolate manufacture is not at present clear, although the indications are that it has no effect on flavour or flow properties.

Acknowledgments

The author wishes to thank the Directors of Messrs. W. & M. Duncan Ltd. for permission to publish this paper. The experimental work was carried out by Mr. D. S. Birrell.

W. & M. Duncan Ltd.
Beaverhall Road
Edinburgh 7

Received 26 September, 1955

References

[1] Saunders, James, *J. Sci. Fd Agric.*, 1955, **6**, 110
[2] Saunders, James, *Int. Choc. Rev.*, 1955, **X**, 275
[3] Greenewalt, Crawford H., *Industr. Engng Chem. (Industr.)*, 1925, **17**, 522
[4] Lea, C. H., & Hannan, R. S., *Biochem. biophys. Acta*, 1949, **3**, 313
[5] Supplee, G. C., *J. Dairy Sci.*, 1926, **9**, 50

STUDIES IN THE COLD STORAGE OF PEANUTS

By P. B. MATHUR, M. PRASAD and K. KIRPAL SINGH

Shelled and unshelled peanuts packed in small gunny bags were stored at four temperature ranges, viz., 32–35° F, 42-45° F, 52–55° F and room temperature (71–92° F) for 9 months. The relative humidities ranged between 85% to 90% in the cold-storage chambers and 50–82% at the room temperature.

A parallelism was observed between the changes during storage in the moisture contents of the kernels and the acid values of the extracted oils and, to a less degree, the changes in peroxide values. So far as germination capacities are concerned, shelled nuts should be stored at 32–35° F and unshelled ones at room temperatures (71–92° F). A free fatty acid content exceeding 1% was found to be associated with seeds of low germination capacity.

Neither the shelled nor the unshelled condition nor the storage temperature had any effect on the early growth of viable peanut seeds. After 9 months at 32–35° F, both shelled as well as unshelled peanuts were found in an excellent condition organoleptically, and were 100% marketable. Shelled nuts would occupy only 40% approximately of the volume as compared with unshelled nuts during storage, assuming that only kernels are required

As a result of this investigation a temperature of 32–35° F and a R.H. of 85–90% are recommended as the optimum conditions for the cold storage of peanuts. Shelled nuts should be stored in gunny bags or some other suitable packages.

Introduction

Peanut or groundnut (*Arachis hypogaea*) is one of the most important oil-seed crops of the world. In 1954, the commercial crop of the world was estimated at 12 million short tons.

Peanut is now an important crop in the warmer areas of all parts of the world, and the present world trade largely depends on the European demand for oil. Following the disruptions caused by the World War II, there was a considerable shortage of edible oils and fats, particularly in Europe, and increased production of peanut (groundnut) oil appeared to offer a practical approach to the problem.

Among the physiological changes during the storage of peanuts, the development of rancidity is the most important both from the point of view of extraction of oil and conversion into various peanut products. Very low moisture contents in peanuts during storage may cause them to become brittle. Higher moisture contents, on the other hand, may render them 'soggy'. According to Garren & Wilson,[1] brittleness develops when the moisture content falls below 4% in seeds and 'sogginess' develops at moisture contents above 10%. Another storage disorder of a physiological nature is the impairment in the viability of the seeds under improper conditions of storage.

Material and methods

Peanuts belonging to the variety Spanish were obtained from the farm attached to the Institute. The peanuts had been cured at the farm and the moisture contents of the kernel and the shell were 4·78 and 10·03%, respectively, at the time of commencement of the experiment. Other data concerning this variety as obtained at the time of storage are: kernels, 79·62%, and shells, 20·38%, by weight; and oil content of the kernels, 50·88% on the basis of cured nuts. Shelled and unshelled peanuts packed in small gunny bags were stored at three cold storage temperature ranges, viz., 32–35° F, 42–45° F and 52–55° F. The relative humidity range in the three chambers was 85–90%. Shelled and unshelled lots in small gunny bags were also stored at room temperature (71–92° F, R.H. 50–82%).

Moisture contents of the kernels as well as the shells were determined on 25-g. samples according to the method recommended by the American Oil Chemists' Society.[2] The peroxide value of the extracted oil was determined by the Wheeler's method[3] and the acid value by the method described by Jamieson.[4] Germination tests were carried out in earthenware dishes filled with sand and suitably watered.

Results

The data concerning the percentage changes in fresh weight in peanuts stored at various temperatures are presented in Table I. It is evident from this table that shelled as well as unshelled peanuts had gained in weight at the end of 9 months' storage at all the cold storage temperature ranges, viz., 32–35° F, 42–45° F and 52–55° F. This is because of low moisture content levels both in the shelled and the unshelled peanuts at the commencement of the experiment (kernel, 4·78% and shell, 10·03%) and the high relative humidity range, viz., 85–90%, in the three cold storage chambers. At room temperature (71–92° F, R.H. 50–82%), however, both the shelled and the unshelled peanuts lost weight during the 9 months' storage period.

The data pertaining to the changes in percentage moisture contents in peanuts and changes in the peroxide values and contents of free fatty acids in the oils extracted from them during storage at various temperatures are graphically shown in Figs. 1–3. The data concerning the changes in percentage moisture contents in shells removed from peanuts stored at various temperatures are recorded in Table II.

Table I

Percentage changes in fresh weight in peanuts (on original weight basis) stored at various temperatures*

Storage temp. °F	Shelled (S) or un-shelled (U)	Original weight, g.	Time of storage, months								
			1	2	3	4	5	6	7	8	9
32–35	S	1000	+3·8	+3·9	+2·5	+2·0	+3·7	+3·2	+2·9	+2·8	+2·7
	U	2000	+4·0	+4·7	+3·5	+3·3	+4·2	+4·2	+4·1	+3·5	+4·5
42–45	S	1000	+6·8	+8·3	+8·4	+7·6	+6·1	+6·0	+6·1	+6·2	+6·2
	U	2000	+6·0	+7·5	+9·9	+8·3	+7·0	+7·0	+6·9	+7·0	+7·3
52–55	S	1000	+5·5	+5·8	+6·0	+6·2	+6·1	+6·4	+6·8	+6·5	+5·6
	U	2000	+6·7	+6·9	+6·9	+6·9	+7·1	+6·9	+6·9	+7·1	+6·6
Room temp. (71–92)	S	1000	−0·5	+0·1	+1·1	+1·0	+0·6	+0·5	+0·5	−0·8	−1·7
	U	2000	−0·2	+0·8	+2·4	+1·8	+1·3	+1·5	−0·4	−2·0	−4·8

* + denotes increase in weight and − decrease in weight.

A perusal of Figs. 1–3 shows that there is a parallelism between changes in moisture contents of peanuts and the peroxide and the acid values of the oils extracted from them at all the storage temperatures investigated. Karon & Altschul[5] have shown that lipolysis in stored cotton seed is faster, the higher is the moisture content of the material. Another point brought out by Figs. 1–3 is that the moisture contents of the kernels as well as the peroxide and the acid values of the oils extracted from them at the end of 9 months' storage are invariably higher in the unshelled peanuts than in the shelled ones. The attainment of a higher moisture content level by the kernels and the accompanying changes in peroxide and acid values in the case of unshelled peanuts can be explained on the basis of a high water-absorbing capacity of peanut shells as illustrated by Table II.

Germination tests

The data regarding the percentage germination in peanuts stored at various temperatures are recorded in Table III and their statistical analysis with regard to the rate of fall in germination capacities provided in Table III*a*. The statistical analysis has been done separately for the two periods, viz., start to end of the 4th month and 4th to 9th month. During the first period, the rates of fall in germination capacities in shelled *versus* unshelled peanuts were found to be the same in all the temperature ranges investigated. During the second period, however, the rates of fall in germination capacities for shelled *versus* unshelled were significantly different at 5% level both at 32–35° F and at room temperature (71–92° F). It follows, therefore, that for storage at 32–35° F shelled nuts should be chosen in preference to unshelled ones and for storage under non-refrigerated conditions unshelled nuts should be preferred over shelled ones. Beattie, Jackson & Currin[6] have reported from U.S.A. that during common storage unshelled peanut seeds were found to germinate better than shelled ones. In India also, nuts in shell are recommended for non-refrigerated storage and transportation.[7]

Attempts have been made by a number of workers to correlate the free fatty acid content of the extracted oil with the germination capacity in the case of cotton seed. For example, it was shown by Hoffpauir, Petty & Guthrie[8] that, for practical purposes, cotton kernels containing more than 1% of free fatty acids will not germinate. Simpson[9] concluded that in cotton seeds with a high moisture content the free fatty acids in the extracted oil increase and the germination capacity decreases during storage. The results in Fig. 3 and Table III would show that the same is true of peanut seeds also.

Data concerning the weights of 100 peanut seedlings from seeds stored at various temperatures are presented in Table IV and their statistical analysis shown in Table IV*a*. For the collection of these data, seeds that failed to germinate were not taken into account and the seedlings were allowed to grow for a period of 10 days before they were washed, dried and their weights recorded. These data were compiled to ascertain whether a viable peanut seed would be affected in its early growth by the shelled or unshelled condition or by the temperature of storage. The statistical analysis provided in Table IV*a* shows that none of the above-mentioned factors have any effect on the early growth of viable peanut seeds. This in no way detracts from the phenomenon of vernalization where the developing embryo is subjected to a temperature treatment and not the dormant seed.[10] However, a gradual decrease in the weight of 100 peanut

seedlings is observed in all the treatments beginning from the commencement of the experiment to the end of the experiment. This appears to be due to the variations in seasons beginning April 1953 and ending January 1954.

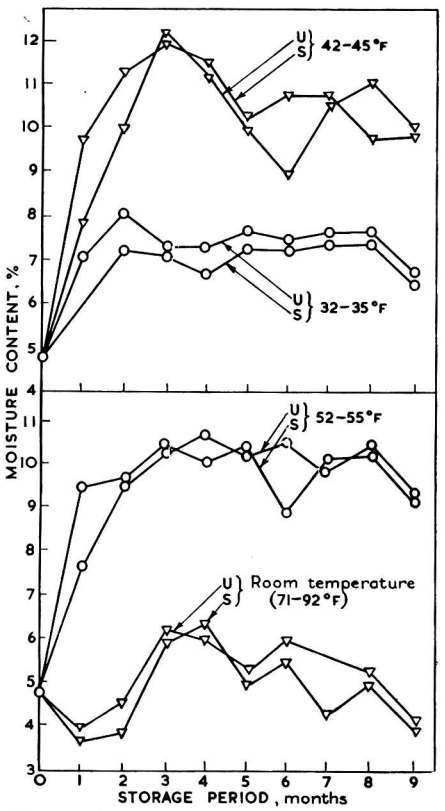


FIG. 1.—*Changes in percentage moisture contents in peanuts stored at various temperatures. In the case of unshelled peanuts, values for kernels only are plotted*

U = unshelled S = shelled

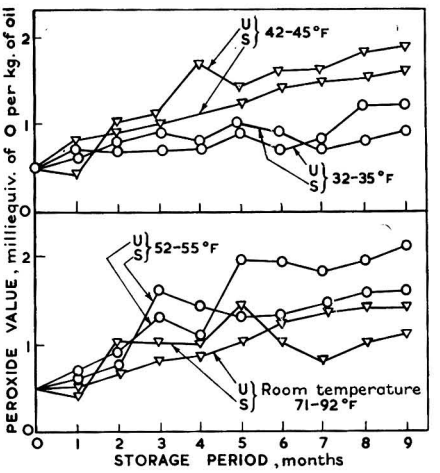


FIG. 2.—*Changes in the peroxide values in oils extracted from peanuts stored at various temperatures. In the case of unshelled peanuts, values for kernels only are plotted*

U = unshelled S = shelled

FIG. 3 (*right*).—*Changes in free fatty acids in oils extracted from peanuts stored at various temperatures. In the case of unshelled peanuts, values for kernels only are plotted*

U = unshelled S = shelled

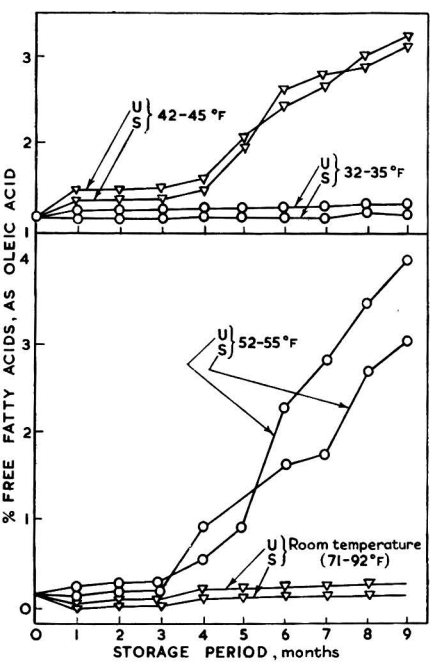


Table II

Moisture contents of shells removed from peanuts stored at various temperatures (original moisture content, 10·03%)

Storage temp. °F	Time of storage, months								
	1	2	3	4	5	6	7	8	9
	%	%	%	%	%	%	%	%	%
32–35	14·90	14·18	12·54	13·92	13·61	13·43	13·62	12·38	12·80
42–45	21·10	17·20	18·76	18·60	17·47	17·39	17·57	17·08	16·23
52–55	18·10	17·00	15·54	17·00	16·18	16·80	16·36	16·15	16·53
Room temp. (71–92)	9·00	9·98	11·56	11·61	10·71	12·05	11·20	10·30	9·19

Table III

Germination in peanuts stored at various temperatures

Storage temp., °F	Shelled (S) or unshelled (U)	Original germination	Time of storage, months								
			1	2	3	4	5	6	7	8	9
		%	%	%	%	%	%	%	%	%	%
32–35	S	96	93	92	91	91	90	90	89	89	88
	U	96	92	92	90	89	88	86	86	85	84
42–45	S	96	88	88	80	78	40	16	14	12	12
	U	96	92	92	90	86	84	72	44	32	16
52–55	S	96	88	86	80	80	36	20	8	8	4
	U	96	89	87	86	84	65	60	52	48	16
Room temp. (71–92)	S	96	92	88	88	86	84	74	70	64	64
	U	96	92	92	90	87	86	80	79	76	76

Table IIIa

Statistical analysis of Table III*

Storage temp. °F	Shelled (S) or unshelled (U)	Rate of fall in germination (transformed variate) from start to end of 4th month (degrees)	Rate of fall in germination (transformed variate) from 4th to 9th month (degrees)	Remarks: From start to end of 4th month	Remarks: From 4th to 9th month
32–35	S	1·42 ± 0·39	0·51 ± 0·06	(1) No significant difference between shelled and unshelled nuts in any of the temp. ranges	(1) Differences between shelled and unshelled nuts in the rate of fall of germination significant at 5% level, at 32–35° F and at room temp.
	U	1·78 ± 0·42	0·81 ± 0·09		
42–45	S	3·93 ± 0·74	7·62 ± 2·32		
	U	2·30 ± 0·41	9·56 ± 0·93		
52–55	S	3·65 ± 0·82	9·46 ± 2·09		
	U	2·68 ± 0·77	7·09 ± 1·27		
Room temp. (71–92)	S	2·49 ± 0·56	3·34 ± 0·45		
	U	2·12 ± 0·39	1·82 ± 0·29		
				(2) Difference for shelled nuts stored at 32–35° F. *vs.* 42–45° F significant at 5% level. Differences between other temp. ranges not significant	(2) Differences for shelled nuts at 32–35° F *vs.* room temp. significant at 0·1% level. Differences for other temp. ranges significant except for 42–45° F *vs.* 52–55° F and *vs.* room temp.
				(3) Differences for unshelled nuts between the various temp. ranges not significant	(3) Differences for unshelled nuts highly significant for all the temp. ranges except for 42–45° F *vs.* 52–55° F

* An angular transformation has been used to convert the percentages in degrees, hence the rates of fall and their standard errors are in angles in degrees.

Table IV

Fresh weights of 100 *peanut seedlings (g.) from seeds stored at various temperatures (period of growth =* 10 *days)*

Storage temp. ° F	Shelled (S) or unshelled (U)	Original weight of 100 seedlings g.	Time of storage, months 1	2	3	4	5	6	7	8	9
32–35	S	57	53	48	41	36	40	37	30	23	24
	U	57	50	42·5	48	33	39	28	32	23	23
42–45	S	57	49	42	35	33	32	30	33	20	20
	U	57	55	34	33	37	40	30	26	26	20
52–55	S	57	49	46	35	33	33	22	43	50	18
	U	57	55	43	42	36	35	44	33	22	19
Room temp. (71–92)	S	57	41	43	43	32	37	42	35	23	21
	U	57	40	35	53	30	33	44	39	53	28

Table IV*a*

Statistical analysis of Table IV

Storage temp. ° F	Shelled (S) or unshelled (U)	Rate of fall in the weight of 100 peanut seedlings (g./month)	Remarks
32–35	S	3·67 ± 0·33	(1) No significant difference between shelled and unshelled nuts in any of the temp. ranges.
	U	3·65 ± 0·46	
42–45	S	3·62 ± 0·46	(2) For shelled nuts, no significant differences for any of the temp. ranges
	U	3·53 ± 0·67	
52–55	S	2·41 ± 1·20	(3) For unshelled nuts, no significant differences for any of the temp. ranges
	U	3·75 ± 0·58	
Room temp. (71–92)	S	2·96 ± 0·64	
	U	1·05 ± 1·14	

Condition of stored nuts

Data concerning the condition and organoleptic evaluation of peanuts at the end of 9 months' storage are provided in Table V. At 32–35° F both shelled and unshelled peanuts were found in an excellent condition at the end of the storage period. At room temperature, however, only unshelled peanuts were in an acceptable condition organoleptically, all the other lots being unacceptable. At 42–45° F and 52–55° F a positive correlation was observed between mould growth and increase in free fatty acid content.

Table V

Storage temp. ° F	Shelled (S) or unshelled (U)	*Condition and organoleptic evaluation of peanuts after 9 months' storage*
32–35	S	Excellent marketable condition. Taste, good
	U	Excellent marketable condition. Taste, good
42–45	S	A number of peanuts mouldy. Taste, stale
	U	A number of peanuts mouldy. Taste, stale
52–55	S	A large number of peanuts mouldy. Taste, stale
	U	A large number of peanuts mouldy. Taste, stale
Room temp. (71–92)	S	Peanuts infested with insects and moulds. Taste, not good
	U	Peanuts infested with insects and moulds. Taste, good

The percentages of marketable peanuts by weight at the end of 9 months' storage at various temperatures are recorded in Table VI. Both for shelled and unshelled peanuts, 32–35° F is a better storage temperature range than room temperature (71–92° F). At 32–35° F, there was no difference between shelled and unshelled peanuts, all the nuts in both lots being in an excellent marketable condition. The percentage of marketable nuts was much higher in the unshelled lot as compared with the shelled one at the room temperature.

Laboratory experiments showed that shelled nuts occupy approximately only 40% of the volume required for the same number of unshelled nuts. This is of importance in view of the fact that only the kernels are required for planting, extraction of oil or conversion into other peanut products.

Table VI

Percentages of marketable peanuts at the end of 9 months' storage at various temperatures

Storage temp. °F	Shelled (S) or un-shelled (U)	% marketable nuts (mean of two replications)	Statistical remarks
32–35	S	100·0	(1) Difference between 32–35° and room temp. very highly significant for shelled nuts
	U	100·0	
42–45	S	77·2	(2) Difference between 32–35° and room temp. highly significant for unshelled nuts
	U	82·1	
52–55	S	0·0	(3) Difference between shelled and unshelled nuts highly significant at room temp.
	U	26·3	
Room temp. (71–92)	S	8·7	
	U	76·9	

Discussion

According to Woodroof *et al.*,[11] low storage temperatures are very effective in minimizing insect infestation, rancidity, absorption of odours and deterioration in colour and flavour of peanuts. Pons *et al.*[12] stored peanuts at about 0° F, 33·8° F and 80·6° F for 4 years. Those stored at 80·6° F were found not viable, while those stored at lower temperatures germinated perfectly. Hull[13] has shown that the time required for breaking the dormancy of Florida Runner and Spanish varieties was increased when stored at 37·4° F and decreased when stored at 68–104° F. In a recent article, Harden[14] has suggested that the present irregular supply position of peanuts in U.S.A. can be solved by cold storing the nuts. Thompson *et al.*[15] have recommended a temperature of 32° F and a R.H. of 60–70% as the best conditions for the cold storage of peanuts. The lower humidity recommended by these authors is contrasted with the higher value of 85–90% advocated in the present work. Under the higher humidity conditions, which are easily attained in cold storage rooms at 32–35° F, the nuts remained in sound marketable condition and had good organoleptic properties even after 9 months' storage. For good germination subsequently, storage of shelled nuts is preferable.

Acknowledgments

Our thanks are due to Dr. V. Subrahmanyan, Director, for his keen interest in this investigation. Our thanks are also due to Mr. A. N. Sankaran for the statistical analysis of part of the data.

Central Food Technological Research Institute
Mysore
India

Received 2 August, 1955

References

[1] Garren, K. H., & Wilson, C., 'Peanut Diseases', 1951 (Washington National Fertilizer Assoc.)
[2] 'Official and Tentative methods of the American Oil Chemists' Society', 1946 (Chicago: Amer. Oil Chem. Soc.)
[3] Wheeler, D. H., *Oil & Soap*, 1932, **9**, 89
[4] Jamieson, G. S., 'Vegetable fats and oils', 1943 (New York: Reinhold Publishing Corp.)
[5] Karon, M. L., & Altschul, A. M., *Plant Physiol.*, 1944, **19**, 310
[6] Beattie, J. H., Jackson, A. M., & Currin, R. E., 1932, *Circ. U.S. Dep. Agric.*, No. 233
[7] 'Marketing of groundnuts in India', Brochure series No. 6, 1950. Directorate of Marketing and Inspection, Min. of Agric., Govt. of India
[8] Hoffpauir, C. L., Petty, D. H., & Guthrie, J. D. *Science*, 1947, **106**, 344
[9] Simpson, D. M., *J. agric. Res.*, 1942, **64**, 407
[10] 'Vernalization and Phasic development of Plants', 1935 (Aberystwyth and Cambridge: Imperial Bureaux of Plant Genetics)
[11] Woodroof, J. G., Thompson, H. H., & Cecil, S. R., *Food Ind.*, 1949, **21**, 16
[12] Pons, W. A., jun., Murray, M. D., O'Conner, R. T., & Guthrie, J. D., *J. Amer. Oil Chem. Soc.*, 1948, **25**, 308
[13] Hull, F. H., *Bull. Fla agric. Exp. Sta.*, 1937, No. 314
[14] Harden, D. H., *Peanut J. & Nut World*, 1954, **34**, [2], 13
[15] Thompson, H. H., Cecil, S. R., & Woodroof, J. G., *Bull. Ga Exp. Sta.*, 1951, No. 268

STUDIES ON THE EFFECTS OF TREATMENT WITH CHLORINE DIOXIDE ON THE PROPERTIES OF WHEAT FLOUR. I.— The Chemical Composition of Protein of Treated Flours

By P. MEREDITH, H. G. SAMMONS and A. C. FRAZER

In this first of a series of four papers, an investigation is described into the possible production of abnormal substances by the action of ten times the normal level of chlorine dioxide treatment of flour. Quantitative aspects of the amino-acid content of the flour protein after treatment have also been studied. Comparison has been made with untreated and normally treated flours and with flour treated with ten times the normal amount of nitrogen trichloride.

No abnormal ninhydrin-reactive substances resulting from the treatment have been found and, of the essential amino-acids, only tryptophan has been reduced in proportion, to an extent greater than 10% after heavy treatment with nitrogen trichloride. Of the non-essential amino-acids, cystine has been reduced to about 75% by heavy treatment with chlorine dioxide or nitrogen trichloride.

The remaining three papers of the series will deal with the biological aspects of the investigation.

Introduction

It has long been known that on storage the baking qualities of wheat flour improve. This is believed to be due to oxidation presumably by oxygen of the atmosphere. For many years it has been usual to use other, quicker methods of oxidation in order to reproduce the effects of ageing in a much shorter time.

Modern treatments make use of such chlorine compounds as nitrogen trichloride (Agene), patented in 1921[1] and chlorine dioxide (Dyox), patented in 1928,[2] or physical aeration,[3] which has basically the same action. The effects of chlorine dioxide on the baking qualities of flour have been described by Ferrari *et al.*[4]

Until recently, nitrogen trichloride was the most frequently used of these improving agents, but doubts first expressed in 1927[5] of the possible harmful effects on the dietary value of gluten were confirmed by Mellanby in 1946.[6] The toxic substance responsible, methionine sulphoximine, was isolated and identified in 1950[7] and in 1951.[8] A possible substitute for nitrogen trichloride had then to be seriously considered. Such a substance is chlorine dioxide, but it was felt that a more thorough examination of its effects on flour was needed, despite the fact that several groups of workers[9–12] have studied the effects on animals and human subjects of flours treated with chlorine dioxide, but have produced no evidence of toxicity.

Both the protein[13] and the lipid[14] fractions of chlorine-dioxide-treated flours have been examined recently by other workers.

An oxidizing agent such as chlorine dioxide might alter the value of proteins to the animal organism by:

(*a*) forming abnormal substances,
(*b*) destruction of essential amino-acids, or,
(*c*) producing modifications of structure affecting the availability of the amino-acids.

The present work is an attempt to investigate possibilities (*a*) and (*b*) for chlorine dioxide treatment.

It was decided to examine first the possibility of the production of abnormal substances by comparing an untreated flour with flours treated with chlorine dioxide at normal and ten-times-normal levels and with nitrogen trichloride and, second, the change in concentration of known amino-acids which might be brought about by the action of these oxidizing agents. Only those substances reacting with ninhydrin to give a colour have been considered.

Experimental

Materials

Preparation of flour.—The original flour used in this investigation was commercially milled, from the following grists:

60% No. 2 Manitobas
5% Garnet
15% Plate
5% Australian
15% English

The flour was true straight-run flour of 78% extraction. It was free from added flours or admixtures, including Creta Preparata. Part was retained as control (Flour 1).

For the commercial treatment with chlorine dioxide (Flour 2) the divides and rates of treatment were as follows:

46% Patents	1·75 g. of chlorine dioxide per sack
34% Middle grade	3·25 ,, ,, ,, ,, ,, ,,
11% Low grade	5·5 ,, ,, ,, ,, ,, ,,
9% Bottom grade	10·0 ,, ,, ,, ,, ,, ,,

This gave an average of 3·42 g. of chlorine dioxide per 280-lb. sack of the straight-run flour (i.e., 27 p.p.m.).

Flour 3 was prepared by further treatment of Flour 2 to a total of 34·2 g. of chlorine per sack.

Flour 4 was heavily agenized by treatment of a portion of the original flour with nitrogen trichloride to an uptake of approximately 65 g. per 280-lb. sack. This is about ten times the normal level of treatment. The extent of treatment was checked by independent observers.

Within two days of receipt these four flours were defatted in order to prevent any further changes occurring due to the possibility of an oxidizing agent remaining in solution in the lipids. The samples were extracted four times with dry ether at room temperature, then three times with ethanol–ether (3 : 1), also at room temperature. They were dried by placing in a desiccator under vacuum and finally allowed to come to equilibrium with the air before being stored in stoppered glass bottles.

Gluten.—Glutens were washed from these flours using tap water. Birmingham tap water is of sufficiently low solids content (40–50 p.p.m.)[15] not to contaminate the samples appreciably and yet it allows a reasonable recovery of gluten.

The gluten from Flour 3 was not coherent and had to be washed over a wire sieve. That from Flour 4, however, was quite easily handled, although it was not of such high quality as those from Flours 1 and 2.

Methods

(*a*) *Examination for abnormal substances*

Hydrolysis.—The wet glutens, in about 0·5-g. quantities, were hydrolysed with 6N-hydrochloric acid under the dilute conditions described by Dustin *et al.*[16] for the maximal recovery of the majority of amino-acids. The dilution is about 1 in 3600.

After boiling for 24 hours under reflux, the solutions were evaporated under vacuum at 40° until most of the excess acid had been removed. The residues were taken up in water and moist silver oxide added until the solution was at pH 4·0. After brief standing, the solution was filtered to remove the precipitated silver chloride.

Removal of acidic amino-acids.—The clear solution at pH 4 was passed through a column (37 cm. by 1 cm.) of Deacidite-E anion-exchange resin in the hydrogen form.

The resin was washed with water to effect quantitative recovery of all but the acidic amino-acids. The latter were recovered as a separate fraction by elution with dilute hydrochloric acid. The resin effluent and washings were evaporated under reduced pressure to about 2 ml. volume.

An equal volume of the chromatography solvent was added and then absolute alcohol added dropwise until only one phase was present. This solution was then ready for addition to the chromatography column.

Column chromatographic separation.—An imitation of the paper system, using Partridge's solvent[17], butanol–acetic acid–water (4 : 1 : 5), was used, the column (3 × 60 cm.) being packed with Whatman cellulose powder (coarse grade) saturated with aqueous phase. The effluent was collected in fractions of about 8 ml.

The separation of the amino-acids exactly followed the order found on paper sheets, with the exception of the basic amino-acids, which could only be eluted by passing *n*-propanol through the column.

A quantitative ninhydrin reaction was carried out on a 0·5-ml. sample from each fraction by the method of Moore & Stein.[18] From these results an elution curve was plotted, on the basis of which the fractions were pooled into 15 larger fractions, representing definite parts of the elution curve. Each of these pooled fractions was then evaporated to dryness under reduced pressure and stored in a stoppered tube. In this way, a total of seventeen fractions was obtained from each flour—fifteen from the chromatographic separation plus acidic and basic fractions. Each sample was dissolved in 250 μl. of N-hydrochloric acid and examined by paper chromatography.

As a preliminary examination, spots of 20 μl. and 50 μl. of each sample (equivalent to 120 and 300 mg. of flour and containing 1–3 major amino-acids) were run uni-dimensionally with phenol as solvent. In general, the smaller quantity gave a clear picture, whilst the pictures obtained from the larger quantity tended to suffer from blurring due to overloading. The heavily loaded papers, however, were of use in deciding the presence or absence of doubtful spots.

The fractions of Flours 1 and 3 were further examined by the two-dimensional paper method. The second solvent used was the same butanol–acetic acid–water mixture as was used for the column. This was considered justified, on the grounds that it was not additional resolving power that was required, but simply a wider spreading of the spots to allow a clearer examination.

Neither the acidic nor the basic fractions gave clear pictures. In order to examine the basic fractions, recourse was made to paper electrophoresis. Using M/20 acetic acid as buffer solution, 40-μl. samples of the basic fractions were separated, at 9 volts per cm. for three hours. At the end of this time the three main basic amino-acids (arginine, lysine, histidine) had just run off the end of the paper strip. The substances remaining on the cathodic half of the paper were eluted by allowing water to flow through. After partial evaporation, the extract was subjected to two-dimensional chromatography in the usual way.

In the case of the acidic fractions, no satisfactory method of examination was found because of the enormous preponderance of glutamic acid which blurred the whole separation. Smaller quantities (5 μl.) were examined by two-dimentional chromatography with a consequent lowering of sensitivity.

(*b*) *Quantitative amino-acid analyses of gluten*

Hydrolysis.—In order to overcome hydration problems, freeze-dried samples (125–150 mg.) were weighed out in equilibrium with the air.[19] At the same time a sample was weighed out for determination of moisture content.

600 ml. of re-distilled constant-boiling hydrochloric acid was boiled under reflux overnight with a constant stream of oxygen-free nitrogen passing through it. This removed atmospheric oxygen from the solution and the apparatus. After addition of the gluten sample, the mixture was refluxed under nitrogen for 24 hours and the acid then distilled off under reduced pressure. The dry residue was dissolved in water and the solutions filtered through a sintered glass plate. The clear and almost colourless filtrate was diluted to exactly 10 ml. Two 4-ml. aliquots were taken and suitable citrate buffer solutions added to bring them to pH 2·5 and pH 4·0, respectively. Each was then diluted to exactly 10 ml. with water.

Total nitrogen determination.—The procedure adopted by Chibnall, Rees & Williams[19] was followed for the digestion and that of Ballantine & Gregg[20] for the determination of ammonia. As a check on the method, the nitrogen content of a sample of gluten, purified by reprecipitation

from acetic acid dispersion, was determined. A value of 17·6% N was found (moisture- and ash-free), this being in good agreement with the findings of Osborne[21] who reported values of 16·66% for gliadin and 17·49% for glutenin.

Chromatography.—The apparatus and procedure used was similar to that described by Moore & Stein,[22] Schramm *et al.*[22] and by Schramm & Bigwood.[24]

The determination of the amino-acid content of the fractions was by the method of Yemm & Cocking.[25, 26]

Readings were interpreted from separate standard curves for each amino-acid. Most of these curves were based on only a single sample of the amino-acid in question and the results cannot, therefore, be considered to be of true analytical accuracy, but provide a basis for comparison of the three gluten hydrolysates.

Determination of tryptophan.—Tryptophan is destroyed by heating with mineral acids in the presence of traces of carbohydrate or certain other amino-acids. The acid hydrolysates were therefore unsuitable for its determination. The choice lay between microbiological determination (the method favoured by Schramm *et al.*[23]), attempted chromatographic determination in an alkaline hydrolysate and a purely chemical method. The last course was chosen. Since a method described for use on the intact protein seemed preferable, Bates' modification[27] of the Voisenet–Rhode reaction was attempted.

The method was first tried exactly as described, using a standard solution. The colour was found to reach a maximum intensity in less than three minutes after dilution and then faded rapidly. On attempting the reaction with an acetic acid dispersion of gluten, the gluten remained in solution on addition of the alkali, but precipitated on addition of the reagents. The method as published was, therefore, considered unsatisfactory for this investigation and attempts were made to modify it.

These efforts were not entirely satisfactory, since the colour yield and stability were affected by the presence of protein (see Tables V, *A* and V, *B*). The figures obtained cannot represent a true assay of tryptophan content, but do enable a comparison of the three glutens to be made. They probably represent minimal values for the tryptophan content of gluten.

The method finally used was as follows:

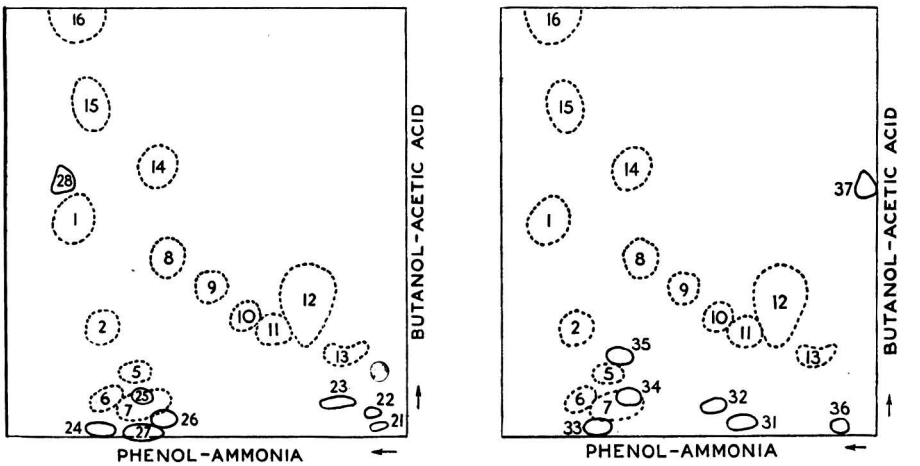
> An air-dry gluten sample of about 240 mg. was weighed out and 1 ml. of 3N-sodium hydroxide added. The mixture was heated for 30 minutes in a boiling water-bath to effect complete dissolution, cooled and diluted to exactly 10 ml. with water.
>
> For the standard solution, about 500 mg. of tryptophan was weighed out, dissolved in 10 ml. of N-hydrochloric acid, and diluted to 250 ml. This solution, diluted 1 in 20, gave a final concentration of about 100 μg. per ml.
>
> A method of addition standards was used since the gluten gave a colour development differing from that of pure solutions of tryptophan.
>
> Suitable quantities of gluten and standard solutions were measured into 25-ml. volumetric flasks. 0·3N-Sodium hydroxide was added to make 2 ml. volume, 20 ml. of concentrated hydrochloric acid were added, followed by 0·5 ml. of 5% *p*-dimethylaminobenzaldehyde solution, and mixed. After 30 minutes, 0·2 ml. of 1% sodium nitrite solution was added, the whole mixed and diluted to 25 ml. with concentrated hydrochloric acid. Readings were taken in a spectrophotometer (Unicam S.P. 350) 30 minutes after the addition of the nitrite, using tubes having a mean light path of 1·61 cm. and at 600 mμ. wavelength.
>
> The calculated results have been obtained by plotting these readings and using this graph as a standard curve in interpreting the readings for gluten alone.

Results

(*a*) *Examination for abnormal substances*

From the one-dimensional papers, no spots were observed for Flours 2, 3 and 4 which were not observed for Flour 1. The pictures obtained for the acidic and basic fractions were not at all clear, since, in the case of the acidic fractions there is an enormous preponderance of glutamic acid and the basic amino-acids do not separate properly.

On examining the two-dimensional papers, no spots were found for Flour 3 that were not present for Flour 1. On the other hand, several faint spots occurred for Flour 1 that did not occur for Flour 3 (Fig. 1, No. 21–28). There were also some spots occurring for both flours that could not be identified (Fig. 2, No. 31–37). The basic fractions showed the same pattern of seven faint spots, one of which had a characteristic orange colour, for all four flours. In the case of the acidic fractions, only two minor spots were found, these being common to all four flours.



FIGS. 1 *and* 2.—*Two-dimensional chromatograms of glutens* 1 *and* 3

KEY

1. Proline
2. Methionine sulphoxide
5. Histidine
6. Arginine
7. Lysine
8. Alanine
9. Threonine
10. Glycine
11. Serine
12. Glutamic acid
13. Aspartic acid
14. Tyrosine
15. Valine–methionine
16. Leucines–phenylalanine

21–28. Spots found with gluten 1 but not gluten 3

31–37. Unidentified spots in glutens 1 and 3

Further examination was made of some fractions for the possible presence of particular substances. The two substances looked for were methionine sulphoximine in Flour 4 and monochlorotyrosine in Flours 2, 3 and 4. Neither was detected in repeated examinations.

(b) Quantitative amino-acid analyses of glutens

The results of control runs on known amino-acids are given in Table I. Elution curves from the 15-cm. column are shown in Fig. 3, whilst those for the 100-cm. column are in Fig. 4.

The amounts of each amino-acid found, as calculated from the data, are given in Table II, together with the analyses for total nitrogen, ash and moisture. No figures are given for proline since this peak is largely overlaid by the relatively enormous peak of glutamic acid.

Table I

Recovery from resin column in control experiments

	Amount taken μmoles	Recovery %
Alanine	1·0	101·0
	2·0	96·2
Cystine	1·0	88·7
	2·0	81·0
Valine	1·0	92·6
	2·0	95·8
Glutamic acid	2·5	92·1
	2·5	102·7
	2·5	104·2
	2·0	100·7

Both glutamic acid and ammonia formed very large peaks, for which accurate measurement of the colour was difficult. No attempt, therefore, was made to calculate either of these two constituents.

The results were re-calculated to an equi-nitrogenous basis and are given in Table III as percentages of control gluten values.

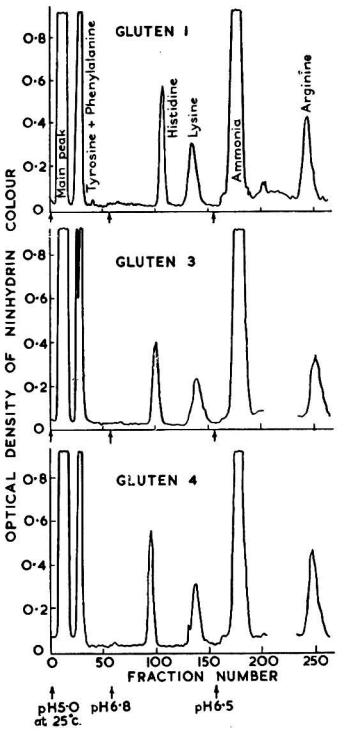


FIG. 3.—*Elution curves of amino-acids in gluten samples from* 15-*cm. column*

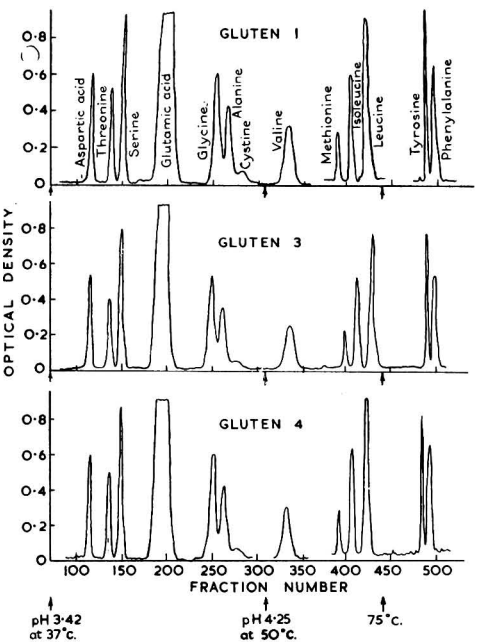


FIG. 4.—*Elution curves of amino-acids in gluten samples from* 100-*cm. column*

A comparison with published results is shown in Table IV. Details of the tryptophan analyses are shown in Table V, *C*, the final results being included in Table III.

Discussion

(*a*) *Examination for abnormal substances*

The general conclusion drawn from the experiment is that no abnormal ninhydrin-reactive substances resulting from chlorine dioxide treatment of flour at ten times the commercial level could be detected. The following reservations must be made:

1. The sensitivity of the method is limited and varies for each amino-acid.
2. The examination has been limited to the gluten fraction of the flour and to those substances giving a colour reaction with ninhydrin.
3. It is possible that an unknown substance present in small proportion may be overlaid by another substance on the paper chromatograms. This is a difficulty inherent in all chromatographic methods.

4. A hydrolysate of the gluten has been examined, and it is possible that an unknown substance may be destroyed in the process.
5. No precautions have been taken against atmospheric oxidation during the handling of the solutions. An unknown substance might, therefore, be destroyed in this way.

Table II

Amino-acids (μmoles) in gluten samples

Gluten No.	1	3	4
Total nitrogen, % dry weight	16·3	15·1	16·3
Ash, % dry weight	0·35	0·21	0·26
Moisture, % dry weight	8·7	9·9	9·7
Amount taken, mg. dry weight	5·036	4·760	5·072
Aspartic acid	1·365	1·150	1·361
Threonine	1·196	1·040	1·199
Serine	2·400	2·070	2·273
Glycine	2·474	2·243	2·340
Alanine	1·857	1·524	1·735
Cystine (½ mole)	0·657	0·426	0·446
Valine	1·857	1·584	1·758
Methionine	0·485	0·429	0·490
*iso*Leucine	1·321	1·296	1·445
Leucine	2·819	2·457	2·854
Tyrosine	1·091	0·893	1·096
Phenylalanine	1·692	1·450	1·808
Amount taken, mg. dry weight	10·072	9·424	10·144
Histidine	1·227	1·089	1·143
Lysine	1·084	0·953	1·072
Arginine	1·797	1·549	1·904

Table III

Amino-acids in gluten samples (% of control gluten values on equi-nitrogenous basis)

	Gluten 3	Gluten 4
Amino-acids essential to man and rat		
*iso*Leucine	112·1	108·6
Leucine	99·5	100·2
Lysine	101·4	98·3
Methionine	101·0	100·4
Phenylalanine	97·9	106·1
Threonine	99·3	99·5
Tryptophan	92·3	87·8
Valine	97·4	94·0
Amino-acids essential to rat, but not man		
Arginine	99·5	105·2
Histidine	102·5	92·5
Amino-acids not essential		
Alanine	93·7	92·8
Aspartic acid	96·2	99·0
Cystine	74·0	67·4
Glycine	103·5	93·9
Serine	98·4	94·0
Tyrosine	93·5	99·8

Gluten 3 was from flour treated with 10 times the normal amount of Dyox
Gluten 4 ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, Agene

The sensitivity attained in this examination is not constant, but is greater for some fractions than for others. With the exception of the acidic fraction, the amount examined was never less than equivalent to 120 mg. of flour. Assuming the limit of detection of an amino-acid to be 2 μg. and that it occurs only in one fraction, this gives a theoretical sensitivity of the order of 1 in 60,000. It is more probable, however, that a substance will be spread over two, or even

Table IV

Amino-acids in gluten samples: comparison with published data (all calculated as g. of amino-acid per 16 g. of nitrogen)

	Literature			Present analysis
Reference No.	29	30	31	
Essential to man and rat				
*iso*Leucine	4·9	4·2	4·6	3·5
Leucine	24·7	7·0	7·7	7·2
Lysine	1·9; 1·3; 1·2; 1·5	1·9	2·0	1·5
Methionine		1·5	1·7	1·4
Phenylalanine	4·1	5·5	5·0	5·4
Threonine	2·7; 2·3	2·5	2·8	2·75
Tryptophan	1·2; 0·9	0·8	0·5	(0·6)
Valine	4·6	4·1	4·3	4·2
Essential to rat, but not man				
Arginine	3·9; 1·9	3·9	3·7	3·0
Histidine	2·2; 2·1	2·2	2·0	1·9
Non-essential				
Alanine	5·0; 2·7	2·8		3·2
Aspartic acid	9·6			3·5
Cystine	1·4	1·9		1·5
Glutamic acid	26·8	27·0		
Glycine	9·0; 7·2	7·0		3·6
Proline	10·0; 8·0	8·0		
Serine		4·0		4·9
Tyrosine	1·3	3·8		3·8

Table V

Determination of tryptophan

Added standard tryptophan solution	Optical density			
	13 min.	30 min.	60 min.	90 min.
A. Colour yield				
Gluten 1 only	0·361	0·353	0·343	0·339
Gluten 1 with added tryptophan solution				
0·5 ml.	0·512	0·501	0·488	0·480
0·8 ml.	0·622	0·618	0·600	0·590
1·0 ml.	0·680	0·675	0·660	0·650
1·3 ml.	0·800	0·798	0·780	0·765
1·0 ml. standard tryptophan solution only	0·410	0·418	0·420	0·420

B. Effect of added gluten on response of 1 ml. of standard tryptophan solution			
Gluten No.	1	3	4
In absence of gluten	0·420	0·430	0·421
In presence of gluten	0·356	0·356	0·360

C. Tryptophan content of gluten			
Total N %	16·3	15·1	16·3
mg. dry weight taken	15·743	15·683	15·617
μg. tryptophan found	107·0	91·0	93·0
Tryptophan g./16 g. of N	0·667	0·617	0·585
% of control		92·3	87·0

three, fractions. The effective sensitivity is thus approximately halved for the peak fraction in which a particular substance occurs. For those examinations in which an aliquot of 20 μl. was examined, the effective sensitivity is probably about 1 in 30,000 parts of flour. In all but three fractions, more than 20 μl. was examined and in one case the aliquot was 100 μl. This 100-μl. fraction would be examined at a sensitivity of about 1 in 150,000. In the case of the acidic fractions, the sensitivity would only be about 1 in 8000. For comparison, it will be remembered that methionine sulphoximine occurs at 1 in 33,000 parts of heavily-treated flour.[28] The fact that the sulphoximine was not detected will be discussed later.

The additional spots shown in Figs. 1 and 2, with the exception of Nos. 35 and 37, behaved in an anomalous manner with regard to the order of their elution from the column. Since these substances were present only in trace concentrations and their presence does not affect the main conclusions, they were not further investigated.

The failure to detect methionine sulphoximine in Flour 4 can be explained by the fact that it is destroyed to the extent of about 80% during hydrolysis. Assuming that 20% of the sulphoximine present in Flour 4 survived the hydrolysis, the remaining concentration would be equivalent to 1 in 165,000 parts of flour. This concentration could not have been detected in the present examination. Campbell, Work & Mellanby[8] note that some destruction occurs during acid hydrolysis. They used 6N-hydrochloric acid, boiling for $3\frac{1}{2}$ hours. Reiner *et al.*[32] also showed that methionine sulphoximine is considerably destroyed by 5N-hydrochloric acid in 24 hours. It would appear, therefore, that most of the sulphoximine originally present in Flour 4 was destroyed in the hydrolysis, the amount remaining being too small to detect by the technique used. This finding serves to emphasize the fourth reservation which was made about the general conclusion.

Monochlorotyrosine was not found, and it is, therefore, probable that no chlorination effects had occurred. Since the chlorine dioxide used in the treatment presumably contains some free chlorine, this result was surprising and a check was made of the stability of monochlorotyrosine to the hydrolysis procedure. No destruction occurred, as judged by the intensities of spots on paper chromatograms.

(b) Quantitative amino-acid analyses of gluten

Considering the results of Table III, it can be seen that even with ten times the normal level of Dyox treatment, no significant effects are seen with any of the amino-acids, except cystine tryptophan, tyrosine, alanine and *iso*leucine.

Consideration of the recoveries of known amino-acids (Table I), of the results as a whole and of the techniques used lead us to the conclusion that only differences of more than 10% can be considered significant, except in the case of tryptophan, where the accuracy is probably within the 5% range. Therefore, only cystine and tryptophan may be considered to be significantly altered by the ten-times Dyox treatment. Of these, only tryptophan, for which the reduction is minimal, is an essential amino-acid. Findings for the ten-times-normal Agene treatment are similar. Preliminary investigations by the authors[33] of acid-hydrolysed glutens, using two-dimensional paper chromatography, showed that the oxidation of methionine was restricted to the sulphoxide and that the concentration of this did not appear to be significantly different in treated and untreated flours. There was no cysteic acid present in detectable concentration. In contrast to these findings, in the present investigation by the Moore & Stein technique there was no detectable methionine sulphoxide. This may be due to the presence of an antioxidant, thiodiglycol, in the eluent.

It is, perhaps, worth while noting that methionine sulphoxide is the product of an easily reversed reaction, whereas methionine sulphone is not so easily reduced. Furthermore, methionine sulphoxide is capable of supporting growth to the same extent as methionine,[34] whereas methionine sulphone is not.[35]

Whilst the commercial level of treatment in both cases definitely improves the flour, both from colour and dough-handling points of view, the heavier treatment has a markedly destructive effect on the mechanical properties of the gluten and, therefore, of the dough. This effect is not great in the case of nitrogen trichloride, although the flour and gluten acquire a slightly yellow colour and the gluten is not quite so coherent as normally. In the case of heavy chlorine dioxide treatment, both the flour and the gluten have a distinct pink colour and the gluten completely loses its coherence, so that it becomes very difficult to wash the starch from the gluten. This probably accounts for the low nitrogen analysis of Gluten 3. The coloration is probably due to oxidation of tyrosine, to give coloured compounds. This reaction between chlorine dioxide and tyrosine has been used as the basis of a method for the determination of chlorine dioxide in water.[36] The low tyrosine figure for Flour 3, but not for Flour 4, may be a reflection of this observation.

Conclusions

1. No abnormal substances have been detected in the treated or overtreated flours which were not present in the untreated material.

2. No detectable level of chloro-derivatives was found; only reversible oxidation products of methionine were observed.

3. *Essential amino-acids.* No significant reduction in the quantity of lysine, phenylalanine, threonine, leucine, *iso*leucine, valine, methionine, histidine or arginine in flour protein was found after treatment with chlorine dioxide at ten times normal level. Tryptophan was slightly reduced at ten times normal level of treatment to about 92% of the level found in the untreated material.

4. *Non-essential amino-acids.* At ten times normal level of treatment with chlorine dioxide, cystine was reduced to about 75% of the level found in the untreated material.

Acknowledgments

The authors are indebted to Messrs. Wallace & Tiernan, Ltd. for supplying the flours and special chemicals, and to Dr. D. W. Kent-Jones and Dr. A. J. Amos for carrying out an independent check on all test materials used.

Department of Pharmacology
Medical School
Edgbaston
Birmingham, 15

Received 22 September, 1955

References

[1] Baker, J. C., U.S.P. 1,367,530
[2] Staudt, E., B.P. 263,760
[3] Rank, Ltd., & Hay, J. G., B.P. 646,311
[4] Ferrari, C. G., Hutchinson, W. S., Croze, A. B., & Mecham, D. K., *Cereal Chem.*, 1941, **18,** 699
[5] Departmental Committee of the Ministry of Health, 'Report on Treatment of Flour with Chemical Substances', 1927 (London: H.M.S.O.)
[6] Mellanby, E., *Brit. med. J.*, 1946, ii, 885
[7] Bentley, H. R., McDermott, E. E., Moran, T., Pace, J., & Whitehead, J. K., *Proc. roy. Soc.*, 1950, [B] **137,** 403
[8] Campbell, P. N., Work, T. S., & Mellanby, E., *Biochem. J.*, 1951, **48,** 106
[9] Radomski, J. L., Woodard, G., & Lehman, A. J., *J. Nutr.*, 1948, **36,** 15
[10] Bentley, H. R., Heathcote, J. G., Booth, R. G., Hutchinson, J. B., Greer, E. N., & Moran, T., *Nature, Lond.*, 1948, **161,** 126
[11] Arnold, A., *Cereal Chem.*, 1949, **26,** 46
[12] Newell, G. W., Gershoff, S. N., Suckle, H. M., Gilson, W. E., Erickson, T. C., & Elvehjem, C. A., *Cereal Chem.*, 1949, **26,** 160
[13] Moran, T., Pace, J., & McDermott, E. E., *Nature, Lond.*, 1953, **171,** 103
[14] Moran, T., Pace, J., & McDermott, E. E., *Nature, Lond.*, 1954, **174,** 449
[15] Bagnall, H. H., Annu. Rep. Birmingham City Analyst, 1953
[16] Dustin, J. P., Czajkowska, C., Moore, S., & Bigwood, E. J., *Analyt. chim. Acta*, 1953, **9,** 256
[17] Partridge, S. M., *Biochem. J.*, 1948, **42,** 238
[18] Moore, S., & Stein, W. H., *J. biol. Chem.*, 1948, **176,** 367
[19] Chibnall, A. C., Rees, M. W., & Williams, E. F., *Biochem. J.*, 1943, **37,** 354
[20] Ballentine, R., & Gregg, J. R., *Analyt. Chem.*, 1947, **19,** 281
[21] Osborne, T. B., 'The Proteins of the Wheat Kernel', 1907, Carnegie Institute of Washington, Publ. 84
[22] Moore, S., & Stein, W. H., *J. biol. Chem.*, 1951, **192,** 663
[23] Schramm, E., Dustin, J. P., Moore, S., & Bigwood, E. J., *Analyt. chim. Acta*, 1953, **9,** 149
[24] Schramm, E., & Bigwood, E. J., *Analyt. Chem.*, 1953, **25,** 1424
[25] Cocking, E. C., & Yemm, E. W., *Biochem. J.*, 1954, **58,** Proc. xii
[26] Yemm, E. W., & Cocking, E. C., *Analyst*, 1955, **80,** 209
[27] Bates, R. W., *J. biol. Chem.*, 1937, **119,** vii
[28] Campbell, P. N., Work, T. S., & Mellanby, E., *Nature, Lond.*, 1950, **165,** 345
[29] Block, R. J., & Bolling, D., 'The Amino-acid Composition of Proteins and Foods', 2nd edn., 1951 (Springfield, Ill.: Thomas)
[30] Block, R. J., quoted in Kleiner, I. S., 'Human Biochemistry', 4th edn., 1954 (London: Kimpton)
[31] Rutgers University Bureau of Biological Research Bulletin, 'Co-operative Determinations of the Amino-Acid Content . . . of Six Selected Protein Food Sources, 1946–50'; quoted in 'Nutritional Data', 2nd edn., 1954 (Pennsylvania: H. J. Heinz Co.)
[32] Reiner, L., Misani, F., Fair, T. W., Weiss, P., & Cordasco, M. G., *J. Amer. chem. Soc.*, 1950, **72,** 2297
[33] Frazer, A. C., Meredith, P., & Sammons, H. G., *Biochem. J.*, 1953, **54,** Proc. xxxvii
[34] Bennett, M. A., *Biochem. J.*, 1939, **33,** 1794
[35] Bennett, M. A., *J. biol. Chem.*, 1941, **141,** 573
[36] Hodgden, H. W., & Ingols, R. S., *Analyt. Chem.*, 1954, **26,** 1224

STUDIES ON THE EFFECTS OF TREATMENT WITH CHLORINE DIOXIDE ON THE PROPERTIES OF WHEAT FLOUR. II.*—Nutritional Value of Proteins of Treated Flours

By A. C. FRAZER, J. R. HICKMAN, H. G. SAMMONS and M. SHARRATT

Feeding tests were carried out and weight gains in relation to food intakes were studied.

1. No differences were demonstrable in the wellbeing or weight gain on unrestricted food intake in animals receiving a diet containing 77% of breadcrumb, whether the flour used was untreated or treated at ten times the normal level with chlorine dioxide.

2. No differences were demonstrable in wellbeing or weight gain on an unrestricted food intake in groups of rats receiving flour protein as the main dietary protein source over a 5-week period, whether the flour used was untreated or treated at ten times the normal level with chlorine dioxide.

3. Lysine supplementation of these diets had an identical effect on the weight gain of groups receiving untreated or treated flour.

4. It is concluded that treatment of flour with chlorine dioxide even at ten times the normal level has no demonstrable effect on the nutritional value of the flour proteins.

It has already been shown by Meredith *et al.*[1] that chemically there is no significant reduction in essential amino-acids after ten times normal level of treatment, with the possible exception of a reduction of not more than 10% of tryptophan. Nevertheless, it seems advisable that this should be checked biologically. The studies reported in this paper were carried out to examine the effect of chlorine dioxide treatment on the nutritional value of flour protein.

Experimental

Materials

Flours used.—These had compositions comparable with those used in Part I. Half the flour was left untreated and half was treated with chlorine dioxide at ten times normal level. Fundamental analyses and degree of treatment were independently checked.

Breadcrumbs.—These were prepared by drying the bread at a temperature not exceeding 60° and grinding. They were used within 14 days and meanwhile were stored in the refrigerator.

Rats.—These were albinos, derived from a Wistar strain. They were taken from our own breeding stock at 30–40 g. body-weight immediately after weaning.

Diets.—The basal diet for Experiments I and II consisted of:

	I	II
	%	%
Breadcrumbs	77	88·5
Yeast	7	7
Casein (crude), Glaxo	11·5	—
Salt mixture (U.S.P. XIV)	4·5	4·5

with supplements of vitamin A acetate (1000 units), Calciferol (0·0025 mg.), α-tocopherol acetate (7 mg.) and Menaphthone (1 mg.) in 0·1 ml. of ethyl laurate given weekly by mouth to each rat.

The basal diet for Experiment III consisted of:

	%
Wheat flour	86
Arachis oil	9
L-Lysine dihydrochloride	0·86
Salts	4
B vitamins	0·14

with supplements of vitamin A acetate (1000 units), Calciferol (0·0025 mg.), α-tocopherol acetate (7 mg.) and Menaphthone (1 mg.) in 0·1 ml. of ethyl laurate given weekly by mouth to each rat.

* Part I: preceding paper

Methods

Groups of male rats were made up from litter mates, the litters being distributed between the groups, the rats being placed in individual cages. The food intake and weight gains were measured during the period of initial rapid growth. To enable the food intake to be measured accurately, the food was placed in a small vessel contained in a larger outer dish. Any food spilt during feeding from the inner pot was collected in the outer one. In case any food was spilt from the outer pot the animals were kept on wire grids about 1½ in. above the bottom tray of the cage. The tray was lined with several thicknesses of absorbent paper to absorb the urine, and any food spilt in the tray could be separated from the faeces and weighed. This system also effectively prevented coprophagy.

The experiments consisted of three parts:

I. An examination of the nutritional value of bread prepared from wheat flour treated with chlorine dioxide.

The experiment consisted of the measurement of food intake and weight gain in two groups of ten rats each, over a period of four weeks. One group was fed with the basal diet, containing breadcrumbs prepared from flour treated at ten times the normal level, and the other group fed with breadcrumbs prepared from the same flour, untreated. The general health was observed carefully, particularly with reference to any signs of dietary deficiency.

II. An examination of the nutritional value of wheat flour after treatment with chlorine dioxide with rats on a restricted protein intake.

Two groups of ten rats were used. The basal diet was as outlined previously, with the substitution of more dried breadcrumbs for the casein. The only sources of protein were now the dried breadcrumb, together with a small amount of yeast protein. One group was fed with a diet containing breadcrumb prepared from flour treated at ten times the normal rate of treatment with chlorine dioxide, and the other group a diet containing breadcrumb prepared from the same flour which had not been treated, each group for a period of five weeks.

III. An examination of the nutritional value of wheat flour protein with lysine supplementation.

Three groups of five rats were used. One group was fed with the diet containing flour treated at ten times the normal rate with chlorine dioxide, and another group was fed with the diet containing the same flour which had not been treated, each group for a period of six weeks. Both these flours were fed *ad libitum*. The third group was fed with the diet containing untreated flour, but the food intake was restricted to that of the group fed with the ten-times-normal-treated flour diet, to overcome palatability differences. This latter problem will be discussed more fully in Part III (following paper).

Treatment of results

The food intakes and weight gains were measured weekly and these figures formed the data from which regression equations were calculated and the corresponding lines were plotted. Average cumulative food intakes and weight gains were also calculated and recorded as points on the graphs. The statistical analysis for variance was made essentially as described by Quenouille.[2] To ensure that these measurements were an accurate assessment of the association between the growth rate and the food intake, an analysis of variance of the regression was carried out. Differences between the regressions were tested by 'Student's t test'.

Results

The results of the three experiments are given in Tables I, II and III, and illustrated in Figs. 1, 2 and 3, respectively. There was no significant difference between the groups of rats used in each experiment.

Table I

Effect of chlorine dioxide treatment on the nutritional value of dried breadcrumb (diet also containing casein)

	Regression coefficient (P = 0·99)	Probability of no differences between regressions
Untreated	0·3163 ± 0·05755	0·6 > P > 0·5
10 × normal ClO_2 treatment	0·3126 ± 0·05021	

Analysis of variance of the association between weight gain and food intake

	M.S.	F.	P.
Untreated			
Variance ascribable to food intake	3869	297·6	> 0·99
Residual variance	13		
10 × normal ClO_2 treatment			
Variance due to food intake	3819	381·9	> 0·99
Residual variance	10		

Table II

Effect of chlorine dioxide treatment on the nutritional value of dried breadcrumb used as the principal protein source (no casein in diet)

	Regression coefficient (P = 0·99)	Probability of no differences between regressions
Untreated	0·2055 ± 0·02025	0·3 > P > 0·2
10 × normal ClO_2 treatment	0·2244 ± 0·001783	

Analysis of variance of the association between weight gain and food intake

	M.S.	F.	P.
Untreated			
Variance ascribable to food intake	2601·4	351·5	> 0·99
Residual variance	7·4		
10 × normal ClO_2 treatment			
Variance ascribable to food intake	2704	541	> 0·99
Residual variance	5·0		

Table III

Effect of chlorine dioxide treatment of wheat flour used as the only source of protein, supplemented with L*-lysine*

	Regression coefficient (P = 0·99)	Probability of no differences between regressions
Untreated (diet *ad lib.*)	0·2173 ± 0·007198	0·2 > P > 0·1
10 × normal ClO_2 treatment	0·2335 ± 0·007747	0·2 > P > 0·1 ; 0·5 > P > 0·4
Untreated (food intake restricted to that on 10 × normal ClO_2 treated flour)	0·1996 ± 0·02073	

Analysis of variance between the association of growth and food intake

	M.S.	F.	P.
Untreated (*ad lib.*)			
Variance ascribable to food intake	4530·9	910·7	> 0·99
Residual variance	19·9		
10 × normal ClO_2 treatment			
Variance ascribable to food intake	4643·3	908·7	> 0·99
Residual variance	5·11		
Untreated (food intake restricted to that on 10 × normal ClO_2 treated flour)			
Variance ascribable to food intake	3391·9	92·67	> 0·99
Residual variance	36·6		

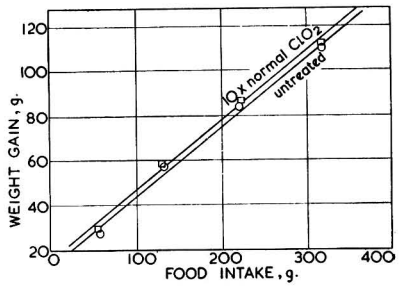


FIG. 1.—*Regression lines and average cumulative food intakes and weight gains—diet of breadcrumbs + casein etc.*

○ Untreated flour. $y - 69{\cdot}75 = 0{\cdot}31632(x - 183{\cdot}00)$
□ 10 × normal ClO_2-treated flour. $y - 71{\cdot}25 = 0{\cdot}31260\ (x - 182{\cdot}25)$

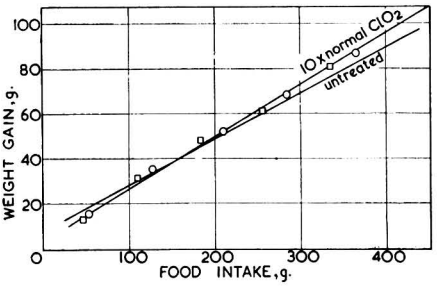


FIG. 2.—*Regression lines and average cumulative food intakes and weight gains—diet of breadcrumbs etc. without casein*

○ Untreated. $y - 50{\cdot}96 = 0{\cdot}2055(x - 210{\cdot}12)$
□ 10 × normal ClO_2. $y - 47{\cdot}58 = 0{\cdot}2244(x - 188{\cdot}24)$

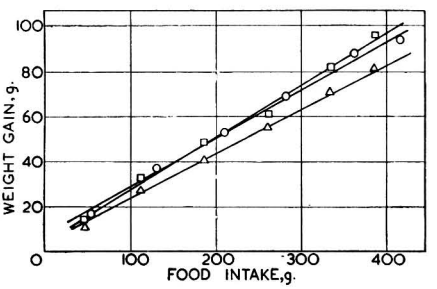


FIG. 3.—*Regression lines and average cumulative food intakes and weight gains—diet of bread crumbs etc. without casein, but with lysine supplementation*

○ Untreated—diet *ad lib.* $y - 59{\cdot}37 = 0{\cdot}2173(x - 243{\cdot}17)$
□ 10 × normal ClO_2—diet *ad lib.* $y - 55{\cdot}60 = 0{\cdot}2335(x - 221{\cdot}23)$
△ Untreated—dietary intake restricted to 10 × normal ClO_2 intake. $y - 47{\cdot}40 = 0{\cdot}1996(x - 221{\cdot}23)$

Discussion

The preliminary experiment showed no gross change in the nutritional value of the flour protein even after ten times the normal treatment with chlorine dioxide. This is in complete accord with the chemical studies and the observation of other workers.[1, 3–6] It seemed advisable, however, to put the treated material to a more stringent test, so the next series of experiments were devised in which the flour protein was practically the only protein source available. Even under these circumstances there was no significant difference between the growth and wellbeing of the rats receiving the overtreated, as compared with the untreated material. Since flour proteins are known to be deficient in lysine, it might be argued that rats receiving flour protein only were suffering from a depression of growth due to lysine deficiency and that this might be obscuring the presence of other deficiencies. To examine this possibility, the third series of experiments were carried out in which the diets used were supplemented with lysine. Again, no differences were found between the animals receiving bread made from flour treated with ten times the normal level of chlorine dioxide and those having bread made from untreated flour. It may, therefore, be concluded that chlorine dioxide treatment of flour, even at ten times the normal level, caused no demonstrable deleterious effects on the nutritional value of the flour proteins.

Acknowledgments

The authors wish to thank Messrs. Wallace & Tiernan, Ltd. for the treatment of flour with chlorine dioxide, Dr. D. W. Kent-Jones and Dr. A. J. Amos for providing the bread baked from treated and untreated flours and for carrying out an independent check on the properties of all the flours used in these experiments, and Barbara Meredith for technical assistance with the dietary control.

Department of Pharmacology
Medical School
Edgbaston
Birmingham, 15

Received 22 September, 1955

References

[1] Meredith, P., Sammons, H. G., & Frazer, A. C., *J. Sci. Fd Agric.*, 1956, **7**, 361
[2] Quenouille, M. H., 'Introductory Statistics', 1950 (London: Butterworth)
[3] Newell, G. W., Gershoff, S. N., Suckle, H. M., Gilson, W. E., Erickson, T. L., & Elvehjem, C. A., *Cereal Chem.*, 1949, **26**, 160
[4] Frazer, A. C., Meredith, P., & Sammons, H. G., *Biochem. J.*, 1953, **54**, xxxvii
[5] Graham, W. D., Teed, H., & Grice, H. M., *J. Pharm. and Pharmacol.*, 1954, **6**, 534
[6] Graham, W. D., & Grice, H. M., *J. Pharm. Lond.*, 1955, **7**, 126

STUDIES ON THE EFFECTS OF TREATMENT WITH CHLORINE DIOXIDE ON THE PROPERTIES OF WHEAT FLOUR. III.*—Lipid Changes and Vitamin Content of Treated Flours

By A. C. FRAZER, J. R. HICKMAN, H. G. SAMMONS and M. SHARRATT

This investigation shows that, in the development of rancidity of the flour lipid by air oxidation or by chlorine dioxide overtreatment of the flour, the palatability of the flour is affected, but that, even so, there is no demonstrable alteration in the nutritional value of the flour protein.

Vitamin E is destroyed by all oxidative methods, but as it contributes only about 10% of the total dietary vitamin E, this, on present evidence, is not considered to be of serious nutritional significance to man.

Introduction

As already described in Parts I and II,[1, 2] the effects of chlorine dioxide on the amino-acids of flour proteins are minimal. From chemical studies the only changes caused by ten-times-normal level of treatment are: a reduction of cystine to about 74% of the level found in untreated flour and a small decrease in the tryptophan content. Biological tests show that there is no significant decrease in the nutritional value of the flour protein. The other main effects that might be expected to occur as a result of oxidation are changes in the lipids and possibly some reduction in vitamins—especially vitamin E. The object of this paper is to describe studies carried out on this aspect of the problem.

Materials and methods

Materials

Breadcrumb was prepared by drying bread at a temperature not exceeding 60° from flour that is (i) untreated, (ii) ClO_2-treated at normal level, or (iii) ClO_2-treated at ten-times-normal level, or for certain experiments, from bread made by an aeration process using untreated flour. In this procedure, half the flour is mixed at high speed with all the water and a little unprocessed

* Part II: preceding paper

soya flour for a few minutes before the remainder of the flour is added to make the dough. The fresh breadcrumb, as used in the feeding experiments, was used within 14 days of preparation and meanwhile was stored in the refrigerator. The stale breadcrumb, as used for the determination of peroxide value only, was prepared by exposing breadcrumb to a warm dry atmosphere for several weeks.

Animals

Groups of rats—litter mate male pairs—were taken immediately after weaning at 30–40 g. body weight. The animals were kept in individual cages throughout the experiment, as described in Part II.[2] Food intakes and weight gains were measured.

Methods

Chemical estimation of peroxides.—The method of Wheeler[3] was employed, using a carbon tetrachloride extract of the flours.

Assessment of effects of rancidity.—The weight gains and food intakes of five litter mate pairs of rats were taken over a period of three consecutive weeks and correlated with peroxide values. One pair was fed rancid breadcrumb from overtreated flour (peroxide value 21), while the other was fed non-rancid breadcrumb from the same flour untreated (peroxide value 5). The diets were as follows:

	%
Yeast	6·0
Breadcrumb	71·5
Arachis oil	11·0
Salt (U.S.P. XIV)	4·5
Casein (crude), Glaxo	7·0

The diets were stored in the refrigerator at 0° after mixing to restrict further oxidation, until required for feeding. Diets were made up weekly.

Fat-soluble vitamins, including α-tocopherol, were given as supplements by mouth.[2]

Assessment of vitamin-E content.—(*a*) The weight gains and food intakes of ten groups of rats, eight males in each group, were measured over a period of 100 days.

(*b*) The relative testes weights $\left(\frac{\text{weight of testes}}{\text{weight of animal}} \times 100\right)$ were determined at the end of this period.

(*c*) The following diets were used:

Vitamin-E-free diet (A)	%
Casein (vitamin free)	15
Lard	10
Dry yeast	10
Steenbock salt mixture	5
Sucrose	60

Group A was fed diet A only. Groups Bi, Bii and Biii were fed diet A, in which sucrose was replaced by breadcrumb made from untreated flour.

Groups Ci, Cii and Ciii were fed diet A, in which sucrose was replaced by breadcrumb made from normally treated flour.

Groups Di, Dii and Diii were fed diet A, in which sucrose was replaced by breadcrumb made from flour treated by the aeration process using untreated flour.

Groups Bi, Ci and Di had no vitamin-E supplement.

Groups Bii, Cii and Dii had 0·5 mg. of vitamin E/rat/day.

Groups Biii, Ciii and Diii had 1·0 mg. of vitamin E/rat/day.

Results

Assessment of effects of rancidity

Peroxide values.—No significant differences were observed between untreated material and material treated with chlorine dioxide at normal level. Ten-times-normal chlorine dioxide

treatment resulted in a higher peroxide value. Allowing the breadcrumb to become stale produced a similar result. These results are summarized in Table I.

The production of peroxides gives only a rough indication of the degree to which oxidative rancidity has developed. It is only a part of a complex process, and various conditions of time and temperature may alter the peroxide level considerably.

Table I

Peroxide values of bread and breadcrumb

	Peroxide value μg. O_2/g.
(i) *Flour or fresh bread*	
Untreated Chlorine-dioxide-treated at normal level	< 5·0 (usually nearer 1·0)
(ii) *Fresh breadcrumb*	
Untreated Chlorine-dioxide-treated at normal level	1–5
Chlorine-dioxide-treated at 10 × normal level	15–25
(iii) *Stale breadcrumb*	
Either from treated or untreated flours	>15

Biological studies to assess the effect of rancidity.—Table II shows weight gain/food intake relationship for litter mate pairs compared with peroxide value of a carbon tetrachloride extract of the diet. Animals receiving untreated material ate more of the diet but the ratio of weight gain/100 g. food intake was the same in both groups.

Table II

Weight gain/food intake relationship compared with peroxide value

Litter mate group	1	2	3	4	5
Weight gain g./rat/day					
A. Diet with overtreated material (Peroxide value = 21)	4·1	4·5	4·6	4·8	4·6
B. Diet with untreated material (Peroxide value = 5)	4·8	5·1	5·1	4·4	4·6
Food intake g./rat/day					
A	9·7	11·7	10·8	12·3	13·3
B	11·8	13·6	12·6	11·7	13·6
Weight gain g./100 g. food intake					
A	42	38	43	39	35
B	41	38	41	38	34

Assessment of vitamin-E content

Chemical estimation of tocopherols.—A marked reduction of the α-tocopherol content of flours occurred after treatment with chlorine dioxide. These observations are summarized in Table III.

Table III

Chemical assay of α-tocopherol content of flour

	α-tocopherols mg./100 g.	S.D.	% 'Normal level'
Untreated flour	1·5	±0·020	100
Chlorine-dioxide treated (normal level)	0·2	±0·016	14
Chlorine-dioxide-treated (10 × normal level)	Trace	—	—

Biological assessment of vitamin E content.—The body weights at 100 days are given and compared in Table IV. No significant differences were observed between any of the groups.

Table IV

Body weight of rats at 100 days

	Vitamin-E supplement mg./rat/day	Body weight at 100 days	Standard deviation
A. Control	0	210	± 34·4
B. Untreated			
i	0	189	± 26·5
ii	0·5	196	
iii	1·0	204	± 20·2
C. Chlorine-dioxide-treated			
i	0	209	± 25·4
ii	0·5	206	
iii	1·0	208	± 17·2
D. Aeration treatment			
i	0	212	± 22·8
ii	0·5	213	
iii	1·0	197	± 17·5

The relative testes weights are recorded in Table V and analysed statistically in Table VI. The results confirm that the vitamin E content of flour is reduced by both chlorine dioxide and aeration treatment. Statistical analysis (Table VI) shows that there is no statistical difference between the mean testes weights in Groups A, C and Di, and that the values in these three groups are significantly different from those in all other groups with the exception of A/Bii, A/Cii, A/Diii and Ci/Cii.

Table V

Relative testes weights of individual animals in each group

Rat No.	Control sucrose A	Bread from untreated flour B			Bread from chlorine-dioxide-treated flour C			Bread made by aeration process D		
		i	ii	iii	i	ii	iii	i	ii	iii
1	9·26	8·37	8·79	9·94	7·30	9·34	8·83	5·96	9·39	9·56
2	12·56	7·75	10·86	8·55	9·87	9·68	13·42	5·23	8·43	10·75
3	3·27	9·29	9·57	8·60	9·11	8·92	10·00	4·96	9·30	8·19
4	3·95	11·18	6·04	5·76	4·50	9·42	8·88	3·41	9·34	10·48
5	5·21	10·56	10·11	8·26	9·09	8·83	10·69	4·36	8·21	10·49
6	8·74	9·36	11·04	10·46	5·62	8·43	9·19	9·86	10·04	9·63
7	3·84	10·79	7·69	10·55	4·56	10·29	9·70	4·41	10·97	8·59
8	4·18	10·59	10·25	10·65	4·01	6·96	8·52	—	10·55	10·46
Mean	6·38	9·75	9·29	9·10	6·76	8·98	9·90	5·46	9·53	9·77
S.D.	±3·30	±1·24	±1·71	±1·67	±2·38	±1·00	±1·52	±2·10	±0·97	±0·96

Discussion

Changes in the fatty acids in flour oil

The lipid material occurring in flour forms about 1·0% of the flour by weight. It consists mainly of glycerides and phospholipids.[5] The unsaturated fatty acids present in flour—especially linoleic and linolenic acid—are readily oxidized in the presence of air. The products of the

Table VI

Assessment of significance of figures shown in Table V by White's Ranking Method (reference No. 7)

	Bi	Bii	Biii	Ci	Cii	Ciii	Di	Dii	Diii	
A	S	S	NS	NS	NS	S	NS	S	NS	A
	Bi	NS	NS	S	NS	NS	S	NS	NS	Bi
		Bii	NS	S	NS	NS	S	NS	NS	Bii
			Biii	S	NS	NS	S	NS	NS	Biii
				Ci	NS	S	NS	S	S	Ci
					Cii	NS	S	NS	NS	Cii
						Ciii	S	NS	NS	Ciii
							Di	S	S	Di
								Dii	NS	Dii
									Diii	////// //////

Probability of groups being from same population

NS = Not significant. $P > 0.05$

S = Significant. $P = 0.05$ *or* $P < 0.05$

oxidation are complex and include peroxides, hydroxy-acids, aldehydes and polymers. A number of volatile substances may be formed that give the off-flavour effect associated with rancidity.

Some rats tolerated the rancid breadcrumb well, but other rats did not, and in consequence they ate less of the material. Moran, Pace & Hutchinson[6] have published studies which clearly demonstrate interference with palatability due to overtreatment. As may be seen from the average figures (Table II), the overall result was a reduction in the food intake. In every case the weight gain ran parallel with the food intake (the weight gain in g. per 100 g. of food intake was not significantly different between any of the litter mate pairs).

These oxidative changes will be prevented, or at least delayed, by the presence of natural antioxidants, such as the tocopherols. As oxidation proceeds and peroxides are formed, so the level of antioxidants decreases. When the antioxidant level becomes very low, rapid development of oxidative chain reactions may take place. The oxidative changes are part of the normal alterations that take place in flour or bread with the passage of time.

It will be seen from Tables III–VI that, both chemically and biologically, vitamin-E activity was considerably reduced by treatment of the flour. The same effect was produced by both chlorine dioxide and aeration treatment. Vitamin E in flour is labile: it decreases during natural ageing and is markedly reduced by baking. On present levels of consumption in this country, the daily intake of vitamin E is of the order of 10 mg. per day, of which flour contributes about 1 mg. If this is, in fact, close to the normal daily requirement, supplementation may be desirable. This would be best achieved by increasing the intake of foods that provide a rich and relatively stable source of vitamin E. Cottonseed and palm oil at 30–60 mg./100 g., soya-bean and groundnut oil at about 10 mg./100 g., would appear to be much more promising sources of dietary vitamin E than bread containing less than 0·5 mg./100 g. Another possible source is oatmeal, which may contain 2–5 mg./100 g. With these considerations in mind, it is difficult to attribute any nutritional significance to the more rapid reduction of the vitamin-E content of flour by chlorine dioxide or other forms of treatment.

Acknowledgments

The authors wish to thank Messrs. Wallace & Tiernan, Ltd. for the supply of treated and untreated flours, Dr. D. W. Kent-Jones and Dr. A. J. Amos for providing the breadcrumb and

for their independent check on all flours used, and Dr. Frances Williams for the chemical assay of vitamin E.

Department of Pharmacology
Medical School
Edgbaston
Birmingham, 15

Received 24 October, 1955

References

[1] Meredith, P., Sammons, H. G., & Frazer, A. C., *J. Sci. Fd Agric.*, 1956, **7**, 361
[2] Frazer, A. C., Hickman, J. R., Sammons, H. G., & Sharratt, M., *J. Sci. Fd Agric.*, 1956, **7**, 371
[3] Wheeler, D. H., *J. Amer. Oil Chem. Soc.*, 1948, **25**, 315
[4] Emmerie, A., & Engel, C., *Rec. Trav. chim. Pays-bas*, 1938, **57**, 1351
[5] Hilditch, T. P., 'The Chemical Constitution of Natural Fats', 1947, 2nd edn. (revised) (London : Chapman & Hall)
[6] Moran, T., Pace, J., & Hutchinson, J. B., *Chem. & Ind.*, 1954, p. 1354
[7] White, C., *Biometrics*, 1952, **8**, 33

ERRATA

In the paper entitled 'The Chemical Composition and Nutritional Value of Bacon' by L. C. Baker, *J. Sci Fd Agric.*, 1956, **7**, 179, the word 'not' should be deleted from the second paragraph on p. 179.

In the paper entitled 'Studies on the Nitrogen Metabolism of the Ensilage Process' by A. R. Kemble, *J. Sci. Fd Agric.*, 1956, **7**, 125, in the heading to Table VI the words '% dry matter' should read '% fresh weight.'

In the paper entitled 'The Role of Lipids in Baking. III' by M. A. Cookson and J. B. M. Coppock, *J. Sci. Fd Agric.*, 1956, **7**, 72, in Table III, 'Unsaponification matter' should read 'Unsaponifiable matter', and in Table IV, line 8 should read 'calculated as % glyceryl monostearate.'

JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE

ABSTRACTS

MAY, 1956

The general arrangement of the abstracts is as follows: 1.—AGRICULTURE AND HORTICULTURE. 2.—FOOD; also appropriate Microbiological Processes; Essential Oils. 3.—SANITATION, including Water; Sewage; Atmospheric Pollution, etc. 4.—APPARATUS AND UNCLASSIFIED.

INDEX OF AUTHORS' NAMES

ANON., 257, 262, 271, 290.
Adams, D. F., 249.
Ahrens, M. C., 284.
Alleksandrova, L. N., 245.
Algida Industria Alimenti Gelati S.r.l., 292.
Allcroft, R., 264.
Allen, M. B., 247.
Allmendinger, D. F., 253.
Ambastha, H. N. S., 254.
Amer. Home Products Corp., 292.
Anantharamiah, S. N., 280.
Andersen, E., 271.
Anderson, E. G., 251.
Anderson, J. O., 267.
Anderson, P. W., 284.
André, P., 274.
Andreae, W. A., 250.
Andrews, F. N., 264, 267.
Andriesse, D., 283.
Anglin, C., 280.
Anstalt Unda, 291.
Arle, H. F., 261.
Arnon, D. I., 247.
Arrington, L. R., 280.
Aso, K., 273, 274.
Ayres, J. C., 282.

BAETZ, G. D., 280.
Bagley, R. A., 267.
Bailey, M. E., 284.
Baker Perkins, Ltd., 292.
Baker Process Co., 291.
Ball, C. D., 251.
Ball, C. O., 275.
Ballinger, W. E., 273.
Banwart, G. J., 282.
Baraud, J., 286.
Barlow, F., 257.
Barr, N. F., 287.
Barrows, H. L., 255.
Bartels, W., 260.
Bartholomew, R. P., 241.
Bartlett, D. E., 264.
Barton, N. L., 246.
Bass, E. J., 277.
Batjer, L. P., 251.
Baumann, E. R., 295.
Beall, G., 287.
Beck, G. E., 251.
Becker, D., 271.
Becker, K., 278.
Becker, R. R., 287.
Beeckler, A. F., 266.
Beeftink, W. G., 243.
Beevers, H., 246, 247.
Bekker, J. H., 294.
Bell, H. K., 253.
Benard, P., 274.
Benedict, R. H., 255.
Bennett, S. H., 257.
Benoit, R. J., 295.
Berg, H. W., 276.
Bergquist, D. H., 283.
Bernardi, A. E., 296.
Bernhart, F. W., 280.
Beroza, M., 294.
Berriozabal, J. M., 291.
Bertram, S. H., 285.
Bethune, J. L., 279.
Betz, A., 246.
Bezeau, L. M., 263.
Bhat, J. V., 282.
Biale, J. C., 246.
Biellier, H. V., 267.
Biely, J., 266.
Bigoui, G., 285.
Bills, G. T., 261.
Binns, W., 267.
Bishop, D., 261.
Bissett, O. W., 274.
Black, D., 272.
Blakemore, L. C., 243.
Blanchet, R., 244.
Blinn, R. C., 294.
Blum, A. E., 286.
Bockelmann, J. B., 277.
Boeke, J. E., 289.
Boettger, S., 271.
Bolhuis, G. G., 255.
Bond, J., 264.
Bonner, J., 250.
Born, D. E., 293.
Bourdet, A., 269.
Boyer, P. D., 271.
Brackeen, L. G., 241.
Brant, A. W., 282.
Bray, D. J., 266.
Brecknell, Munro & Rogers, Ltd., 292.
Breidenstein, B. C., 262.
Brenner, M. W., 278.
Brown, D. A., 255.
Brown, D. R., 275.
Brown, H. D., 273.
Brown, M. L., 286.
Brown, R. T., 255.
Brueckner, A. L., 268.
Bruns, V. F., 261.
Bryan, B. B., 255.
Bryner, J. H., 264.
Buchowicz, J., 249.
Bungenberg de Jong, H. G., 283.
Bunnell, R. H., 266, 268.
Burdine, H. W., 261.
Burger, M., 278.
Buringh, P., 241.
Burmester, B. R., 267.
Burnett, B. B., 289.
Burris, M. J., 283.
Burris, R. H., 248.
Burroughs, W., 265.
Buswell, A. M., 295.

CAHILL, V. R., 283.
Cain, J. C., 247.
Callahan, V. O., 241.
Cameron, J. W., 251.
Campbell, J. D., 254, 260.
Cann, G., 249.
Carlström, G., 264.
Carman, G. E., 294.
Carrick, C. W., 264.
Cass, L. M., 259.
Causa, A. N., 247.
Chabert, E., 259.
Chapman, R. A., 280.
Chatterji, R. K., 270.
Cheftel, H., 287.
Childers, N. F., 253, 259.
Chitale, R. P., 272.
Christensen, C. M., 290.
Christian, J. E., 267.
Christiansen-Weniger, E., 258.
Clark, K. G., 245.
Cleland, J. E., 291.
Cleven, C. C., 275.
Coanda, H., 268.
Columbia-Southern Chem. Corp., 292.
Cook, A. H., 276.
Corbett, R. E., 288.
Corns, W. G., 250.
Cotter, D. J., 258.
Cottrall, G. E., 266.
Couch, J. F., 254.
Couch, J. R., 266.
Craft, C. C., 247.
Creek, R. D., 264.
Croom, A. G., 265.
Crosby, E. S., 296.
Cuendet, L. S., 290.
Culbertson, C. C., 265.
Cummings, J. G., 245.
Curry, J. J., 295.
Czarnecki, H. T., 277.
DACRE, J. C., 282.
Dain, J. A., 263.
Dame, C., jun., 273.
Darby, R. T., 248.
Das, K. G., 285.
Dastur, N. N., 281.
David, W. A. L., 256.
Davidson, R. H., 293.
Davis, G. K., 263.
Deatherage, F. E., 283.
De Bakker, A., 283.
Degman, E. S., 251.
Deibner, L., 274.
Dekker, J., 259.
Denington, E. M., 267.
Denisen, E. L., 253.
De Sollano, C. S. F. D., 291.
Deszyck, E. J., 253, 259.
Dewey, D. H., 273.
Dickson, A. D., 277.
Dietrich, W. C., 275.
Dimick, K. P., 273, 275.
Dimond, A. E., 257.
Dorman, D. A., 295.
Dougherty, R. W., 263.
Dow Chem. Co., 269.
Drago, P., 286, 287.
Draper, C. I., 267.
Drosdoff, M., 241, 255.
Dubetz, S., 255.
Dunn, C. G., 278.
Dunn, H. O., 263.
Dye, W. B., 272.

EASLEY, J. F., 263.
Eaton, H. D., 287.
Ecklund, O. F., 289.
Edelman, C. H., 241.
Edwards, D. H., 242.
Edwards, L. D., 267.
Eheart, J. F., 254.
Elehwany, N. E., 275.
Emilsson, B., 252.
Emmert, E. M., 262.
Emmert, F., 248.
Enders, C., 279.
Endo, A., 262.
Engel, C., 280.
Engler, K., 241.
Englis, D. T., 289.
Ethyl Corp., 269.
Evans, B. S., jun., 289.
Everson, E. H., 261.

FARNHAM, R. S., 241.
Fawcett, C. H., 256.
Fawcett, Ltd., E., 291.
Fay, R. W., 294.
Fazio, T., 278.
Feldman, A. E., 295.
Ferrari, T. J., 243.
Fieger, E. A., 284.
Finn, L. A., 284.
Flanzy, M., 274.
Flunc, J. A., 293.
Foskett, R., 254.
Foster, R. J., 250.
Fouts, E. L., 280.
Fox, R. L., 248.
Foy, C. D., 247.
Francis, D. W., 268.
Francis, F. J., 276.
Frank, A. H., 264.
Frenzel, B., 249.
Fritz, G., 246.
Fritzsche, H. W., 275.
Fulton, J. M., 252.

GADDY, V. L., 245.
Gardiner, B. O. C., 256.
Gardner, R., 245.
Garratt, R. H., 279.
Gasser, W., 281.
Gates, C. W., 257.
Geddes, W. F., 271, 290.
Genevois, L., 286.
Geraldson, C. M., 259.
Gerhardt, F., 290.
Gernon, G. D., jun., 276.
Gersdorff, W. A., 293.
Getty, M. R., 253.
Gibbs, H. S., 242.
Gibbs, M., 247.
Gideon, J. C., 244.
Gilbreath, J. C., 266.
Gilles, K. A., 269.
Girolami, R. L., 282.
Glabe, E. F., 284.
Glenister, P. R., 278.
Gnagy, R. M., 249.
Goldblith, S. A., 289.
Goldman, P. F., 284.
Goll, M., 261.
Golubchuk, M., 290.
Good, N. E., 250.
Gorringe, B. S., 293.
Gradwell, M. W., 242.
Grainger, M. M., 294.
Gray, P. P., 279.
Green, S. R., 278.
Greenleaf, C. A., 289.
Greenwood, D. A., 267.
Greig, J. K., 252.
Guatelli, M. A., 288.
Gunther, F. A., 294.
Guy, E. J., 281.
Guyer, R. B., 274.
Gyles, N. R., 266.
Gyoergy, P., 292.

HAAS, G. J., 277.
Habid, A. T., 273.
Hadaway, A. B., 257.
Hagan, R. M., 246.
Haines, C. E., 263.
Hale, W. H., 265.
Hall, C. V., 252.
Hall, J. L., 283.
Hall, J. R., 291.
Hall, N. S., 241.
Hamada, S., 273.
Hamilton, R., 241.
Hammer, C. L., 251.
Hand, D. B., 275.
Hanna, A. D., 260.
Harcourt, D. G., 259.
Hardenburg, R. E., 274.
Hardesty, J. O., 245.
Harding, H. G., 295.
Harms, R. H., 266.
Harper, W. J., 265.
Harries, J. M., 289.
Harris, J. G., 275.
Harris, R. H., 270.
Harrison, D. L., 283.
Hassall, K. A., 256.
Hatano, T., 263.
Hathaway, M. L., 286.
Hauge, S. M., 264.
Hayes, R. E., 270.
Heatherington, W., 260.
Heck, M. C., 283.
Heiss, R., 287.
Held, H. R., 279.
Henrickson, R. L., 283.
Henson, J. H., 282.
Heukelekian, H., 296.
Highkin, H. R., 250.
Hill, E. G., 265.
Hill, F. W., 266.
Hill, K. W., 255.
Hinkle, D. A., 241.
Hinton, S. A., 265.
Hintzer, H. M. R., 270.
Hodgson, J. M., 261.
Holben, F. J., 254.
Holm, L., 251.
Holton, R. W., 248.
Homeyer, P. G., 265.
Hoover, M. W., 254.
Hopkins, L., 252.
Hopkins, R. H., 276, 277
Horn, M. J., 286.
Hornstein, I., 293.
Horton, O. H., 264.
Hoshing, B. H., 272.
Howell, M. J., 250.
Howlett, F. S., 252.
Hoy, J. M., 257.
Hummel, B., 290.
Humphrey, R. R., 262.
Humphries, E. C., 260.
Hurst, J. S., 267.

IMPERIAL CHEM. INDUSTRIES, LTD., 269.
Instituto de la Grasa, 285.
Iya, K. K., 280.

JACKS, H., 259.
Jager, H., 288.
Janovsky, H. L., 287.
Jenny, J., 249.
Jha, I. B., 254.
Johns, A. T., 262.
Johnson, G. A., 294.
Johnson, J. A., 271.
Jones, A. R., 263.
Jordan, P. S., 265.
Jordan, R. M., 265.
Judenko, E., 260.
Jungherr, E. L., 267, 268.

KACZKOWSKI, J., 248.
Kaler, H. A., 249.
Kanngiesser, W., 260.
Karim, A., 244.
Karla, A., 244.
Kassanis, B., 260.
Katz, A., 288.
Kaufman, J., 274.
Kayama, M., 284, 285.
Kearns, C. W., 293.
Keeney, P. G., 280.
Kelley, J., 255.
Kelley, V. W., 250.
Kellog, H. B., 257.
Kendall, W. A., 250.
Kennard, W. C., 253.
Kennedy, J. G., 280.
Kenwood Mfg Co., Ltd., 291.
Kenworthy, A. L., 253.
Ketchum, B. H., 295.
Ketterer, H., 278.
Khan, D. H., 244.
Kimball, L. B., 275.
King, C. G., 287.
King, J., 292.
Kleber, W., 279.
Klose, A. A., 284.
Knight, S. G., 282.
Knollenberg, H. F. R., 291.
Knusekoff, H. H., 241.
Kofranek, A. M., 255.
Kohl, H. C., 255.
Kokatnur, M. G., 285.
Kolbach, P., 279.
Kolbezen, M. J., 294.
Koller, D., 246, 250.
Kondo, F., 263.
Koppe, R. K., 249.
Kornberg, S. R., 271.
Kortleven, J., 245.
Kozeff, A., 267, 268.
Kraft, A. A., 282.
Krienke, W. A., 280.
Kristoffersen, T., 281, 282.
Kuhn, R., 292.
Kuiper, L., 288.
Kuipers, H., 252.
Kung, H.-C., 287.
Kunkel, R., 245.

Kunkle, L. E., 283.
Kymal, K., 270.
Kymal, P. K., 270.

Lafourcade, S., 276.
Lagasse, F. S., 255.
Lancy, L. E., 291.
Langenberg, G. J., 270.
Larsen, R. P., 253.
Larson, N. L., 266.
Lawrence, C. H., 258.
Lawson, C. W., 292.
Laxminarayana, H., 280.
Layton, M. H., 241.
Lee, J. G., 263.
Leonard, S. J., 273.
Lesher, S., 206.
Lesher, S. W., 267.
Lewis, R. W., 266.
Lewis, V. M., 292.
Linquist, D. A., 294.
Lindquist, F. E., 275.
Link, C. B., 255.
Linn, M. B., 255.
List, P. H., 286.
Lloyd-Jones, C. P., 257.
Longenecker, J. B., 291.
Lott, R. V., 253.
Love, R., 267.
Lubitsch, T. M., 271.
Lucas, A. M., 267.
Lucas, H. L., jun., 287.
Luchsinger, E. B., 276.
Luh, B. S., 273.
Lund, A. J., 289.
Lunt, O. R., 255.
Lutz, J. M., 274.
Lyons & Co., Ltd., J., 292.
Lyr, H., 261.

Mabbitt, L. A., 282.
McArdle, F. J., 287.
McCallum, G. J., 242.
McCauley, R. H., jun., 294.
McClary, C. F., 267.
McCollum, J. P., 255.
McDonald, D. C., 242.
McFarlane, W. D., 279.
McIntyre, C. L., 241.
McIntyre, R. T., 270.
McKee, H. S., 247.
Mackintosh, D. L., 283.
McLaren, J. B., 265.
MacLeod, P., 280.
Maclinn, W. A., 275.
McPherson, J. B., jun., 294.
McRae, D. H., 250.
Mader, P. B., 249.
Mahlstede, J. P., 251.
Mahon, J. H., 280.
Makower, B., 272, 273, 275.
Malan, H., 290.
Manders, G. R., 248.
Mannheim, H. C., 287.
March, B. E., 266.
Marlowe, G. A., jun., 254.
Marsh, G. L., 273, 276.
Marshall, N. L., 257.
Martin, L. F., 272.
Martin, W. P., 243.
Massey, P. H., jun., 254.
Mather, G. P., 272.
Mathur, L. B., 287.
Matson, W. E., 284.
Matterson, L. D., 266, 267.
Matthews, W. A., 252.
Mayfield, H. L., 266.
Mayhew, D. J., 249.
Meade, F. M., 255.
Meade, R. J., 265.
Mecham, D. K., 271.
Mehta, T. N., 285.
Meijer, A., 273.
Mellen, W. J., 266.
Meredith, W. O. S., 277.
Merker, P. C., 267.
Merrill, M., jun., 255.
Meyer, F. L., 286.
Miles, J. W., 289.
Miller, B. S., 271.
Miller, D., 271.
Miller, J. G., 256.
Miller, T. B., 282.
Miller, W. M., 274.
Minges, P., 254.
Minister of Supply, 292.
Ministry of Agric., Fisheries & Food, Food Standards Commee, 288.
Mitra, S. N., 270, 281.
Moghrabi, H., 254.
Money, R. W., 292.
Monsanto Chem. Co., 268.
Monvoisin, J., 287.
Moore, E. L., 251.
Moorefield, H. H., 293.
Moreno Calvo, J., 273.
Morgan, M. E., 280.
Mortensen, J. L., 243.
Mossell, D. A. A., 288, 294.
Mountier, N. S., 256.
Moyer, J. C., 275.
Mukherjee, S., 272.
Murwin, H. F., 252.

Naghski, J., 254.
Nair, K. V., 285.
Nakayama, T., 274.
Neal, A. L., 263.
Negbi, M., 250.
Nelson, A. I., 270, 275, 287.
Nelson, F. E., 281, 282.
Nestel, L., 247.
Nielsen, H., 267.
Nielsen, T. R., 247.
Noll, C. R., jun., 248.
Noordzij, P., 290.
Nordfeldt, S., 262.
Normand, W. C., 261.
Northern Dairy Engrs, Ltd., 291.
Norton, H. W., 275.
Notevarp, O., 292.
Novak, A. F., 284.
Noworytko, J., 296.
N.V. Octroolen-Maats. "Activit," 291.

Österreichische Stickstoffwerke A.-G., 268.
Ohira, K., 246.
Ohms, J. I., 264.
Oki, N., 274.
Olcott, H. S., 271.
Olsen, S. R., 245.
Oserstreet, R., 247.
Oort, A. J. P., 256, 258, 259.
Orr, H. L., 267.
Ørum-Hansen, S., 292.
Oser, B. L., 287.
Owades, J. L., 278.
Owen, B. D., 263.

Padfield, C. A. S., 259.
Pahnish, O. F., 265.
Palmer, K. J., 272.
Palmer, L., 249.
Pandit, T. K., 282.
Parker, H. E., 264.
Parkin, E. A., 261.
Parsons, C., 276.
Patton, S., 280.
Paukner, E., 279.
Pearson, C. S., 287.
Peebles, D. D., 281.
Peeters, G. P., 274.
Pence, J. W., 271.
Perry, C. C., 259.
Peryam, D. R., 289.
Peterson, A., 290.
Peterson, M. L., 246.
Pew, W. D., 252.
Peynaud, E., 276.
Pfeil, E., 260.
Pilgrim, F. J., 289.
Pillay, P. P., 285.
Pippen, E. L., 284.
Piquett, P. G., 293.
Plaisted, P. H., 251.
Pluygers, C. W., 256.
Polin, D., 266.
Pomeroy, R., 295.
Pool, M. F., 284.
Popence, J., 247.
Porges, N., 296.
Posthethwaite, J. D., 242.
Potasse et Engrais Chimiques, 268, 269.
Potter, G. F., 255.
Potter, L. M., 266, 267.
Pouradier, J., 286.
Powers, L., 251.
Prescott, L. H., 261.
Process Millers, Inc., 291.
Procter, B. E., 289.

Radwan, A. A. M., 250.
Raeside, J. I., 264.
Rahn, E. M., 251.
Raible, K., 279.
Raleigh, G. J., 261.
Ramachandran, K., 248.
Ransford, J. R., 275.
Rao, M. B., 281.
Rao, M. N., 289.
Rao, S. N. G., 272.
Rao, S. V., 248.
Rappaport, L., 253.
Rayner, J. W. R., 269.
Reagan, R. L., 268.
Rebstock, T. L., 251.
Refai, F. Y., 271.
Reid, B. L., 266.
Reid, J. T., 263.
Reifer, I., 248, 249.
Ribereau-Gayon, J., 276.
Rigby, F. L., 279.
Riker, A. J., 248.
Ritter, C. M., 253.
Roald, A. S., 292.
Roberts, E. J., 272.
Robertston, R. N., 247.
Robinson, W., 267.
Robinson, W. B., 275.
Rockland, L. B., 276.
Roehm, R. R., 266.
Rogers, B. J., 247.
Rollins, H. A., jun., 252.
Rolston, L. H., 258.
Romsdal, S. D., 245.
Rosella, E., 259.
Roth, G. A., 257.
Rothwell, D. F., 244.
Roubicek, C. B., 265.
Rousseau, J. E., jun., 287.
Roy, H. K., 295.
Roy, S. C., 281.
Ruby, E. S., 283.
Ruf, R. H., 261.
Ruminska, A., 248.
Russell, G. C., 255.
Rust, R. H., 242.
Rutz, W. D., 280.
Ryall, A. L., 274.
Rygg, G. L., 253.

Safley, C. E., 265.
Sahai, R., 287.
Sahasrabudhe, M. R., 296.
Salisbury, F. B., 250.
Sando, W. J., 254.
Sanford, P. E., 266.
Sarnecka-Keller, M., 296.
Sato, A., 274.
Saunders, W. M. H., 243.
Sawyer, C. N., 295.
Sawyer, R. L., 258.
Schafer, M. L., 263.
Schippers, P. A., 252.
Schlegel, V., 290.
Schlichting, E., 244.
Schmehl, W. R., 245.
Schmidt, J. L., 290.
Schoorl, P., 265.
Schreiber, R. A., 289.
Schröder & Co., 291.
Schultz, T. H., 275.
Schutz, H. G., 289.
Scott, L. E., 247, 252.
Scott, R. W., 248.
Searle, G. H., 292.
Sell, H. M., 251.
Semb, G., 244.
Seymour, J., 245.
Shallis, N., 253.
Shapter, R. E., 248.
Sharpless, G. R., 267.
Shaw, C. G., 249.
Shear, C. B., 255.
Shearman, J. W., 291.
Sherard, H., 241.
Sherwood, C., 255.
Shewfelt, A. L., 275.
Shirley, R. L., 263.
Shrader, W. D., 241.
Shupe, J. L., 267.
Sibbitt, L. D., 270.
Sijpesteijn, A. K., 256.
Singsen, E. P., 266, 267, 268.
Sipple, H. L., 287.
Sites, J. W., 253.
Skodje, M. T., 295.
Sletnes, P. A., 292.
Slodowski, P. C., 276.
Sluijsmans, C. M. J., 245.
Slump, H., 281.
Smith, A. K., 284.
Smith, C. B., 249.
Smith, F., 269.
Smith, F. G., 246.
Smith, G. D., 241.
Smith, R. M., 266.
Somade, H. M. B., 293.
Sorensen, C. M., 291.
Sorger-Domenigg, H., 290.
Sotier, A. L., 278.
Spence, E. R., 280.
Spencer, D. M., 256.
Spencer, J. V., 284.
Springer, M. E., 241.
Springs Cotton Mills, 290.
Stadelman, W. J., 284.
Stallcup, O. T., 262.
Standridge, N. N., 271.
Stanley, E. B., 265.
Steffen, A. J., 295.
Steinberg, M. P., 270, 275, 287.
Steinkarys, G., 285.
Stier, E. F., 275.
Stiles, W. C., 259.
Stinson, L. D., 266.
Stone, I., 279.
Stonestreet, G. A., 292.
Strandskov, F. B., 277.
Strocchi, P. M., 286, 287.
Strong, D. C., 267.
Strzemienski, K., 249.
Stubbs, R. W., 255.
Sturkie, P. D., 266.
Subrahmanyan, V., 286.
Suhovecky, A. J., 260.
Sullivan, W. N., 293.
Sund, K. A., 262.
Swaminathan, M., 289.
Swanson, E. W., 265.
Sweet, A. T., 241.
Swenson, G. A., 241.
Swirski, M., 287.
Szabo, A., 245.

Taylor, G. A., 248.
Taylor, J. W., 254.
Taylor, O. C., 249.
Teas, H. J., 251.
Tenney, R. I., 277, 279.
Teubner, F. G., 254.
Thomas, F. B., 254.
Thomas, P., 241.
Thomas, W. D. E., 257.
Thompson, C. D., 261.
Throneberry, G. O., 246.
Tilara, K. S., 287.
Timmers, H. J., 241.
Timmons, F. L., 261.
Ting, S. V., 253, 259.
Tollenaar, D., 260.
Tollenaar, F. D., 288.
Torrie, J. H., 264.
Touchburn, S. P., 266.
Trebler, H. A., 295.
Troop, F. J., 275.
Troy, V. S., 278.
Tsao, C. H., 293.
Tsuchiya, Y., 284, 285.
Tucakov, J., 288.
Tuckett, E. S., 242.
Tuckey, S. L., 296.
Turian, G., 257.
Turner, C. W., 264, 267.
Tveit, M., 258.

Udy, D. C., 270.
Uhlen, G., 244.
Union Starch & Refining Co., 291.
Uota, M., 274.
Upchurch, R. P., 246.
U.S. Dep. Agric., 294.

Vail, G. E., 283.
Van Beukering, J. A., 241.
Van Dam, J. G. C., 243.
Van de Kamer, J. H., 270.
Van der Kerk, G. J. M., 256.
Van der Kloot, A. P., 277.
Van der Molen, W. H., 243.
Van Duin, R. H. A., 242.
Vanecko, S., 247.
Van Engel, E. L., 277.
VanEseltine, W. P., 245.
Van Raalte, M. H., 256.
Van Rummelen, F. F. F. E., 241.
Van Schuylenburgh, J., 241.
Van Wijk, W. R., 241.
Varela, G., 284.
Varier, N. S., 285.
Varner, J. E., 247.
Veldhuis, M. K., 274.
Vermeulen, F. H. B., 243.
Von Lillienskiold, M., 271.
Voss, T., 252.

Wadsworth, R. V., 286.
Waggoner, P. E., 257.
Wain, R. L., 256.
Waldo, F., 292.
Wall & Sons, Ltd., T., 292.
Wallace, H. D., 263.
Wallace & Tiernan Process Co., 291.
Wangerin, R. R., 261.
Warnick, A. C., 263.
Washko, J. B., 254.
Waters, N. F., 266, 267.
Watts, B. M., 284.
Watts, J. G., 257.
Webster, G. C., 247.
Weijers, H. A., 270.
Weiss, C. M., 296.
Wellington, G. H., 263.
Wells, F., 283.
Wesseling, J., 241.
Westhoff, V., 242.
White, H., 291.
White, J. W., 254.
White, P., 292.
Whiting, F., 263.
Whitnah, C. H., 280.
Wieck, F. E., 257.
Wiederspahn, F. E., 253.
Wierbicki, E., 283.
Wilcox, F. H., jun., 267.
Wilcox, L. V., 242.
Wildermuth, R., 241.
Wilkowske, H. H., 280.
Willcox, O. W., 245.
Willett, E. L., 264.
Williams, B. H., 241.
Williams, R. F., 248.
Williams, R. M., 249.
Wilson, S. L., 295.
Wind, G. P., 241, 246.
Winters, H. F., 253.
Winton, B., 267.
Wittwer, S. H., 250, 251, 254.
Wong, C-K., 288.
Wong, F. F., 275.
Wood, R. K. S., 258.
Wright, E., 265.
Wright, H. J., 286.
Wright, K. E., 246.

Yamaguchi, M., 254.
Yamauchi, F., 273.
Yancey, F., 268.
Yerkes, W. D., jun., 249.
Young, R. E., 246.
Young, R. W., 254.

Zaheer, S. H., 248.
Zeevaart, J. A. D., 258.
Zeuthen, C., 291.
Zilliken, F., 292.
Zimmerman, P. W., 296.
Zoch, L. L., 277.
Zonnefeld, H., 273.

ERRATUM

	Col.	Line	
i,	184	3*	*For* 2 : 4-dinitro *read* 2 : 4-dichloro.

*From bottom

JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE

ABSTRACTS

MAY, 1956

I.—AGRICULTURE AND HORTICULTURE

General: Soils and Fertilisers

Soil survey of [A] Elmore Co., Alabama, [B] St. Charles Co., Missouri. [A] L. G. Brackeen, H. Sherard, R. S. Farnham, Philip Thomas, V. O. Callahan, C. L. McIntyre, R. Wildermuth, B. H. Williams, G. A. Swenson, M. Drosdoff, and M. H. Layton. [B] W. D. Shrader, H. H. Krusekopf, A. T. Sweet, N. S. Hall, M. E. Springer and Guy D. Smith (*U.S. Dep. Agric., Soil Conserv. Service*, A 1955, Series 1939, No. 26, 116 pp.; B 1956, Series 1939, No. 38, 49 pp.).—Descriptions with maps of the various types of soil present in the areas named, with their uses and management. H. S. R.

Regional development and agricultural extension (in the Tropics). J. A. van Beukering (*Neth. J. agric. Sci.*, 1955, **3**, 93—99).—An address. A. H. CORNFIELD.

Soils of the alluvial plain of Iraq, south of Baghdad. P. Buringh and C. H. Edelman (*Neth. J. agric. Sci.*, 1955, **3**, 40—49).—The application of aërial photography to the soil survey of the area is described. Soil association maps of selected areas are presented. A. H. CORNFIELD.

Genesis and classification of "mountain soils" developed on turfs in Indonesia. J. van Schuylenburgh and F. F. F. E. van Rummelen (*Neth. J. agric. Sci.*, 1955, **3**, 192—215).—Physical and chemical characteristics of a no. of profiles are presented. Parent material exerted a profound effect on type of soil formed. Brown podsolic soils were formed on liparatic tuffs, grey-brown podsolic soils on andesitic tuffs and brown forest soils on basalto-andesitic tuffs. A. H. CORNFIELD.

Mineralogical investigations of some Gold Coast soils. R. Hamilton (*Neth. J. agric. Sci.*, 1955, **3**, 127—134).—The mineralogical analysis of dark-coloured soils from the dry savannah plains (melanites and fluviomarine soils) and of bright-coloured soils (rubrites) is reported. A. H. CORNFIELD.

Some problems concerning aërial photo-interpretation in soil survey. P. Buringh (*Neth. J. agric. Sci.*, 1955, **3**, 100—105).—The value of aërial photographs as an aid in soil surveys is discussed. A. H. CORNFIELD.

Determination of soil permeability *in situ*. H. J. Timmers (*Neth. J. agric. Sci.*, 1955, **3**, 119–126).—The method of determining permeability, based on non-stationary movement of soil water, with a view to indicating whether irrigation of the area is justifiable is described. A. H. CORNFIELD.

Optimal depth of drainage. J. Wesseling and W. R. van Wijk (*Neth. J. agric. Sci.*, 1955, **3**, 106—118).—It was shown mathematically that under Dutch conditions no shortage of water is likely to occur for cereal crops and potatoes in heavy clay soils when drainage is deeper than 130 cm. With a grazed pasture or cut grass crop water shortage may occur if drainage is below 50 cm. When the water supply was $< 0{\cdot}7$ times potential evapotranspiration a decline in yield of several crops occurred. A. H. CORNFIELD.

Capillary rise of moisture in a heavy clay soil. G. P. Wind (*Neth. J. agric. Sci.*, 1955, **3**, 60—69).—The rate of capillary rise of moisture in a heavy clay was calculated by means of water balance. Moisture movement in this way supplied about 15 cm. of water in 1953. Under favourable conditions a rise of 3—4 mm. of water a day occurred. A graph relating height above the water table, pF, and capillary rise is presented. A. H. CORNFIELD.

Soil and water losses in southwest Arkansas. R. P. Bartholomew, D. A. Hinkle and K. Engler (*Arkansas agric. Exp. Sta.*, 1955, *Bull.* 550, 47 pp.).—The effect of rainfall characteristics and soil management practices on run-off and erosion from a fine sandy loam with a 2·9% slope was studied. The greatest run-off occurred on unploughed fallow soil. Ploughing reduced run-off for periods ranging from a few days to several months. Once a good cover crop of oats, rye or vetch was established, it was as effective as a Bermuda grass sod in preventing run-off. Soil losses were usually correlated with water losses, except that during intense rainfall soil losses were much higher in relation to water losses. A rye cover crop reduced soil losses by about 25% whilst a Bermuda grass sod practically eliminated soil losses. A. H. CORNFIELD.

Water tables, equipotentials and streamlines in drained soil with anisotropic permeability. D. H. Edwards (*Soil Sci.*, 1956, **81**, 3—18).—Using a recording paper, having one electrically conducting face, analogues of steady state water drainage in soils whose permeability is anisotropic have been constructed. Varying rainfall, soil permeability, drain diameter and depth of impermeable layer below the drain have been studied. T. G. MORRIS.

Measurement of soil moisture. J. D. Posthethwaite and E. S. Tuckett (*J. agric. Eng. Res.*, 1956, **1**, 89—95).—Various methods for determining soil moisture are briefly considered. A system involving measurement of the electrical resistance of blocks of nylon fabric encased in stainless steel gauze and covered with a thin layer of plaster embedded in soil, is described. A. G. POLLARD.

Determination of specific gravities of soils as influenced by clay-mineral composition. M. W. Gradwell (*N.Z. J. Sci. Tech.*, 1955, **37, B**, 283—289).—Fluid displacement methods of determining sp. gr. of clay subsoils were used with water and toluene; the values obtained with water invariably exceeded those obtained with toluene. The discrepancies were appreciable only with soils containing amorphous allophane in a finely divided state or considerable amounts of expanding-lattice minerals. Determinations on two allophane clays by He gas displacement gave results intermediate between those obtained with water and toluene. (12 references.) J. S. C.

Breakdown of particles in pumice sands due to mechanical dispersion treatment. D. C. McDonald (*N.Z. J. Sci. Tech.*, 1955, **37, B**, 351—353).—Dispersion for mechanical analysis of soils is usually produced either by stirring the suspension in a modified milk-shake machine (**I**) or by shaking it in an end-over-end machine (**II**). Tests with a pumice-containing brown sand showed that greater breakdown takes place in 1 min. of treatment in **I** than in 30 min. of treatment in **II**. It is therefore recommended that **I** be not used for this type of sand and that treatment in **II** be limited to 30 min. J. S. C.

Tillage in relation to rainfall intensity and infiltration capacity of soils. R. H. A. van Duin (*Neth. J. agric. Sci.*, 1955, **3**, 182—191).—The relationship between depth of cultivation and amount of rainfall which can be stored by the soil is studied mathematically. A. H. CORNFIELD.

Evaluation of diffusion-porosity relationships in soils and other porous media using radioactive carbon dioxide in a non-steady-state self-diffusion system. R. H. Rust (*Dissert. Abstr.*, 1955, **15**, 1950—1951).—Limitations of the steady-state diffusion system for studying diffusion–porosity relationships are given. Advantages of a non-steady-state self-diffusion system are, (i) the error that may arise from mass flow is very small, (ii) the problem of maintaining a constant partial pressure differential is eliminated and (iii) experimental time is shorter. A two-phase, non-steady-state diffusion equation was solved for boundary conditions appropriate to a closed two cell system using an Illinois analogue computer. A diffusion-pycnometer was operated under constant temp. and R.H. An equation for the diffusion-porosity relationship on air-dry media is given. O. M. WHITTON.

Relationship between vegetation and surrounding medium, in particular the soil. V. Westhoff (*T.N.O Nieuws*, 1955, **10**, 9—15).—Factors concerned in relationships between plant associations and soil conditions in Dutch soils include NaCl content, grazing, grassland manuring, level and composition of ground-water and soil structure, chemical composition, humus content and pH. The use of plant associations as indices of soil conditions and the value of vegetation maps in pedological studies are described. SOILS & FERT. (A. G. P.)

Natural radioactivity of soils. H. S. Gibbs and G. J. McCallum (*N.Z. J. Sci. Tech.*, 1955, **37, B**, 354—368).—Techniques for measuring β- and γ-radiations from soil are described and the radioactivity of principal horizons of a no. of soils was examined for relationships to properties used in the identification and classification of soil profiles. It was found that soil radioactivity depends partly on the rock materials from which the profiles are developed and which determine the initial level of radioactivity, and partly on the extent of weathering and leaching of the profiles. J. S. C.

Classification and use of irrigation waters. L. V. Wilcox (*U.S. Dep. Agric.*, 1955, *Circ.* 969, 19 pp.).—The concn. and nature of the

dissolved constituents of waters determine their quality for irrigation. Methods of analysis are described for electrical conductivity, sol.-Na %, Na-adsorption ratio, residual Na_2CO_3, B, dissolved solids, pH, cations and anions, and their significance and use in the classification of irrigation waters are explained. The effects of various types of water on soils and crops are described.
J. S. C.

Effect of soil-conditioner–fertiliser interactions on soil structure, plant growth and yield. J. L. Mortensen and W. P. Martin (*Soil Sci.*, 1956, **81**, 33—46).—HPAN (hydrolysed polyacrylonitrile) and VAMA [copolymer of vinyl acetate and the partial methyl ester of maleic acid mixed with $Ca(OH)_2$] were incorporated at a rate of 0·12% in ploughed silty clay loam. After fertilisation with N, K and P maize was sown. At harvest the total % of water-stable aggregates (modified Yoder wet sieving method) and % aëration porosity were significantly increased by the conditioners, VAMA being the more effective. There was a highly significant fertiliser–conditioner interaction. Moisture equiv., water holding capacity, field moisture %, pH or cation-exchange capacity were unaffected by the treatment. In growth and general appearance plants on conditioner-treated and N-fertilised plots were superior to other plants. During drought, wilt and leaf roll occurred on plants not receiving conditioner. Roots were more extensive on treated plants. Grain from N-fertilised conditioner-treated plants was drier than that from untreated. N fertilisation increased the N content of the grain; the conditioner enhanced this. K and P in the grain were unaffected by treatment. Yields were increased by treatment. Oats were sown in the second year, no conditioner being applied. The effect of the previous conditioner treatment was maintained and the soil was easier to till. The previous N fertilisation increased the N content of the oats except on the conditioner-treated plots where it was significantly less than on untreated, possibly due to increased microbial activity and loss of N as NO_3'. P accumulation in the oats was significantly increased by the conditioner treatment and significantly decreased by N treatment. Yields were significantly increased by the previous fertilisation. T. G. Morris.

Desalinisation of soil as a column process. W. H. van der Molen (*Soil Sci.*, 1956, **81**, 19—27).—The desalinisation by rainfall of Netherlands soils drained after wartime inundation has been followed by periodical sampling at fixed spots down to a depth of 80 cm. Homogeneous saline profiles were used for testing the Glueckhauf theory of column processes. A good qualitative correlation was found between theory and field observations even for non-homogeneous profiles. Quantitative agreement was better for light than for heavy soils. T. G. Morris.

Examination of soils and crops after sea-water flooding. II. Influence of salt on some vegetable crops. J. G. C. van Dam. **III. Sensitivity to salt of fruit crops.** W. G. Beeftink (*Neth. J. agric. Sci.*, 1955, **3**, 1—14, 15—34).—II. The growth of 26 species of plants on soil which had been flooded with sea water and then drained was studied. Germination, particularly of small-seeded species was slow, and many species failed to germinate. A surface application of gypsum to the seed bed helped germination in many cases. Growth of plants was slow and maturation was delayed. Lettuce and spinach tended to bolt. Characteristic salt-toxicity symptoms appeared on many species. Yields of cabbage, chicory and endive were reduced slightly by increasing salt content of the soil, whilst yields of other species were reduced to a much greater extent. The presence of salt increased the incidence of blackleg in some species. Details of treatment of affected soils prior to growing crops are described.

III. The sensitivity of various species of fruit to salt in the soil is presented. There were varietal differences among species in tolerance to salt damage. Sensitivity of apple trees to salt was not related to vigour of the rootstocks. Sensitivity as related to salt content of the soil water, duration and height of flooding, and age of trees is described. Cultivation and other measures, which sometimes resulted in the saving of affected trees, are also described.
A. H. Cornfield.

Changes in the base status of a soil after treatment with sulphur or sulphuric acid. W. M. H. Saunders and L. C. Blakemore (*N.Z. J. Sci. Tech.*, 1955, **37, B**, 276—282).—The effects on soil of S and H_2SO_4 applications (each equiv. to 7·5 cwt. of S per 6-in. acre) were studied over a period of one year. It is shown that such additions can reduce the pH and exchangeable-base content of soil within three months, but that the cations displaced from the exchange complex may persist for a considerable time before being leached away. It is therefore suggested that, in following a process of soil acidification, pH or total-exchangeable-base values may give a low indication of the amount of basic cations present. (13 references.)
J. S. C.

Soil heterogeneity and soil testing. T. J. Ferrari and F. H. B. Vermeulen (*Neth. J. agric. Sci.*, 1955, **3**, 265—273).—Analytical errors in the Laboratory for Soil and Crop Testing, Groningen, are 4%. The overall error (sampling + analytical) is ~10% for P, K and Mg determinations, 5% for clay and humus determinations and 0·1 unit for pH measurements. Errors were of the same order from arable and grassland soils and were not related to size of field.
A. H. Cornfield.

Comparison between sodium bicarbonate and lactate methods for determination of available phosphorus in soil. G. Semb and G. Uhlen (*Acta Agric. scand.*, 1955, **5**, 387—389).—In comparison with the lactate method, the $NaHCO_3$ method (cf. Olsen *et al.*, *Anal. Abstr.*, 1954, **1**, 2851) gives higher values for available P in soils of pH <5·5, and lower values in soils of pH >6·0. Agreement between the two methods and between the analytical results of both methods and the results of cropping trials are considered fairly good.
P. S. Arup.

Colorimetric determination of phosphorus in soil extracts. A. Karla (*Acta agralia fenn.*, 1955, **83**, 25—47).—In the colorimetric Mo-blue method, P in soil extracts (up to 2·5 p.p.m.) may be determined satisfactorily with min. ion-interference, by addition of equiv. proportions of H_2SO_4 and HCl to produce 0·8N, in the solution, by using $(NH_4)_6Mo_7O_{24}$ (3·2 mg. per ml.) reagent in the ratio, molybdate : acid = 4 : 1 and small amounts of $SnCl_2$ as the reducing agent. Soils & Fert. (A. G. P.).

Nature and determination of the available forms of phosphorus in Illinois soils. J. C. Gideon (*Dissert. Abstr.*, 1955, **15**, 1946).—The most promising results for (i) total adsorbed forms of P in soils and (ii) total easily acid-soluble forms of available P were obtained by 10-min. extraction with 0·03N-NH_4F, in (i) 0·005N-HCl and (ii) 0·1N-HCl, at a soil : extractant ratio of 1 : 50. The coeff. of simple correlation for P extracted by test (i) was 0·908 and by (ii) 0·882. The results are compared with those from previous tests. Investigations of the effects of pH (e.g., liming) on the forms of soil P are reported and discussed. O. M. Whitton.

Available phosphoric acid and cultural value of granitic soils. R. Blanchet (*C. R. Acad. Agric. Fr.*, 1955, **41**, 745—750).—Results of treatment with P_2O_5 by various methods, of granitic soils on farms in Montmarault are discussed, the soils containing originally coarse gravel and sand with very little clay, H_3PO_4, or lime, but having 0·4 to 0·5 pt. per 1000 of exchangeable K_2O, and pH ~5. The comparison of various methods of determination of available H_3PO_4 in such soils indicates that the results given by the Chaminade and Morgan–Barbier methods are the most representative of cultural values. In the latter method the use of dry, sifted soil, definite time of shaking and careful colorimetric assessment are recommended. In these soils P retains its full activity only if the pH is raised previously to ~7; org. reserves of the soil should be maintained. E. M. J.

Vertical distribution of nitrogen, phosphorus and potassium in some soils of East Pakistan. A. Karim and D. H. Khan (*Soil Sci.*, 1956, **81**, 47—56).—The distribution of org. N, NH_3- and NO_3'-N, available P, inorg. P, org. P, sesquioxide-bound P, Fe- and Al-bound P, adsorbed P, available K_2O, adsorbed K_2O and K_2O fixed in colloidal and non-colloidal fractions is reported for profiles of some podsolised soils of East Pakistan. T. G. Morris.

Binding and fixing of copper [in soils]. E. Schlichting (*Acta Agric. scand.*, 1955, **5**, 313—356).—Distinction is drawn between combined (bound but available) and fixed (non-available) soil-Cu, and doubt is cast on published data concerning the fixation of Cu by humus. This doubt is confirmed as far as three podsol profiles (one from Schleswig-Holstein and two from Sweden) are concerned. The capacity for binding Cu is directly related to the humus contents of the soils under examination; humus and the humic acid fractions have high storage capacities for combined Cu, but no evidence is found (by the *Aspergillus* spore-blackening technique) of the fixation of appreciable amounts of Cu by humus. For the determination of Cu in soils, chemical extraction is preferable to the potentiometric method, but the latter is quite suitable for the analysis of the humic acid fractions. Humic acid fractions are preferably extracted by means of aq. NaF and pptd. by H_2SO_4; the ions Cl' and $Fe^{\cdots}$ should be excluded from the process as far as possible. The accuracy of the *Aspergillus* test for available Cu can be improved by multiple testing with different wt. of the soil sample. Measurements of availability can be compared only if carried out at the same pH. (49 references.) P. S. Arup.

Influence of temperature and nitrogen on the decomposition of plant materials mixed with soil. D. F. Rothwell (*Dissert. Abstr.*, 1955, **15**, 1965).—Temperature will cause the decomposition products of plant materials of the same composition to vary. At 45°, 60° and 70° the addition of N to plant materials low in N generally will not conserve C but will encourage its loss.
O. M. Whitton.

Processes of the interaction of humic substances with the mineral fraction of the soil. L. N. Aleksandrova (*Pochvovedenie*, 1954, No. 9, 23—24).—The fundamental phases of the absorption of humic material at the surfaces of soil particles are the formation of water-insol. humic material on the surface of the particles and the cementing of the org. and organo-mineral films as they form. The insol. humic matter formed at the particle surface retains a high degree of mobility for some time, gradually becoming firmly fixed as the surface films dry out. Fixation is greatest in soils rich in highly dispersed fractions under conditions inhibiting the intensive mineralisation of humus and favouring removal of moisture from the sphere of action. SOILS & FERT. (A. G. P.).

Influence of liming on humus content [of soils]. J. Kortleven (*Landbouwk. Tijdschr 's Grav.*, 1955, **67**, 33—44).—Lowering of humus content by liming was much greater in sandy soils than in other types examined. Four groups of soils are distinguished according to humus contents of, <8, 8—11·5, 16—18·5 and >21·5. The fall in humus content with increasing pH was very small in the first group and became progressively greater in the following three groups. SOILS & FERT. (A. G. P.).

Occurrence of *Azotobacter* in certain western South Carolina soils. W. P. VanEseltine (*Soil Sci.*, 1956, **81**, 29—32).—*Azotobacter* was found to be present in each of 50 soil samples tested. Higher concentrations were found in autumn than in spring, in sandy clay loams and sandy loams than in loams or fine sandy loams, in soils of pH >5·85 and in soils of high Ca and Mg content. *Azotobacter* concentrations also tended to be higher in soils rich in K, N and P. T. G. MORRIS.

Effects of formulation on granulation of mixed fertilisers. J. O. Hardesty, A. Szabo and J. G. Cummings (*J. agric. Food Chem.*, 1956, **4**, 60—63).—A study is made of the moisture requirements for optimum agglomeration of mixed fertilisers. Replacement of $(NH_4)_2SO_4$ with NH_4NO_3 (≡7 units of N) in ammoniated mixed fertilisers containing triple or ordinary superphosphate and KCl, reduces the moisture required for optimum agglomeration from 14 to 2% for 1 : 1 : 1 ratios and from 16 to 6% for 1 : 2 : 1 ratios. N. M. WALLER.

High analysis fertilisers. J. Seymour (*Farm. Chem.*, 1955, **118**, No. 9, 38—40).—The production of an " enriched " superphosphate is based on the interaction of $Ca(PO_3)_2$ (**I**), rock phosphate and H_2SO_4 involving the hydrolysis of **I** and the simultaneous conversion of rock phosphate into superphosphate. The product may be ammoniated and K salts may be incorporated to provide mixed fertilisers of varying N : P : K ratios. A. G. POLLARD.

Availability of phosphate fertilisers in calcareous soils in Colorado. W. R. Schmehl, S. R. Olsen, R. Gardner, S. D. Romsdal and R. Kunkel (*Colo. agric. Exp. Sta.*, 1955, *Tech. Bull.* 58, 44 pp.).—Calcium metaphosphate was as effective a source of P for a no. of crops on calcareous soils as was superphosphate when it was mixed with the soil but was less effective when it was band-placed or broadcast. Nitro-phosphate was as effective as superphosphate when mixed with the soil or band-placed but not when broadcast. Rhenania was as effective as superphosphate except when band-placed. $CaHPO_4$ was not as effective as superphosphate whatever method of application was used. H_3PO_4 and $NH_4H_2PO_4$ applied in irrigation water were as effective as $NH_4H_2PO_4$ or conc. superphosphate band-placed or mixed with the soil. Superphosphate ploughed under was as available as was band-placed superphosphate. A. H. CORNFIELD.

Composition and nitrification of some sewage and industrial sludges. K. G. Clark and V. L. Gaddy (*Farm. Chem.*, 1955, **118**, No. 10, 41—45).—Detailed analyses of 18 sludges are recorded. Rates of nitrification of the materials decreased in the general order of the types: (i) activated (anaërobic) sludges, (ii) activated-digested sludges (preliminary aëration followed by anaërobic digestion), (iii) digested (aërobic) sludge and (iv) industrial sludges. A. G. POLLARD.

Agrobiologic percentage method of evaluating fertiliser tests. III. Quantitative agrobiologic analysis of a factorial experiment. O. W. Willcox (*Soil Sci.*, 1956, **81**, 57—69).—The use of variance analysis for results of field tests with fertilisers is discussed and criticised as not giving satisfactory information. Strip tests and the use of the Mitscherlich–Baule yield curve is advocated. The results of a Belgian field test on sugar beet are considered. T. G. MORRIS.

Advantages of visual observations with special reference to magnesium investigations. C. M. J. Sluijsmans (*Landbouwvoorlichtung*, 1955, **12**, 16—21).—Grading of oats and potatoes by visual symptoms of Mg deficiency was closely correlated with subsequent yields. Similar grading for rye agreed reasonably well with determinations of soil-Mg. especially when pH was taken into account. In oats deficiency symptoms develop fully at a height of 10—20 cm. Observations in rye should be made 3—4 weeks earlier. SOILS & FERT. (A. G. P.).

Plant Physiology, Nutrition, Biochemistry

Respiration of growing root-tips. A. Betz (*Planta*, 1955, **46**, 381—402).—Respiration experiments with selected segments of the roots of maize and pea seedlings show the degree of respiration, based on the protein-N, to be lower in the apical meristem than in the stretching zone. As shown by Ruhland *et al.* (cf. *ibid.*, 1938, **28**, 471) the apical meristem produces more CO_2 than can be accounted for by the O_2-intake. The production of the " extra CO_2 " decreases with the maturing of the tissue. The significance of these findings is considered with reference to the metabolism of root growth. (34 references.) P. S. ARUP.

Stimulation of citrus fruit respiration by carbon dioxide. J. C. Biale and R. E. Young (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet.*, *East Lansing*, Sept., 1955, 48).—Increases in CO_2 content of the air between 0 and 10% cause increases in respiration of citrus fruits. When ethylene (10 p.p.m.) was added also, the extra CO_2 did not suppress the ethylene-induced stimulation of respiration. The CO_2 suppressed yellowing of the fruit both in the absence and presence of ethylene. L. G. G. WARNE.

Cytochrome oxidase content and respiratory rates of etiolated wheat and barley seedlings. G. Fritz and H. Beevers (*Plant Physiol.*, 1955, **30**, 309—317).—Extracts from etiolated seedlings of pea, wheat and barley contain cytochrome oxidase at all stages of development (up to 12 days) and this content is more than adequate to account for the observed respiratory activity of the tissue from which it is derived. In wheat and barley roots the enzyme is present at all stages of growth but amounts extracted were insufficient to catalyse all the respiratory O_2 intake. E. G. BRICKELL.

Relation of respiratory and enzymic activity to maize seed viability. G. O. Throneberry and F. G. Smith (*Plant Physiol.*, 1955, **30**, 337—343).—Changes in respiratory capacity and in the activity of malic and alcohol dehydrogenases and cytochrome oxidase of maize embryos were measured during the early stages of germination. Loss of viability appears to be closely associated with respiratory failure in most seeds but malic dehydrogenase activity was more closely correlated with germination percentage and respiratory capacity than that of the other two enzymes. E. G. BRICKELL.

Effect of soil-moisture content on the rate of photosynthesis and respiration in ladino clover (*Trifolium repens*, L.). R. P. Upchurch, M. L. Peterson and R. M. Hagan (*Plant Physiol.*, 1955, **30**, 297—303).—A special apparatus for controlling plant environment and measuring CO_2 exchange is described. Rate of photosynthesis (apparent or corrected) is affected little by removal of available moisture until the time when first visible signs of wilting appear. Respiration rates of the aërial portions of the plant tend to increase slightly as wilting appears. E. G. BRICKELL.

Regulation of germination in seeds (Review). D. Koller (*Bull. Res. Counc. Israel*, 1955, **5D**, 85—108).—This review summarises the recognised relationships between germination and the various factors which regulate it. The following are discussed: moisture, gases temp., mechanical factors in the coats enclosing the embryo, exogenous chemical effects, illumination, dispersal units and the definition of the term " dormancy." (203 references.) E. M. J.

Flow of water through plant roots. G. P. Wind (*Neth. J. agric. Sci.*, 1955, **3**, 259—264).—The pressure gradients required to ensure varying rates of flow of moisture through grass roots was calculated by applying Poiseuille's Law. The rate of flow through roots at various depths was compared with that through soil. A. H. CORNFIELD.

Transpiration and the absorption and distribution of radioactive phosphorus in plants. K. E. Wright and N. L. Barton (*Plant Physiol.*, 1955, **30**, 386—388).—The effect of transpiration upon the absorption and translocation of radioactive P in the sunflower plant (var. Mammoth Russian) is described using the autoradiogram technique. A positive relationship between water transport and ^{32}P accumulation in the leaves is demonstrated, higher rates of water loss being associated with greater amounts of ^{32}P in the leaves. E. G. BRICKELL.

Absorption and translocation of phosphorus and iron by rice plants. K. Ohira (*Tohoku J. agric. Res.*, 1955, **5**, 345—353).—Rice seedlings were grown in water culture using a nutrient solution containing Fe and Mn in varying proportions. After four weeks radio-P and -Fe were included in the nutrient. Absorption and translocation of P was favoured by low [Fe] in the culture solution. A high-Fe nutrient permitted appreciable intake of P but suppressed its translocation. In chlorotic Fe-deficient plants the uptake of P was depressed considerably. Plants grown in high-Mn low-Fe media showed a decline in P uptake and severe Mn toxicity. High-Mn, high-Fe nutrients did not induce symptoms of Mn toxicity but permitted an increased P intake. The intake and translocation of Fe

in the plants was inversely related to the [Fe] in the tissues. High [Mn] in the plant tissues restricted the translocation of Fe.
A. G. POLLARD.

Magnesium absorption mechanisms in maize. C. D. Foy (*Dissert. Abstr.*, 1955, **15**, 1963).—The investigations reported suggest that the difference in Mg levels in the leaves of the maize inbreds is due, primarily, to an immobilisation of Mg in the stems. The importance of amounts and ratios of Mg, Ca and K fertilisation in Mg yields, Mg deficiency symptoms, and leaf composition of maize hybrids is assessed. O. M. WHITTON.

Rôle of the hydrogen ion in the mechanism of potassium absorption by excised barley roots. T. R. Nielsen and R. Ooerstreet (*Plant Physiol.*, 1955, **30**, 303—309).—Changes in H ion concn. of KBr solutions in the pH range 4 to 6 had a marked effect on the rate of K absorption by excsed barley roots, absorption decreasing with increasing pH. Cu^{++} in the solution tended to decrease the effect.
E. G. BRICKELL.

Absorption and breakdown of urea by leaves of coffee, cocoa and banana. J. C. Cain (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 3).—Coffee and cocoa leaves absorbed up to 95% of urea given as sprays in 5 to 6 hr. Bananas absorbed urea more slowly. Breakdown of the absorbed urea in the leaves is rapid and is accompanied by an increase in glutamine and asparagine.
L. G. G. WARNE.

Nitrite metabolism in higher plants. S. Vanecko and J. E. Varner (*Plant Physiol.*, 1955, **30**, 388—390).—Manometric experiments with NO_2 and experiments with $^{15}NO_2'$ show that nitrite is an intermediate in nitrate reduction. E. G. BRICKELL.

Incorporation of radioactive amino-acids into the proteins of plant tissue homogenates. G. C. Webster (*Plant Physiol.*, 1955, **30**, 351—355).—Incorporation rates vary greatly according to the method of preparation of the homogenate. The process is dependent on adenosine triphosphate and is considerably enhanced by Mg but inhibited by most other divalent ions. Incorporation of one amino-acid may be promoted by the presence of a mixture of the other amino-acids normally found in protein. E. G. BRICKELL.

Incorporation of radioactive acetate and sucrose into amino-acids and protein of excised organs of red kidney bean. B. J. Rogers (*Plant Physiol.*, 1955, **30**, 377—379).—*Phaseolus vulgaris* was studied. Incorporation of amino-acids proceeds at a considerably greater rate into protein of excised roots than into protein of excised leaves. E. G. BRICKELL.

Conversion of carbon-14-labelled urea into amino-acids in leaves. G. C. Webster, J. E. Varner and A. N. Causa (*Plant Physiol.*, 1955, **30**, 372—374).—Incorporation of the C of urea-^{14}C into amino-acids is demonstrated for bean (*Phaseolus vulgaris*) leaves, the pattern being almost identical with that obtained with $NaH^{14}CO_3$.
E. G. BRICKELL.

Physiology of the pea fruits. II. Soluble nitrogenous constituents in the developing fruit. H. S. McKee, L. Nestel and R. N. Robertson (*Aust. J. biol. Sci.*, 1955, **8**, 466—475).—Sol. N compounds in the seeds and hulls of developing fruits of the pea (*Pisum sativum*, var. Canner's Perfection) are reported for successive stages of growth. Of the 26 compounds studied, some were not detected in all samples, but all decreased in the seeds during periods of intense protein synthesis. The results are discussed in relation to those of other workers. S. C. JOLLY.

Nitrogen-fixing blue-green algæ. I. Growth and nitrogen fixation by *Mabæna cylindrica*, Lemm. M. B. Allen and D. I. Arnon (*Plant Physiol.*, 1955, **30**, 366—372).—The presence of Ca was essential for growth whether nitrate or mol. N was used and Ca was not replaceable by Sr nor Mo by V. Growth increased with increasing light intensity up to 16,000 lux. E. G. BRICKELL.

Glucose dissimilation in the higher plant. Effect of age of tissue. M. Gibbs and H. Beevers (*Plant Physiol.*, 1955, **30**, 343—347).—Through the use of a method involving the measurement of the rate of glucose-1-^{14}C and glucose-6-^{14}C oxidation by plant tissue (stem, root, leaf, cotyledon, hypocotyl, coleoptile) it was found that while immature tissue respired glucose either exclusively or to a large extent via the Embden–Meyerhof–Parnas glycolytic sequence the participation of the direct oxidation path was increasingly pronounced as the tissues aged and differentiated.
E. G. BRICKELL.

Effects of some metabolic inhibitors on sugar accumulation in potato discs during partial desiccation. C. C. Craft (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept., 1955, 50).—Sugar accumulated in potato discs during partial desiccation only in the presence of O_2. L. G. G. WARNE.

Some effects of potassium nutrition and crop load on the seasonal foliar analysis of peach trees. J. Popence and L. E. Scott (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept., 1955, 2).—Application of KCl gave an increased K and a decreased Ca and Mg content in peach leaves. Removal of the fruit increased leaf-P and -K and reduced leaf-N, -Ca and -Mg. L. G. G. WARNE.

Effect of gradual reductions of nitrogen on the distribution of macro-elements in the foliage of apple trees grown in gravel culture. F. Emmert (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept., 1955, 3).—One-year-old apple trees in gravel culture were given a complete nutrient solution until July 1st, and then deprived of either K, N or Mg. A reduction in N supply reduced leaf-P, -K, -Ca and -Mg. L. G. G. WARNE.

Growth and nutrition in barley and rye as affected by low-water treatment. R. F. Williams and R. E. Shapter (*Aust. J. biol. Sci.*, 1955, **8**, 435—466).—The relative and absolute contents of Ca, Mg, K, Na, Cl, Mn, N, P, Si and ash at various stages of growth are recorded for barley (*Hordeum vulgare*) and rye (*Secale cereale*) grown in pot experiments and subjected to high- and low-water conditions. Drought conditions caused highly significant reductions in growth in both species; the severity of the effects on various plant parts depended on the stage of development of the parts, those growing most actively suffering the greatest check in growth. Drought conditions also had very small immediate effects in many cases on distribution indices for dry-wt. change, and the exceptional behaviour of rye in this respect may be relevant to its drought resistance.
S. C. JOLLY.

Soil fertility and the quality of seeds. R. L. Fox (*Dissert. Abstr.*, 1955, **15**, 1962—1963).—Wheat and brome grass plants were grown under various conditions of soil fertility and climatic conditions and their seeds tested for germination ability and vigour of the resulting seedlings. Added N and P nutrients have considerable effect on the composition of seed and embryo, and the properties of the seed and its performance are changed by the conditions under which the seed is grown. O. M. WHITTON.

Effects of sporulation medium and age on fungus spore physiology. R. T. Darby and G. R. Mandels (*Plant Physiol.*, 1955, **30**, 360—366).—Results of exploratory studies relating to the respiratory activity, viability, and dry wt. changes are reported for *Myrothecium verrucaria, Memnoniella echinata* and *Aspergillus luchensis*. Sporulation media has a profound effect on spore physiology; *M. verrucaria* spores from a cellulosic substrate being much longer lived than those from succinate, peptone, potato dextrose, or sucrose plus yeast extract, cultures. Basal salts markedly stimulated endogenous respiration of *M. echinata* and *A. luchensis* from certain media.
E. G. BRICKELL.

Influence of ferricyanide on the yield and tropine alkaloid content of leaves of *Datura stramonium*, L. I. Reifer, A. Ruminska and J. Kaczkowski (*Acta biochim. polon.*, 1955, **2**, 315—320).—Seeds of *D. stramonium* were soaked in aq. 1% $K_3FeC_6N_6$ and after germination the seedlings were watered with more of the solution. Treated plants produced 25% more leaves having, on average, 13% more alkaloid and yielding 36% more alkaloid per plant than did control plants. A. G. POLLARD.

Survey of the non-volatile organic acids in seedlings of some grasses and legumes. R. W. Holton and C. R. Noll, jun. (*Plant Physiol.*, 1955, **30**, 384—386).—Tabular data of the acid anions detected in various plant extracts are presented. E. G. BRICKELL.

Non-volatile organic acids of crown galls, crown gall tissue cultures and normal stem tissue. R. W. Scott, R. H. Burris and A. J. Riker (*Plant Physiol.*, 1955, **30**, 355—360).—The individual org. acids from normal stems, crown galls and crown gall tissue cultures of marigold, periwinkle and sunflower, and from tomato stems and galls, were determined chromatographically. Fumaric acid was a major constituent of the acids from marigold and sunflower stem tissues; periwinkle and sunflower tissue cultures contained unusually large amounts of α-ketoglutaric acid. E. G. BRICKELL.

Seed-cake of *Annona squamosa* (Sitaphal). I. Nitrogenous constituents of the seed-cake. S. Venkob Rao, K. Ramachandran and S. H. Zaheer (*J. Indian chem. Soc., Industr. Edn*, 1955, **18**, 133—138).—The defatted seed-cake of the custard apple contains N 4·86 and protein 20·9%, of which 63·5% is extractable with water and the remainder with dil. salt solutions. Approx. 33% of the amino-acid N is present as basic amino-acids. A papain hydrolysate of the cake may be used as an accessory nutrient in the lactic fermentation of sugar-cane molasses. S. C. JOLLY.

Effectiveness of five cleaning procedures in the preparation of leaf samples for analysis. G. A. Taylor (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 1).—Apple leaves sprayed with Pb arsenate or Fermate or Dithane or Tag were wiped with damp cheese cloth (**I**), immersed in aq. Versene and detergent and rinsed with water (**II**), immersed in detergent solution and rinsed

with water (**III**), immersed in distilled water only (**IV**) or not cleaned (**V**), and the leaves analysed for N, P, K, Ca, Mg, Fe, Mn, Cu and B. Treatments (**I**), (**II**) and (**III**) were most effective and (**IV**) least effective in removing Fe, but (**II**) and (**III**) were much less laborious than (**I**). None of the treatments leached any of the elements from the leaves. L. G. G. WARNE.

Importance of respiration losses in the preparation of leaf samples for analysis. C. B. Smith (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 1).—Apple and peach leaves were collected and (i) dried at three different temp., (ii) stored in a refrigerator and (iii) sent by post to the laboratory. With peach but not with apple leaves, posting resulted in respiration losses which caused an increase of approx. 10% in the apparent nutrient element contents. Drying at 30° or storage in a refrigerator for seven days before drying at 65° or 100° caused smaller increases. L. G. G. WARNE.

Ålvik's method for determining carbon dioxide [in plant assimilation and respiration experiments]. B. Frenzel (*Planta*, 1955, **46**, 447—466).—The method is critically examined in the light of published data, and condemned on the grounds that a satisfactory equilibrium between the atm. CO_2 in the apparatus and the CO_2 content of the indicator solution cannot be established under the experimental conditions, and that the plant material is subjected to unnatural conditions in the apparatus. (72 references.) P. S. ARUP.

Total and radioactive phosphorus determination in small plant samples using the gravimetric method of Lorenz. K. Strzemieński [Appendix, R. M. Williams] (*N.Z. J. Sci. Tech.*, 1955, **37, B**, 243—257).—A method of determining total and radioactive P in the course of tracer experiments on small plant samples is described. Total P is determined gravimetrically after pptn. as phosphomolybdate. The same ppt. is then converted to $Mg(NH_4)PO_4$ and radioactivity measured, the amount of ppt. being equalised to eliminate self-absorption corrections. In the Appendix, a method is described for estimating the technical error originating from experimental procedures, as distinct from the error caused by random fluctuations in radioactivity. (13 references.) J. S. C.

Micro-determination of tropine alkaloids in plant material. I. Reifer and J. Buchowicz (*Acta biochim. polon.*, 1955, **2**, 187—198).—The *p*-dimethylaminobenzaldehyde method is modified by use of 60% H_2SO_4 in place of glacial acetic acid and by dissolving the reagent in ethanol instead of H_2SO_4. Determinations of tropine alkaloids in the range 1—80 μg. in plant material or pharmaceutical prep. may be completed in 45 min. A. G. POLLARD.

Determination of carotene in dehydrated lucerne meal treated with *NN'*-diphenyl-*p*-phenylenediamine. H. A. Kaler (*J. agric. Food Chem.*, 1956, **4**, 70—71).—A modification of the A.O.A.C. method for the determination of carotene in lucerne is described. This eliminates interference of *NN'*-diphenyl-*p*-phenylenediamine, a carotene anti-oxidant. The diamine causes a yellow colour when chromatographed on magnesia as in the official method; this is removed from the carotene eluate by the addition of dilute alcoholic $SnCl_2$. Five ml. of reagent (≡10 mg. $SnCl_2$) is adequate to reduce all diamine ordinarily encountered in analysis. N. M. WALLER.

Some effects of air-pollution of citrus trees and fruits. O. C. Taylor (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 33).—Grapefruit trees developed toxicity symptoms in the leaves when exposed for 16 hr. to air containing ozone (4 p.p.m.) and hexene. Lemon, Valencia orange, sweet orange and sour orange showed no symptoms. Abnormal leaf growth occurred. Detached fruits showed no skin injury after three weeks' fumigation with air containing 1 p.p.m. of the contaminants. L. G. G. WARNE.

Effects of polluted atmospheres on organic acid composition in plant tissues. P. B. Mader, G. Cann and L. Palmer (*Plant Physiol.*, 1955, **30**, 318—323).—Preliminary work is reported on the effect of smog in the Los Angeles Basin on spinach leaves. Chromatographic analysis indicate that a consistent and very substantial increase in formic acid content of the plant tissues takes place. E. G. BRICKELL.

Relationship of atmospheric fluoride levels and injury indexes on gladiolus and Ponderosa pine. Donald F. Adams, C. G. Shaw, R. M. Gnagy, R. K. Koppe, D. J. Mayhew and W. D. Yerkes jun. (*J. agric. Food Chem.*, 1956, **4**, 64—66).—The relationship between atm. F′ levels and observed foliar injury is shown to be approx. linear at the levels existing at the three test sites (averages 2·36, 0·49 and 0·77 parts per 10^9 of HF) for the two species examined. N. M. WALLER.

Protection against frost in agriculture. J. Jenny (*Industr. aliment. agric.*, 1955, **72**, 651—655).—Measures taken to protect vegetation against spring frosts are discussed: (*a*) protection by retarding bud development, or pruning; (*b*) by covering the plants (e.g., vines) with straw, (*c*) by formation of fog, (*d*) by ventilation, movement of the air, (*e*) by small fires of wood or other fuel or the use of the "Frostguard" apparatus which is described, (*f*) by heat and ventilation, and heating by electricity. E. M. J.

Effects of various chemical and cold-hardening treatments on resistance of sugar beet seedlings to freezing. W. G. Corns (*Canad. J. Bot.*, 1956, **34**, 154—158).—Either a Na salt formulation or free acids of TCA (trichloroacetic acid) and Dalapon (2 : 2-dichloropropionic acid) or the Na salt of 2 : 2 : 3-trichloropropionic acid produced highly significant differences in cold resistance between treated and control plants. The sugar beet seedlings grown in solutions 4 and 8 p.p.m., in the dark at 21° were given short exposures to −10°. In tests involving periodic sampling and freezing of Dalapon-treated illuminated seedlings during a 24-day period of storage at 6°, the chemically treated plants were more resistant than the controls. E. M. J.

Flower-promoting activity of pea seed diffusates. H. R. Highkin (*Plant Physiol.*, 1955, **30**, 340).—An extract from pea seeds may be used to replace the low-temp. treatment of other seeds for vernalisation; this extract is effective in reducing the no. of nodes to the first flower in vernalisable pea varieties. E. G. BRICKELL.

Formation of indole-acetylaspartic acid in pea seedlings. W. A. Andreae and N. E. Good (*Plant Physiol.*, 1955, **30**, 380—382).—Data from chromatographic analyses are presented. E. G. BRICKELL.

Auxin–antiauxin interaction at high auxin concentration. R. J. Foster, D. H. McRae and J. Bonner (*Plant Physiol.*, 1955, **30**, 323—327).—The effects of antiauxin (4-chloro-phenoxy*iso*butyric acid) on the growth of *Avena* coleoptile sections are discussed. Auxin-induced growth may be inhibited by high auxin concn. or by added auxin antagonists. The interaction of antiauxin and auxin is quant. that expected for interaction between a monofunctional inhibitor and a bifunctional substrate. E. G. BRICKELL.

The effects of 2 : 4-D on flowerng in the sweet potato. M. J. Howell and S. H. Wittwer (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 35).—Sprays of 2 : 4-D (100 and 500 p.p.m.) induced flowering in sweet potato plants grown in the greenhouse. Flowering was generally associated with reduced growth of the storage roots. The higher concn. of spray caused damage in one variety. L. G. G. WARNE.

Dual rôle of auxin in flowering. F. B. Salisbury (*Plant Physiol.*, 1955, **30**, 327—334).—Evidence is presented to show that flowering of *Xanthium pennsylvanicum* is inhibited by auxins only if these are applied before translocation of the flowering stimulus from the leaf is complete. Auxin applied after this time causes an increased rate of floral bud development. E. G. BRICKELL.

Germination-regulating mechanisms in some desert seeds. V. *Colutea istria*, Mill. D. Koller and M. Negbi (*Bull. Res. Counc. Israel*, 1955, **5D**, 73—84).—Various methods were tried for increasing permeability of the seed coat of *C. istria*, e.g., treatment for 30—60 min. with conc. H_2SO_4, or vigorous shaking in a glass jar for 6 hr. Acid treatment resulted in more rapid subsequent swelling, permeable seeds germinating equally well in light or darkness, at temp. between 20 and 30°. The inner coat of the embryo in the "unripe" sample provides some protection against decay and the outer coat in both "ripe" and "unripe" samples contains a water-sol. growth inhibitor which retards embryo growth. Two eight-month-old nursery seedlings were successfully transplanted to field conditions in the Negev Highlands. E. M. J.

Effect of naphthylacetic acid on the transpiration rate of Jonathan apple shoots. V. W. Kelley (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 43).—Detached apple shoots dipped in aq. naphthylacetic acid (30 p.p.m.) showed an increased transpiration rate. L. G. G. WARNE.

Effect of certain metabolic inhibitors on translocation of ^{32}P in bean plants. W. A. Kendall (*Plant Physiol.*, 1955, **30**, 347—350).—Translocation of ^{32}P was inhibited when dinitrophenol or NaF was placed in the vicinity of the phloem cells through which the transport occurred; Na fluoracetate, 2 : 4-D, indolylacetic acid or tri-iodobenzoic acid had little or no effect. E. G. BRICKELL.

Effect of certain growth regulators on the yield, earliness and quality of tomatoes. A. A. M. Radwan (*Dissert. Abstr.*, 1955, **15**, 1964).—The effect of *p*-chlorophenoxyacetic acid, *o*-chlorophenoxypropionic acid, maleic hydrazide and α-cyano-β-(2 : 4-dichlorophenyl)acrylic acid on the yield, earliness and quality of tomatoes was studied. The mineral content in the leaves and mineral uptake by the plants was not affected by any of the substances used, and no alteration of the content of pigments in the leaves was observed. Fruit quality was influenced only to an insignificant degree. O. M. WHITTON.

Pretreatment of ornamental plants with growth inhibitors to facilitate handling. J. P. Mahlstede (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 19).—Roses and privet sprayed with maleic hydrazide (100 to 2000 p.p.m.) when in full leaf and later lifted, pruned, packed in polyethylene bags and stored showed at the higher concn. a reduction in mould development with no adverse effects on planting out subsequently. Sprays given to strawberry plants reduced runner production and allowed long storage of lifted plants. Similar results were obtained with *Altheæ, Artemisia* and *Platycodon*. L. G. G. WARNE.

The effect of growth-regulating substances on premature seeding in cabbage. E. L. Moore and S. H. Wittwer (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 36).—"Large," "medium" and "small" cabbage plants were sprayed with α-o-chlorophenoxypropionic acid (250 p.p.m.) (**I**) or 2 : 4-dichlorophenoxyacetic acid (15 p.p.m.) (**II**) or tri-iodoacetic acid (250 p.p.m.) (**III**) or maleic hydrazide (250 p.p.m.) (**IV**) during a cold treatment. Sprays of **I** given in the middle of the low-temp. treatment to large plants delayed, to medium plants prevented flowering, and to small plants increased firmness of the heads. Sprays given at the beginning or end of the cold treatment accelerated flowering. **II** had a similar but less pronounced effect and **III** was without effect. **IV** had no effect if given before the cold period but accelerated flowering if given in the middle of the low-temp. exposure. Given after the cold treatment it killed the terminal buds and retarded growth. L. G. G. WARNE.

Effects of certain cultural and growth-regulator treatments on pod-set and yield of lima beans. E. M. Rahn (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 36).—Sprays of *N*-*m*-tolylphthalamic acid (100 gal. per acre, 125 p.p.m. concn.) given when many blooms were at anthesis and a few small pods present, increased the yield of lima beans by 26%. L. G. G. WARNE.

Effect of maleic hydrazide on vegetative growth and flower production of carnations. G. E. Beck and L. Holm (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 46).—Young carnation plants were sprayed with maleic hydrazide (500, 1000 and 2000 p.p.m.). The axillary buds grew at a slightly slower rate than those of plants pinched in the usual manner. Thereafter all plants grew at the same rate but flower production was reduced in the sprayed plants. L. G. G. WARNE.

Delayed effects of 2 : 4 : 5-trichlorophenoxypropionic acid sprays on Anjou pears. E. S. Degman and L. P. Batjer (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 42—43).—Aq. sprays of 2 : 4 : 5-trichlorophenoxypropionic acid applied to Anjou pears three weeks before harvest caused an increased fruit set the following year. L. G. G. WARNE.

Suppression of tomato plant terminal growth by α-cyanocinnamic acids and related compounds. P. H. Plaisted (*Contr. Boyce Thompson Inst.*, 1955, **18**, 231—242).—The activity of α-cyanocinnamic acids was correlated with substitution in the benzene ring. The monosubstituted α-cyanocinnamic acids showed greatest growth inhibition when the substituent in the *para* position was either Cl or Br. Max. activity with the disubstituted compounds was associated with a Br or Cl in the 2 and 4 position of the ring. Max. activity among the 2 : 4-dihalocinnamic acid derivatives was obtained only when the compound possessed the cyano group on the α-C. (16 references.) R. H. HURST.

Inhibition of plant growth by 2-mercaptobenziminazole analogues. T. L. Rebstock, C. D. Ball, C. L. Hamner and H. M. Sell (*Plant Physiol.*, 1955, **30**, 382—384).—Several compounds related to benziminazole were synthesised and tested as growth inhibitors on cranberry bean seedlings. Those having Cl substituted in the 5 position were most active. E. G. BRICKELL.

Components of variance method and partitioning method of genetic analysis applied to weight per fruit of tomato hybrid and parental populations. L. Powers (*U.S. Dep. Agric.*, 1955, *Tech. Bull.* 1131, 64 pp.).—A modified randomised complete block experiment for *Lycopersicon esculentum*, Mill. var. Criolle and Sioux is described in which the data are analysed by (i) analysis of means, (ii) Fisher's and Wright's method, (iii) dividing wt. per fruit with component characters, (iv) calculating relative per cent variance accounted for by regression, and (v) partitioning frequency distributions on the basis of certain geno types. No one method provides all the information available; the methods are not mutually exclusive but supplemental to each other. (39 references.) E. G. BRICKELL.

Rôles of embryo and endosperm in determining niacin content of starchy and sugary maize endosperms. H. J. Teas, E. G. Anderson and J. W. Cameron (*Plant Physiol.*, 1955, **30**, 334—337).—Data from a series of assays on maize kernels in which the *Su* and *su* genes occurred in various relationships, indicate that the embryo plays no decisive part in determining the niacin level of the endosperm. E. G. BRICKELL.

Crops and Cropping

Growing sweet maize in Arizona. W. D. Pew and L. Hopkins (*Ariz. agric. Exp. Sta.*, 1955, *Bull.* 264, 12 pp.).—Nitrogen should be applied at 100—150 lb. per acre, and, where P is deficient, 50 lb. P_2O_5 per acre should be applied. Applications can be made before planting or as side-dressing before the plants are 12 in. tall. The maize earworm is controlled by 5% DDT dust applied to the silk every 2—3 days. A. H. CORNFIELD.

Relationship between available soil-moisture levels and potato yields. J. M. Fulton and H. F. Murwin (*Canad. J. agric. Sci.*, 1955, **35**, 552—556).—Yields are progressively increased by the maintenance, by irrigation, of available soil-moisture levels (at 6 in. below the surface) up to ~50%. No further advantage is gained by increasing the level to 75%. Increased yields are due to increased tuber-size. On sandy loam, suitable irrigation intervals are 5—8 days. P. S. ARUP.

Frost damage to potatoes. T. Voss (*Phytopath. Z.*, 1955, **25**, 196—222).—The literature of the subject is reviewed. Types of experimentally induced frost damage (lethal, local, and necrosis of vascular tissue) are described with illustrations, and compared with symptoms described in the literature. Data are given for times elapsing after thawing, before the symptoms of various types of damage appear on storage at 4° or 26°. Characteristic symptoms are pointed out by means of which recent injuries (due to frost or mechanical damage) can be distinguished from those of long standing. (95 references.) P. S. ARUP.

Treating ware potatoes with sprout-inhibiting chemicals. B. Emilsson (*Acta Agric. scand.*, 1955, **5**, 390—406).—Results obtained by the author and his co-workers are summarised and examined. Dusting prep. based on five chemicals, and a spraying-prep. based on maleic anhydride are compared for sprouting-inhibiting activity, and also for their influence on loss in wt., losses due to disease, and cooking quality. The most generally satisfactory prep. are those based on 2 : 3 : 5 : 6-tetrachloro-1-nitrobenzene (**I**) (3%) and *iso*-propyl *N*-phenylcarbamate (**II**) (3%) respectively. The latter is 10 times as active as the former, and much more economical in use, but it unfits potatoes for use as seed. The prep. of **I** gives some control of dry-rot. Reductions in loss of wt. (0·5—1·5%) are insufficient to compensate for the cost of treatment, except, perhaps, in cases where sprouting would be heavy due to prolonged storage. The effects of spraying the plants with the maleic anhydride prep. are occasionally uncertain and depend largely on the time and conditions of application; the treatment unfits the potatoes for use as seed. (29 references.) P. S. ARUP.

Factors influencing the keeping qualities of potatoes. P. A. Schippers (*Neth. J. agric. Sci.*, 1955, **3**, 305—310).—An address. A. H. CORNFIELD.

Relation between soil structure, nitrogen supply and yield of sugar beet. H. Kuipers (*Neth. J. agric. Sci.*, 1955, **3**, 170—181).—Yields of beet and sugar increased with rate of N application; optimum yields were obtained with 140 kg. of N per hectare. The type of response to increasing N applications was similar in soils of good or poor structure. The % of sugar in the beet decreased slightly and the % of dry matter in the tops decreased considerably with increasing N applications. Yields decreased with delay in sowing (March 18 to April 23). A. H. CORNFIELD.

Influence of chemical treatments on sprouting of sweet potato roots. C. V. Hall and J. K. Greig (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 35).—Sweet potato roots were treated with ethylene chlorohydrin (175 p.p.m.), 2 : 4-dichlorophenoxyacetic acid (10 p.p.m.) or thiourea (3%) by dipping in aq. solution for 5 sec. (or 3 hr. for the thiourea). 2 : 4-D reduced sprouting with all varieties, but the other substances showed a pronounced variety interaction, giving decreases with some and increases with other varieties. L. G. G. WARNE.

Mineral uptake of a rye cover crop under differential fertiliser treatments. L. E. Scott and W. A. Matthews (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 45).—A rye cover crop fertilised with a 10—10—10 N : P : K fertiliser at the rate of 500 lb. per acre in January doubled the amount of rye ploughed-in in April and more than doubled the amount of mineral nutrients in the crop. The uptake of N and K by the rye exceeded the amount supplied in the fertiliser, but only one-third of the added P was recovered in the crop. L. G. G. WARNE.

Factors affecting the hardiness of the apple. H. A. Rollins, jun. and F. S. Howlett (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 23).—Some varieties (e.g., Hibernal) are very hardy early in the dormant season, increase in hardiness quickly and become frost-susceptible early in the spring. Others (e.g.,

Baldwin) are tender in the autumn and attain max. hardiness slowly and become frost-susceptible slowly in the spring. L. G. G. WARNE.

Manganese survey of soils and leaf tissue in apple orchards in New Jersey. F. E. Wiederspahn and N. F. Childers (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 2).—Typical Mn deficiency symptoms were associated with leaf-Mn concn. between 2·0 and 18·5 p.p.m. L. G. G. WARNE.

Effects of differential nitrogen fertilisation on young peach trees: I, N, P, K, Ca, Mg and Mn content of the foliage. C. M. Ritter (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 40).—Peach trees received no N, $\frac{1}{8}$, $\frac{1}{4}$ or $\frac{1}{2}$ lb. of NH_4NO_3 per year of the trees' age. The successive increments of N increased the leaf N and Mn and the heaviest N application showed a lowered K and P content as the season progressed, but the K levels were not as low as those of the no-N trees. L. G. G. WARNE.

Spectrophotometric measurement of colour changes during the ripening of Halehaven and Elberta peaches. R. V. Lott (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 29).—Even immature fruits stored at 18·3° (but not at 0·6°) developed a good yellow colour, but the highest quality was obtained in mature fruits ripened at 0·6°. L. G. G. WARNE.

Leaf potassium as influenced by different sources of potash as fertilisers and solutions at planting time. A. L. Kenworthy (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 2).—KNO_3 and K_2SO_4 given at planting time result in a greater absorption of K by peach trees than when KCl is used. L. G. G. WARNE.

Measuring the internal colour of Florida red and pink grapefruit with the Hunter colour-difference meter. S. V. Ting, J. W. Sites and E. J. Deszyck (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 28).—The red colour decreased in intensity during Dec. and Jan. and then remained constant up to March. Varietal differences were greatest near the skin. On light soils and with young trees the fruit was more coloured than with older trees and heavy soil. Trees on rough lemon stock had more highly coloured fruits than those on sour orange rootstock. L. G. G. WARNE.

Seasonal changes in Arizona and California grapefruit. G. L. Rygg and M. R. Getty (*U.S. Dep. Agric.*, 1955, *Tech. Bull.* 1130, 44 pp.).—Tabular data for colour, wt. and size, rind thickness, core diameter, juice content, texture and flesh colour, and chemical composition are presented and discussed. E. G. BRICKELL.

Effects of applications of nitrogen, phosphorus, potassium and magnesium fertilisers on petiole analyses and yields of Concord grapes. H. K. Bell, R. P. Larsen and A. L. Kenworthy (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 4).—Under low-K conditions, K fertilisers increased yields of Concord grapes and increased the K, but decreased the Mg, P, Mn and Fe content of the petioles. N(>40 lb. per acre) and P and Mg fertilisers had no effect on yields. L. G. G. WARNE.

Effect of 2 : 4 : 5-trichlorophenoxypropionic acid application on the size, maturation and quality of amini mangos (*Manigifera indica*, L.). W. C. Kennard and H. F. Winters (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 34).—Sprays of 2 : 4 : 5-trichlorophenoxypropionic acid (80 to 800 p.p.m.) given to mangos three weeks after flowering accelerated ripening and reduced fruit size. Later sprays had less effect and a spray given four weeks before harvest was without result. Sprays at all concn. and all times increased fruit colour and decreased the sol. solids content of the fruit. No foliage or fruit injury occurred but seed from sprayed trees showed reduced germination. L. G. G. WARNE.

Chemical inhibition of strawberry runners in the matted row. E. L. Denisen (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 4).—Sprays of maleic hydrazide (1000 or 2000 p.p.m.) and dichloralurea (5000 or 10,000 p.p.m.) were applied to strawberry plants in matted rows on three dates between July 31 and Sept. 7. Dichloralurea had little effect on runner production, but maleic hydrazide especially at the higher conc. reduced runner production and also gave the highest yields of fruit and the largest fruits in the following year. L. G. G. WARNE.

Red currant spacing, pruning and potash carriers. N. Shalis (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 6).—The yield of red currants was the same with spacings of 800 to 2400 bushes per acre. KCl was inferior to K_2SO_4 as a fertiliser and caused leaf scorch and a reduced yield. L. G. G. WARNE.

Effect of some pruning and fertiliser treatments on yield of red raspberries. D. F. Allmendinger (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 6).—Raspberries with 12 canes per hill gave higher yields than with 9 canes and 9 canes higher than 6 canes. Thirty lb. of N per acre increased yields but 60 lb. gave no further increase. None of the treatments affected berry size. L. G. G. WARNE.

Electron irradiation of blueberries and peaches. F. B. Thomas (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 29).—Irradiation of blueberry fruit with cathode rays ($1·0 \times 10^6$ rep at 2·6 mev.) resulted in "commercial sterilisation" of the fruit. L. G. G. WARNE.

Differential cation absorption and yield response by vegetable crops grown at various levels of calcium, potassium and sodium. J. D. Campbell (*Dissert. Abstr.*, 1955, **15**, 1961—1962).—The effect of various fertiliser ratios of Ca, P and Na on the yield of each of 17 crops and on the content of these elements and of Mg in the crop was measured and the significance of the results obtained was evaluated statistically. O. M. WHITTON.

Temperature and photoperiod effects on the development of leaf lettuce. L. Rappaport and S. H. Wittwer (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 6).—"Bibb" lettuce with a 16-hr. photoperiod produced 50 leaves more than with a 9-hr. photoperiod (with night temp. of 15·6° and 21·1°) and flowered about 50 days earlier. Photoperiod had little effect on leaf production and flowering in the Grand Rapids variety. L. G. G. WARNE.

Effect of variety, season and pruning on the development and nutritive value of broccoli inflorescence and leaves. P. H. Massey, jun., J. F. Eheart and R. W. Young (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 26).—In sprouting broccoli (Calabreese), the leaves are edible and as rich in ascorbic acid and richer in carotene than the inflorescences. Removal of five leaves per shoot did not reduce the yield of inflorescences whilst early removal of the terminal inflorescence increased the yield of axillary ones but reduced the total yield. L. G. G. WARNE.

Potash and boron relationships in celery nutrition. P. Minges and M. Yamaguchi (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 44).—In sand culture experiments with celery, "brown checking" followed three days later by "crack stem" occurred with high-K and intermediate-B levels. At low-B levels both maladies occurred simultaneously. L. G. G. WARNE.

Some effects of temperature upon the growth of southern peas. M. W. Hoover (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 6).—Southern peas (*Vigna sinensis*) had a "base growth" temp. of 5° under controlled conditions and of 6·7° under field conditions. Germination took four times as long with a soil temp. of 15·6° as with one of 26·7°. L. G. G. WARNE.

Effects of varying levels of nitrogen, phosphorus, potassium and magnesium on the growth, leaf composition and fruit production of the tomato (*Lycopersicon esculentum* var. *commune*, Bailey).—G. A. Marlowe, jun. (*Dissert. Abstr.*, 1955, **15**, 1964).—The effects of nutrient supply on vegetative development, fruit production and leaf development of the tomato at various stages of growth, were studied under greenhouse and field conditions. Results are given. O. M. WHITTON.

Influence of cold temperature exposure of tomato seedlings on flower formation. S. H. Wittwer and F. G. Teubner (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 7).—Exposure of tomato seedlings during the two weeks following cotyledon expansion to low temp. (10—13° as against 17—21°) promotes formation of flower clusters and reduces the no. of leaves preceding the first truss. L. G. G. WARNE.

Fruit-set in tomatoes as affected by high temperature treatments. H. Moghrabi and R. Foskett (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 24).—High temp. (40·6—43·3°) reduce fruit set in tomatoes and this effect is increased if the plants are darkened for 36 hr. before exposure to the high temp. Flowers pollinated just before or just after high-temp. exposure develop fruits more quickly than those pollinated 48 hr. before the high-temp. treatment. L. G. G. WARNE.

Effects of agronomic factors on the rutin content of buckwheat. J. Naghski, J. F. Couch, J. W. Taylor, W. J. Sando, J. W. White, F. J. Holben and J. B. Washko (*U.S. Dep. Agric.*, 1955, *Tech. Bull.* 1132, 50 pp.).—Five varieties of *Fagopyrum esculentum* were grown in four districts of central and eastern Pennsylvania. Tartary buckwheat proved the most valuable source of rutin. The effects of age of plants, date of planting, rate of seeding, fertilisers, and manner of harvesting, are reported. (23 references.) E. G. BRICKELL.

Assessing ratooning potentialities of the strains of *Sorghum* for fodder. H. N. S. Ambastha and I. B. Jha (*Indian J. Dairy Sci.*, 1955, **8**, 135—142).—Strains of *Sorghum* were selected to give the max. of cuts of green feed within min. time at regular intervals,

*

without the elaboration of HCN, when left to ratoon, in concentrations fatal to cattle; 10—35% more green feed was obtained from satisfactory strains cut at 2-month intervals than from the main crop. There was no appreciable increase in the HCN concn. when the strains under trial were ratooned for taking the second crop of fodder. E. M. J.

Influence of calcium and other elements on fructfication of the groundnut. G. G. Bolhuis and R. W. Stubbs (*Neth. J. agric. Sci.*, 1955, **3**, 220—237).—Of the major elements in the fruiting medium only Ca was essential for fructification. K, Mg and NH_4 were harmful when present alone in the fruiting medium. A high Ca/K or Ca/Mg ratio was satisfactory for, whilst a low ratio was harmful to, fructification. Fructification was better with a high Ca/K or Ca/Mg than with a similar Ca/H ratio in the fruiting medium. A. H. CORNFIELD.

Irrigation of cotton in Arkansas. D. A. Brown, R. H. Benedict and B. B. Bryan (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 552, 40 pp.).—Significant increases in cotton yields due to irrigation were obtained in all of five years on a silt loam. Yield increases were similar whether water was applied when available soil moisture ranged from 20 to 50% or from 30 to 60%. Maintaining available soil moisture level at 50% or higher was necessary for optimum yields. There was no advantage in applying more than 400 lb. of a 6—8—12 (N–P_2O_5–K_2O) fertiliser to the irrigated soil. Subsoiling and placement of lime and fertiliser at 14—18 in. depth did not increase yields of cotton, and had no effect on infiltration rate. Irrigation had no effect on maturity date, quality of lint, % of lint, lint or seed index or germination of the cotton seed. Values for consumptive use of water under the various treatments are given. A. H. CORNFIELD.

Toxic effects of urea fertiliser on mature tung trees. M. Drosdoff, H. L. Barrows, C. B. Shear and F. S. Lagasse (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 32).—Trees receiving 1·2 or 3·6 lb. of urea per tree annually for five years developed toxicity symptoms consisting of necrotic spots near the margin of the leaves. The spots developed between the veins and later coalesced. High K reduced the severity of the symptoms. L. G. G. WARNE.

Responses of mature tung trees on Red Bay soil to boron and magnesium. M. Merrill, jun., R. T. Brown and G. F. Potter (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 32).—Tung trees receiving 0·15 lb. of Na borate and 4 lb. of $MgSO_4$ annually over four years showed no increase in growth. The treatments respectively increased the leaf content of B and Mg, and the B applications reduced leaf-K. L. G. G. WARNE.

Converting timber stands of low-grade hardwood to conifers in the Arkansas Ozarks. F. M. Meade (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 551, 26 pp.).—Results of trials in a no. of areas are reported. A. H. CORNFIELD.

Bleaching and disinfecting discoloured pepper seed with sodium hypochlorite. J. P. McCollum and M. B. Linn (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 25).—Treatment of discoloured pepper seed at harvest time or later for 20 min. with aq. NaOCl removed most of the discoloration without effect on the germination. Longer treatment reduced the germination. L. G. G. WARNE.

Effect of bicarbonate and other constituents of irrigation water on growth of azaleas. O. R. Lunt, H. C. Kohl and A. M. Kofranek (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 11).—Azaleas tolerate high concn. of Na, Ca and SO_4'' and moderate concn. of Mg, NH_4, K and Cl′, but are adversely affected if the concn. of salts in the soil solution exceeds 50 mequiv. per l. High levels of HCO_3', PO_4''' and NO_3' reduce plant growth, but the chlorosis induced by HCO_3' in irrigation waters is reduced if Ca is maintained at a high level and is cured by Fe citrate sprays. L. G. G. WARNE.

Life of cut roses and snapdragons as affected by water and chemical additives. J. Kelley and C. Sherwood (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 19).—Cut antirrhinums had their life doubled if kept in demineralised water with 2% of sucrose plus phenol. L. G. G. WARNE.

Soil mixtures and fertilisers of varying phosphorus–potassium ratios for potted azaleas. C. B. Link (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 27).—Azaleas were grown in soil, peat, soil plus Krilium, soil plus sand plus peat mixture, and in a soil, sand plus peat plus Krilium mixture with various fertiliser treatments. Peat was a good medium if P was added but in other rooting media little response to P was obtained. Additions of K had little effect. Krilium was beneficial when added to soil only, but not when added to the soil, peat, sand mixture. L. G. G. WARNE.

Crop sequence studies on irrigated land in Southern Alberta. S. Dubetz, G. C. Russell and K. W. Hill (*Canad. J. agric. Sci.*, 1955, **35**, 564—567).—In comparative field experiments with seven crops during four seasons, the following (descending) order of merit as preceding crops was found: field-beans, potatoes or canning-peas, and barley or sugar-beet. Canning-maize or wheat could be grown equally satisfactorily in any rotation-sequence. Potatoes after potatoes gave the least satisfactory results. Infestation with weeds was highest after peas, and lowest after inter-tilled crops. Barley interfered with sequence-management by shattering and subsequent volunteer-growth. Summer-fallowing failed to give economic results. P. S. ARUP.

Border row effect in wheat trials with different spacings between plots. Jean G. Miller and N. S. Mountier (*N.Z. J. Sci. Tech.*, 1955, **37, A**, 287—299).—Significant differences in plot yields were nearly always recorded for spacings between plots of 7, 14, 18 and 24 in. when the outside rows were included. The yields of the second rows from the edge did not vary with the spacings between plots. There was no advantage in using 7- or 28-in. spacings instead of the standard 14-in. Coefficients of variation were increased when border rows were included if the error was calculated to include variations due to different spacings. Where the difference in spacings does not contribute to error (e.g., in a very accurately drilled trial), the coefficients of variation were not affected by the inclusion of outside rows at the 14- or 18-in. spacings. Thus, while in some cases whole plots may be harvested, in most cases, where the drilling is not extremely accurate or competition may exist, the trial will be improved by the removal of outside rows. The results apply to variety trials only, and only to trials where there are no extreme differences of habit or yield between varieties. R. H. HURST.

Pest Control

Plant chemotherapy. M. H. van Raalte, A. K. Sijpesteijn, G. J. M. van der Kerk, A. J. P. Oort and C. W. Pluygers (*Meded. LandbHoogsch., Gent*, 1955, **20**, 543—555).—The compound *S*-carboxymethyl-*NN*-dimethyldithiocarbamate (**I**) and several of its deriv. are weak growth-substances and partly protective of cucumber plants against *Cladosporium cucumerinum* when applied through the roots. On substitution of both of the two H atoms at the α-C atom by Me, the growth-modifying, but not the protective property of **I** is destroyed. It is shown that compounds of the type examined, whilst increasing the resistance of the leaf-tissue below the epidermis, do not act as systemic fungicides proper, but rather as systemic or internal protectants. Fungicidal action of **I** occurs only at phytotoxic concn. (> 500 mg. per l. The compounds are similarly protective against *Cladosporium fulvum* of tomatoes and *Mycosphærella pinodes* of peas. P. S. ARUP.

Investigations on fungicides. I. Fungicidal and systemic fungicidal activity in certain aryloxyalkane carboxylic acids. C. H. Fawcett, D. M. Spencer and R. L. Wain (*Ann. appl. Biol.*, 1955, **43**, 553—568).—The systemic fungicidal activity of 54 aryloxyalkanecarboxylic acids and the direct fungicidal activity of 20 of the compounds were tested. There was no relationship between direct and systemic fungicidal activity of the compounds. α-Phenoxy*iso*butyric acid, 2 : 4 : 6-trichlorophenoxyacetic acid, 3-phenoxybutyric acid and 5-phenoxycaproic acid conferred systemic fungicidal protection of broad beans against *Botrytis fabæ* and of tomatoes against *Alternaria solani*. Other compounds showed no systemic effect or were phytotoxic. A. H. CORNFIELD.

Relationships between the chemical constitution and fumigant toxicity of the alkyl iodides. K. A. Hassall (*Ann. appl. Biol.*, 1955, **43**, 615—629).—The fumigant action of 19 alkyl iodides on the grain weevil was studied. The secondary and tertiary isomers were generally less toxic than the primary (as measured by molar LD_{50} or p/p_s values). Despite differences in LD_{50} isomeric primary iodides often acted at about the same p_i/p_s values, indicating that phase distribution in addition to chemical reactivity determines fumigant action. Toxicities of mixtures of iodides varied from 1·0 to 1·25 times the value predicted from the toxicities of single iodides. With the exception of methyl and the tertiary iodides used, all iodides have the same type of chemical action on the organisms. A. H. CORNFIELD.

Aphicidal action of some systemic insecticides applied to seeds. W. A. L. David and B. O. C. Gardiner (*Ann. appl. Biol.*, 1955, **43**, 594—614).—When large seeds such as broad beans were soaked in certain systemic insecticides, notably Demeton, the plants which they produced were toxic to aphids. Little toxicity occurred with small-seeded plants. The insecticidal activity of the plant was directly related to the quantity of solution absorbed by the seed. After 4 hr. soaking there was more insecticide in the seed coat than in the cotyledon, whilst after 24 hr. there was more in the cotyledons. The toxic material in the cotyledon could pass directly to the grow-

ing plant although some was transmitted through the soil and roots. A given quantity of Demeton was more effective as an aphicide when absorbed by the seed than when watered on to the soil around it. Plants from seed which had been soaked in Demeton, dried and stored for one month prior to germination were toxic to aphids.
A. H. CORNFIELD.

New antibiotic spray. Anon. (*Farm Chem.*, 1955, **118,** No. 8, 41).—A brief note on a streptomycin–glycerol prep. (Merck) which has given promising results in the treatment of bacterial blight of beans. A. G. POLLARD.

Thioneb ; fungicide and seed protectant. C. W. Gates (*Farm Chem.*, 1955, **118,** No. 12, 44).—Brief notes are given of the nature and relevant properties of Thioneb (a polyethylene thiuram sulphide).
A. G. POLLARD.

PVP-iodine in agricultural pest control. H. B. Kellog (*Farm Chem.*, 1956, **119,** No. 1, 41—43).—The production, nature and properties of polyvinylpyrrolidone (PVP) are described briefly. Its uses as a herbicide and, in the form of an I-compound, as an insecticide, fungicide, nematocide and virucide are noted.
A. G. POLLARD.

Absorption, breakdown and systemic behaviour in plants of ^{32}P-labelled Demeton-S. W. D. E. Thomas, S. H. Bennett and C. P. Lloyd-Jones (*Ann. appl. biol.*, 1955, **43,** 569—593).—Following application to leaves of beans, apples and Coleus Demeton-S disappeared from the leaf surfaces within a few hours by evaporation, breakdown into toxic non-volatile compounds and absorption. A fumigant action on *Aphis fabæ* was noted. The extent of translocation of toxic materials from treated leaves was not sufficient to kill aphids on untreated leaves. Unchanged Demeton-S could not be found elsewhere in the plant following leaf application. Demeton-S was translocated in the plant following application to the roots of beans ; aphids feeding on shoot tips were killed after two days.
A. H. CORNFIELD.

Effects of insecticides on phytotoxicity and off-flavour. J. G. Watts (*Farm Chem.*, 1955, **118,** No. 5, 47—53).—A short review of the appropriate literature concerning DDT, BHC, lindane, chlordane, toxaphene and Aldrin. A. G. POLLARD.

Effects of ziram (zinc dimethyldithiocarbamate) on the metabolism and growth of fungi. N. L. Marshall (*Dissert. Abstr.*, 1955, **15,** 1988).—The effects of ziram on the respiration of growing and non-growing conidia of *Fusarium roseum* (**I**) and on the growth of **I** and of *Saccharomyces pastorianus* are described and explained.
O. M. WHITTON.

Aqueous suspensions of insecticides. V. Sorption of insecticides by soils. F. Barlow and A. B. Hadaway (*Bull. entom. Res.*, 1955, **46,** 547—559).—Suspensions of insecticides, e.g., DDT, were sprayed on to blocks of soil and the rate of disappearance of active material from the surface was determined. This rate was high when the vapour of the insecticide was readily adsorbed by the soil. The sorbed insecticide accumulated near the surface of the block and slowly diffused into the interior. In one soil DDT was quant. recovered 1 yr. after sorption. High adsorptive capacities of soil may be measured (method described) by use of non-polar liquids (CCl_4, C_6H_6). Adsorption of DDT by mud blocks (for building) was diminished by lime-washing the surface. Treatment with size prevented adsorption but lowered the efficiency of the insecticide.
A. G. POLLARD.

Bioassay of mercury vapour arising from a phenyl mercury compound. A. E. Dimond and P. E. Waggoner (*Plant Physiol.*, 1955, **30,** 374—376).—A method, based on the prevention of abscission in bean explants, which can be completed in four days, requires no special materials, is reasonably selective, and is quant. in the range 0·06—0·9 mg. Hg per cu. m. of air, is described.
E. G. BRICKELL.

Toxicity of some hydrocarbon insecticides to earthworms. J. M. Hoy (*N.Z. J. Sci. Tech.*, 1955, **37, A,** 367—372).—In soils of moderate org. matter content, significant mortality of earthworms occurred with application of DDT at 80 lb. per acre, but not at 40 lb. per acre, or with γ-BHC at 40 lb. per acre, or crude BHC at 20 lb. per acre. In soil of low org. matter content, 21 lb. of crude BHC per acre killed all earthworms. Thus, the three insecticides should not harm earthworms if applied at the rate of 2 lb. effective isomer per acre as used to control *Costelytra zealandica* (White) in pasture.
R. H. HURST.

Factors affecting air-spray distribution. F. E. Wieck and G. A. Roth (*Farm Chem.*, 1955, **118,** 43—46).—Experimental data demonstrate relationships between median droplet size, spray-nozzle orifice, spray pressure, speed of aircraft and distribution of spray.
A. G. POLLARD.

Effect of boric acid on fructification of *Sordaria*. G. Turian (*Phytopath. Z.*, 1955, **25,** 181—189).—Sporulation of a strain of *S. macrospora*, Auersw. (on a medium containing a glucose : biotin ratio normally favouring sporulation) is progressively inhibited by increasing concn. of H_3BO_3 (50—200 p.p.m.) ; mycelial growth is progressively inhibited and finally checked in the higher concn. range. The effect is due to antagonism of boric acid to the indispensable sporulating and growth factor, biotin. The growing H_3BO_3-inhibited fungus produces a yellow diffusible pigment. Addition to the Fries medium of $CaCO_3$ or $MgSO_4$ (normally stimulating sporulation) does not reduce the anti-sporulating effect of H_3BO_3. Lower concn. of H_3BO_3, however, (especially 20 p.p.m.) in the Fries–sucrose medium stimulate the formation of perithecia. (29 references.) P. S. ARUP.

Distribution and interrelationship of physiological races of yellow rust (*Puccinia glumarum*) of wheat in Europe. A. J. P. Oort (*Tijdschr. PlZiekt.*, 1955, **61,** 202—219).—A survey of published data for Europe and Turkey, in which the races are classified as general or local, with discussions of recent changes in distribution and connexions between interrelationships and distribution. (12 references.)
P. S. ARUP.

Southwestern maize borer in Arkansas. L. H. Rolston (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 553, 40 pp.).—Characteristics of the pest are described. Cultural methods as yet offer the best method of control of the pest. Overwintering larvæ are killed by freezing when stubble is brought to the surface in the autumn, and moth emergence is reduced by burial of stubble in the spring. EPN (1 lb.), Isodrin (0·5 lb.) and Endrin (0·125 lb. per acre) in 100 gal. of spray have given good control of the pests in young plants. Older plants require excessive vol. of spray. A. H. CORNFIELD.

Control of *Fusarium* blight in oat seedlings with antagonistic species of *Chætomium*. M. Tveit and R. K. S. Wood (*Ann. appl. Biol.*, 1955, **43,** 538—552).—Of 47 isolates representing 27 species of *Chætomium* only certain isolates of *C. cochloides*, Pall. and *C. globosum*, Kunze, controlled seedling blight of oats (caused by *Fusarium* spp.) in pot and field tests. There was little antagonism between the organisms in plate tests. Good control of blight was obtained when infected seed was sown in soil which had been treated with a *C. cochloides* culture 10 months previously. A. H. CORNFIELD.

Amino-acids as source of carbon for *Fusarium oxysporum* in vascular tissue of lupins. J. A. D. Zeevaart (*Tijdschr. PlZiekt.*, 1955, **61,** 76—78).—Data (unpublished) obtained by Saaltink prove the presence of *Fusarium oxysporum lupini*, Sn et H. in both resistant and non-resistant varieties of *Lupinus luteus*. The saps exuded from decapitated lupins contain no sugar, but do (in most cases) contain detectable amounts of aspartic and (exceptionally) glutamic acid. Since the amounts of aspartic acid found in the resistant are much smaller than those found in the non-resistant plants, the fungus found in the former probably uses the aspartic acid of the sap as its sole source of C. Experiments *in vitro* have shown that the fungus can subsist on inorg. salts and one amino-acid.
P. S. ARUP.

Method of isolating actinomycetes from scabby potato tissue and soil with minimum contamination. C. H. Lawrence (*Canad. J. Bot.*, 1956, **34,** 44—47).—Actinomycetes can be isolated from either infected potato-tubers or from soil by a 10-min. treatment of the material with phenol 1 : 140. Higher concn. of phenol progressively diminished the no. of actinomycetes until growth was inhibited at 1 : 70. Optimum development of the actinomycetes from potatoes was observed on glucose-aspargine agar cultures at pH 6·5, but material taken from soil grew best on Czapek's agar. In comparative tests using Na propionate 1 : 250 in Czapek's agar at pH 7·0, there were fewer actinomycetes and a greater no. of contaminants.
E. M. J.

Influence of physiological metabolism on reaction of potato tubers to *Phytophthora infestans*, de By. E. Christiansen-Weniger, née Kotte (*Phytopath. Z.*, 1955, **25,** 153—180).—The tissue-infiltration technique is used for determining the influence of specific enzyme-inhibitors and -substrates on the growth and sporulation of the fungus on a resistant (Aquila) and a non-resistant (Erdgold) variety of potato. Concn. of 20 substances tolerated by the tissue are generally 10^{-5}—10^{-2}M. Inhibition of polyphenoloxidase activity by NaN_3, phenylurethane, NaF, etc. renders possible the growth and sporulation of the fungus on Aquila. The polyphenoloxidase-stimulating substances protocatechuic and chlorogenic acids inhibit growth and sporulation on Erdgold. The respiration-inhibitors pyrocatechol and tyrosine stimulate growth on Aquila. The enolase-inhibitor NaF partly inhibits growth and sporulation on Erdgold, but promotes growth on Aquila. Malonic acid or malachite-green reduce sporulation on Erdgold. Pyruvic, succinic, malonic and fumaric acids render (temporary) sporulation possible on Aquila, and promote sporulation on Erdgold. The relationship of certain metabolic mechanisms to the problem of immunity to the fungus are discussed. (45 references.) P. S. ARUP.

Influence of irradiation on black spot and reducing substances of potatoes. D. J. Cotter and R. L. Sawyer (*Amer. Soc. hort. Sci.*, 52*nd*

Annu. Meet., East Lansing, Sept. 1955, 49).—Irradiation of potato tubers with γ-rays from ^{60}Co (10,000 to 60,000 r.) resulted in an increase in " black spot " in two varieties (but not in a third).
L. G. G. WARNE.

Effects of urea in early season spray schedule combinations on finish and cracking of the Stayman apple. W. C. Stiles and N. F. Childers (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 22).—Addition of urea to the fungicide and insecticide sprays given to Stayman apples did not increase russeting of the fruit. L. G. G. WARNE.

Factors affecting incidence of superficial scald in Rome Beauty apple and its coloured sport, Frimley Beauty. C. A. S. Padfield (*N.Z. J. Sci. Tech.*, 1955, **37, A,** 312—317).—Early picking (late March) favoured the development of scald and its incidence was markedly increased by delay between picking and cool storage. The use of oiled wraps for both varieties is recommended ; although they did not eliminate scald, their use consistently reduced the percentage loss. R. H. HURST.

Comparative efficacy of different quaternary ammonium compounds against certain phytopathogenic fungi particularly in vine-growing. E. Rosella and E. Chabert (*C. R. Acad. Agric. Fr.*, 1955, **41,** 741—745).—The resistance of, e.g., *Botrytis cinerea* or *Penicillium glaucum*, and the use of too small a dose at too long intervals are responsible for lack of success in treatment of vines with quaternary ammonium compounds. Eight such compounds were tested in concentrations of 5, 10, 20 mg./l. against *B. cinerea*, the best results being obtained with dimethylbenzylalkylammonium chloride; 20 mg./l. gave greater protection than did 10 mg. or 5 mg./l. The possibility of these substances being effective against brown rot, mildew and oidium in vines is discussed. E. M. J.

Effect of lead arsenate sprays on the sucrose content of grapefruit. E. J. Deszych and S. V. Ting (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 47—48).—Post-bloom sprays of Pb arsenate applied to grapefruit cause a low acid content and an increased sucrose content in the fruit. L. G. G. WARNE.

Gypsy moth. C. C. Perry (*U.S. Dep. Agric.*, 1955, *Tech. Bull.* 1124, 27 pp.).—The 1952 appraisal by the Plant Pest Control Branch for the eradication and/or control of *Porthetria dispar*, (L.) in the U.S. is reported. E. G. BRICKELL.

Screening tests with fungicides for control of celery leaf spot. (*Septoria apii*, Chester). H. Jacks (*N.Z. J. Sci. Tech.*, 1955, **37, A,** 373—378).—Of 30 fungicides tested for control of *S. apii*, the most effective were those based on ferbam, thiram, zineb, Maneb, Dichlone, Captan, nitrobenzene, dinitrophenyl crotonate, chloranil, lime sulphur and ziram. When treated plants were watered to simulate very heavy rain (1 in. in 6 min.), ferbam, zineb and Dichlone were the most effective fungicides for control of the disease.
R. H. HURST.

[A] **Antibiotics in control of plant diseases with special reference to internal disinfection of seed.** J. Dekker (*Meded. Dir. Tuinb.*, 1955, **18,** 623—638). [B] **Internal seed disinfection with rimocidin, an antibiotic from *Streptomyces rimosus*.** A. J. P. Oort and J. Dekker (*Meded. LandbHoogsch., Gent*, 1955, **20,** 381—387).—[A] The literature of the subject is reviewed. The active constituent of suspensions of *Streptomyces rimosus*, which controls *Ascochyta pisi* in pea-seeds without affecting germination, is rimocidin. In practice, the rimocidin is best applied to the peas by the method described in the following abstract. Rimocidin is more active at 6—12° than at 14—30°. (70 references.)

[B] Peas infected with *Ascochyta pisi* with few exceptions, can be completely disinfected by soaking during 18—24 hr. in aq. rimocidin at the optimum concn., viz. 100—150 p.p.m. Retardation of germination occurs only at concn. ⩽200 p.p.m. Rimocidin acts as a systemic disinfectant. A method of seed-dressing recommended for practical use consists in soaking the peas (100) in a slurry composed of rimocidin (150 mg.), carboxymethylcellulose (40 mg.) and water (400 mg.). Rimocidin is similarly effective against *Mycosphærella pinodes* of peas, *Colletotrichum lindemuthianum* of French beans, *Stemphylium* spp. of carrots, and *Alternaria* spp. of radishes. P. S. ARUP.

Method for controlling blossom-end rot of tomatoes. C. M. Geraldson (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 50).—The incidence of blossom-end rot of tomatoes is negatively correlated with the level of the Ca supply and is largely prevented if the soil solution contains Ca equal to 20% of the total sol. salts. L. G. G. WARNE.

Control of caterpillars on cabbage in the Ottawa valley, 1953/54. D. G. Harcourt and L. M. Cass (*Canad. J. agric. Sci.*, 1955, **35,** 568—572).—Sprayings or dustings with the following insecticides (applied four times during late July and all Aug.) gave excellent to fair control of *Pieris rapæ*(L.), *Plutella maculipennis* (Curt.) and *Trichoplusia ni* (Hbn.) in the (descending) order of merit : (*a*) Endrin emulsifiable concentrate (20%) at 0·25 lb., wettable DDT powder (50%) at 1 lb., or DDT dust (3%) at 1 lb. ; (*b*) Malathion dust (4%) at 1·5 lb. or Dieldrin emulsifiable concentrate at 0·25 lb. ; (*c*) wettable Malathion powder (25%) at 1·5 lb. or Isodrin emulsifiable concentrate (20%) at 0·25 lb. per acre. No evidence has been obtained of the build-up of resistance against DDT.
P. S. ARUP.

Control of Sigatoka (banana leaf-spot disease) with cuprous oxide mists. D. Tollenaar (*Neth. J. agric. Sci.*, 1955, **3,** 70—83).—Mist blowing with 100 l. of 3% Banecobre-Sandoz (finely dispersed Cu_2O + sticking agent) per hectare at 3—4 weekly intervals gave satisfactory control of banana leaf-spot disease. Mist-blowing was very much more economical with respect to amount of Cu_2O used than were high-vol. spraying or fogging. A. H. CORNFIELD.

Systemic insecticides for the control of insects transmitting swollen-shoot virus disease of cacao in the Gold Coast. A. D. Hanna, E. Judenko and W. Heatherington (*Bull. entom. Res.*, 1955, **46,** 669—710).—Dimefox was far more efficient than schradan, parathion or paraoxon when applied as a spray on seedling trees or in solution to the soil around the trees. Promising results were obtained by injecting Dimefox into the trunks of the trees.
A. G. POLLARD.

Effects of darkness on the constitution of tobacco leaves and susceptibility to virus infection. E. C. Humphries and B. Kassanis (*Ann. appl. Biol.*, 1955, **43,** 686—695).—The NO_3' content and the no. of lesions on the leaves of tobacco infected with tomato aucuba mosaic virus increased whilst the plants were in darkness for four days and then decreased when the plants were brought into the light for four days. The contents of other nitrogenous fractions in the leaf were not related to no. of lesions. In other tests there was no residual correlation between lesion no. and NO_3' content of the leaf when dry matter content had been allowed for. Dry matter and water content of leaves were significantly correlated with lesion no.
A. H. CORNFIELD.

Inactivation of tobacco mosaic virus by extracts and secretions of higher plants and certain micro-organisms. Contribution to the problem of composting of virus-infected plant material. II. Influence of extracts of green and withered foliage on the virus. W. Bartels (*Phytopath. Z.*, 1955, **25,** 113—152).—Data are given for the inactivating effect of aq. extracts (in two concn.) of the foliage of 67 plants on an aq. NaCl extract of the virus. The effects vary widely with different extracts, 100—80% inactivation being obtained with the higher concn. of foliage-extracts of 26 of the plants. Somewhat better effects are obtained with virus-infected press-juice. Laboratory composting experiments show that complete inactivation cannot be obtained by composting with foliage during six weeks, that buffering at pH 7 reduces the inactivation effect, and that the inactivation is reversible. Serological experiments confirm the view that the virus is not destroyed in the experiments. Inactivating effects are demonstrated for the root-drainings of six plants, and are examined in detail. The temp. attained during the steaming of compost are sufficient to destroy the virus in leaf- and root-press-juices, but not the virus in dried tobacco leaves. Previous results obtained for the inactivating effects of micro-organisms (cf. *ibid.*, 1955, **24,** 117) are recapitulated and discussed in relation to the above findings. The problem of the complete destruction of the virus in composted material requires further investigation. (29 references.) P. S. ARUP.

Paper-electrophoretic investigation of phosphatides of healthy and virus-infected plants in different stages of disease. II. E. Pfeil and W. Kanngiesser (*Z. PflKrankh.*, 1955, **62,** 705—711 ; cf. *Biochem. Z.*, 1953, **325,** 12).—Experimental conditions for the electrophoretic determinations are described in detail. The electrophoretic diagrams obtained for the phosphatides of turnip leaves infected with turnip-yellow virus show no abnormality within a period of three months after infection, viz., long after the appearance of visible symptoms. The abnormality shown after 4·5 months by the phosphatides of centrifuged press-juice differs considerably from that shown by the phosphatides of MeOH extracts of the leaves. The phosphatides extracted from healthy potatoes cannot be clearly distinguished from those tubers affected with leaf-roll virus.
P. S. ARUP.

A *Phytophthora* root rot of soya-beans. A. J. Suhovecky (*Dissert. Abstr.*, 1955, **15,** 1991—1992).—A *Phytophthora* root rot of soya-beans, its effects and its prevention by soil steaming are described. Susceptibilities of different varieties were determined.
O. M. WHITTON.

New rose fungicide. J. D. Campbell (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 38).—Copper dihydrazinium sulphate as 50% wettable powder (½ to ¾ lb. in 100 gal. of

water per acre) gave good control of powdery mildew of roses with no appreciable toxic effect. L. G. G. WARNE.

Occurrence of peroxidase in wood-destroying *Basidiomycetes*. H. Lyr (*Planta*, 1955, **46**, 408—413).—The production of peroxidase by the fungi can be shown with certainty only when it is (practically) the sole oxidising enzyme present in the culture-filtrate. The problem is complicated by the presence of laccase. Two fungi known to produce peroxidase (*Phelinus igniarius* and *Ph. pini*) and two laccase-producing fungi (*Fomes annosus* and *Trametes confragosa*) show practically the same pattern of specificity towards 15 O-acceptors as does the peroxidase of sea-radish. Peroxidase and laccase do not differ appreciably as regards heat-sensitivity. Peroxidase activity is partly inhibited by CO, and wholly inhibited by KCN (10^{-4}M.). The possible rôle of peroxidase in the destruction of wood by fungi is discussed. (28 references.) P. S. ARUP.

Insecticidal dusts for protection of stored peas and beans against bruchid infestation. E. A. Parkin and G. T. Bills (*Bull. entom. Res.*, 1955, **46**, 625—641).—Damage to the stored peas and beans by *Acanthoscelides obtectus* and *Callosobruchus chinensis* was prevented by admixture with dusts of colloidal SiO_2, colloidal Al pentasilicate, diatomite, γ-BHC or on diatomite or kaolin at the rate of 6—8 oz. per 200 lb. of beans. An experimental technique for determining the efficiencies of insecticides for this purpose is described. A. G. POLLARD.

Emergence of larvæ of *Heterodera rostochiensis* under conditions of constant and of alternating temperature. D. Bishop (*Ann. appl. Biol.*, 1955, **43**, 525—532).—The % emergence of *H. rostochiensis* larvæ was greater when temp. was alternated between 15° and 25° daily than when it was kept constant at 25°. The % emergence varied with the concn. of anhydrotetronic acid (**I**) used (0·125—0·0800). After one week optimum emergence occurred with 0·2% of **I** and after five weeks with 0·1% of **I**. A. H. CORNFIELD.

Preservative for harvesting containers. M. Goll and C. D. Thompson (*Farm Chem.*, 1955, **118**, No. 5, 26—29).—Wooden packing boxes, etc., were preserved from decay by treatment with a proprietary prep. (Cellu-San) of a Zn petroleum sulphonate product which acts as a water repellent and fungicide. It leaves no odour in the wood and has no detrimental action on the skins of operatives. A. G. POLLARD.

Control of weeds and brush in Louisiana pastures with herbicides. L. H. Prescott (*Dissert. Abstr.*, 1955, **15** 1990).—Various formulations of 2 : 4-D, 2 : 4 : 5-T and other herbicides were evaluated in different oil, water, and oil and water emulsions carriers as to their effect on trees, brush and miscellaneous weeds in pastures. O. M. WHITTON.

Use of aromatic solvents for control of submersed aquatic weeds in irrigation channels. V. F. Bruns, J. M. Hodgson, H. F. Arle and F. L. Timmons (*U.S. Dep. Agric.*, 1955, *Circ.* 971, 33 pp.).—Aromatic or cyclic hydrocarbons of either petroleum or coal-tar origin complying with specifications established at the U.S. Bureau of Reclamation Chemical Engineering Laboratories give satisfactory control of most kinds of submersed aquatic weeds. Materials and equipment, channel and water factors, and weed growth factors are discussed together with details of the toxicity of solvents to weeds, crop plants, soil bacteria, farm animals, fish and other aquatic animal life. (14 references.) E. G. BRICKELL.

Control of Johnson grass. H. F. Arle and E. H. Everson (*Ariz. agric. Exp. Sta.*, 1955, *Bull.* 265, 9 pp.).—General infestations of Johnson grass are best controlled by a dry summer fallow. Spot treatment of the grass with CCl_3COONa or $NaClO_3$ gave good control in cultivated fields. These two chemicals and undiluted aromatic oils gave good control on ditchbanks and lined canals. A. H. CORNFIELD.

Some effects of herbicides on cotton. W. C. Normand (*Dissert. Abstr.*, 1955, **15**, 1989).—Thirteen varieties of cotton were treated with alkanolamine salts of dinitro-*o*-*sec*.-butylphenol, *iso*propyl *N*-(3-chlorophenyl)carbamate, 3-(*p*-chlorophenyl)-1 : 1-dimethylurea (CMU) and 3-(3 : 4-dichlorophenyl)-1 : 1-dimethylurea. No differential responses of any of the varieties receiving any of the treatments was found. The effect of CMU on physiological processes of cotton plants is described. O. M. WHITTON.

Effect of varying rates of chloro-PIC (*iso*propyl N^3-chlorophenylcarbamate) for onion weed control on subsequent growth of rye and oats. H. W. Burdine, R. H. Ruf and G. J. Raleigh (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 36—37).—Applications of 0·8, 16 or 24 lb. per acre on May 10 and July 14 did not affect onion yields, but all the rates of application reduced the growth of rye sown on September 29 or on April 15 (in the following year). L. G. G. WARNE.

CDAA controls weed grasses in grass-family crops. R. R. Wangerin (*Farm Chem.*, 1955, **118**, No. 12, 47—49).—Experimental trials demonstrate the value of CDAA (α-chloro-*NN*-diallylacetamide) in the control of annual grasses in cereals. A. G. POLLARD.

Stauffer's Vapam fumigant. Anon. (*Farm Chem.*, 1955, **118**, No. 7, 52—54).—Vapam (*N*-methyldithiocarbamate dihydrate) effectively destroys weeds and weed seeds and has shown promise as a fungicide and as a soil fumigant for controlling arthropods. A. G. POLLARD.

Aminotriazole as a weed-killer. Anon. (*Farm Chem.*, 1955, **118**, No. 5, 58).—A short note on recent tests of this material. A. G. POLLARD.

Residual activity of 3-amino-1 : 2 : 4-triazole in soils. K. A. Sund (*J. agric. Food Chem.*, 1956, **4**, 57—60).—A colorimetric method for determining the substance is based on the reaction of aminotriazole (**I**) with a modified Na nitroprusside reagent. By use of this method it is shown that the disappearance of **I** in soils is dependent on soil type. The chemical becomes adsorbed to soil particles and partakes in the soil base-exchange system. It also shows a tendency to form complexes with metals. Toxic effects on tomato seedlings were proportional to the amount of **I** in the soil. N. M. WALLER.

Use of pigmented polyethylene for weed control and for forcing and irrigating vegetables. E. M. Emmert (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 26).—Large seeds, planted by jabbing through black polyethylene sheets into the soil germinate more rapidly than usual (due to higher soil temp. and non-crusting of soil). Few weeds appear and a better stand of seedlings is obtained. The plastic covers the rows but not the whole ground and makes furrow irrigation possible whilst drying out of the ground is retarded. L. G. G. WARNE.

Animal Husbandry

Forage production on Arizona ranges. IV. Range condition in Coconino, Navajo and Apache Counties. R. R. Humphrey (*Ariz. agric. Exp. Sta.*, 1955, *Bull*, 266, 84 pp.).—The types of range in the area and the grazing value of some common plants are described. Management methods are discussed. A. H. CORNFIELD.

Pasture quality and ruminant digestion. I. Seasonal change in botanical and chemical composition of pasture. II. Levels of volatile acids and ammonia in rumen of sheep on high-production pasture. A. T. Johns (*N.Z. J. Sci. Tech.*, 1955, **37, A**, 301—311, 323—331).—I. The change in composition of a pasture of short-rotation ryegrass and clover was determined at frequent intervals. Values for total N, non-protein N, free and bound amino-N, and sol. carbohydrate are recorded. The most marked change is the rapid fall of protein level in the late spring and its rapid rise in the autumn.

II. The volatile acid and NH_3 levels in the rumen of sheep on the pasture were compared with the concn. resulting from a diet of hay. Max. post-feeding NH_3—N levels varied between 35 and 130 mg. per 100 ml. of rumen contents. Differences occurred in the % of individual acids, particularly when pasture was compared with hay. These differences may be related to animal metabolism. R. H. HURST.

Ensilage. II. Ecological aspects of the actions of yeasts in the process. A. Endo (*Tohoku J. agric. Res.*, 1955, **5**, 291—303).—Some biochemical characteristics of strains of yeasts isolated from silage are examined. Their probable rôle in the process of ensilage is discussed. A. G. POLLARD.

Effects of oat silage and of legume-grass silage on beef carcass quality. B. C. Breidenstein (*Dissert. Abstr.*, 1955, **15**, 1953).—The effects of legume-grass silage and of oat silage on beef carcass quality were determined and objective measures of certain carcass traits which contribute to beef quality derived. The results are given in detail. O. M. WHITTON.

Comparison of silage preservatives. O. T. Stallcup (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 557, 16 pp.).—Sodium metabisulphite, Ca formate (**I**), and Ca formate–$NaNO_3$ (**II**) were good preservatives for high-moisture-containing crops such as oats, crimson clover and lucerne but did not help in the preservation of coarse materials such as cotton plants or clover harvested in the advanced stage of maturity. Oat silage treated with **I** or **II** was more acceptable to animals than where whey powder or molasses was used. Lucerne silage treated with whey powder was more acceptable than lucerne treated with beet pulp or **II**. SO_2 was a poor preservative. A. H. CORNFIELD.

Molasses: nitrogen-enriched molasses products and dry molasses as fodder. S. Nordfeldt (*Socker Handl. I*, 1955, **11**, 81—84).—The ways of using molasses in fodder and its value are reviewed. Research (not yet concluded) on N-enriched molasses indicates that N from urea is more easily assimilated than is N from NH_3. Beet pulp

is recommended as a carrier for dried molasses; carriers of poor nutritional value do not give a very economic feedstuff and are too expensive to compete with other feedstuffs.

SUG. IND. ABSTR. (E. M. J.).

Nutritive value of D-tryptophan. M. L. Schafer (*Dissert. Abstr.*, 1955, **15**, 2001—2002).—The nutritive value of D-tryptophan was studied. Young growing rats fed a diet complete in all other known nutrients except niacin, but containing 4% of hydrolysed casein which was sufficient to maintain body wt. but not to promote growth, showed no apparent difference in the utilisation of D- and L-isomers of tryptophan as indicated by total pyridine nucleotides (PN) in the liver tissue, maintenance of wt., and general appearance. When fed the control diet, containing 18% of hydrolysed casein, young growing rats did not utilise the D-tryptophan as readily as the L-isomer as indicated by depreciated appearance of coat, rate of growth, and PN content of the liver tissue. O. M. WHITTON.

Detoxication of Tung meal. Jordan G. Lee (*J. agric. Food Chem.*, 1956, **4**, 67—68).—Tung meals non-toxic to chicks are demonstrated to be non-toxic to albino rats. For both species the same detoxification procedure, comprising alcohol extraction, moistening and steaming, is necessary. The meals are not economical sources of protein since they require lysine supplementation for good feed utilisation. N. M. WALLER.

Effects of mould growth on digestibility and feeding value of grains for swine and sheep. A. R. Jones, L. M. Bezeau, B. D. Owen and F. Whiting (*Canad. J. agric. Sci.*, 1955, **35**, 525—532).—Mouldiness reduces the digestibility of oats by pigs and lambs, but not that of wheat by pigs. In growing and fattening pig-rations containing 25 and 36% of oats, respectively, the substitution of mouldy for sound oats or of mouldy for sound wheat (~60%) does not appreciably affect the growth-rate or feeding-efficiency of pigs. The performance of lambs deteriorates on increasing the % of mouldy oats in the ration. The mouldy grains are not unpalatable to pigs or lambs. P. S. ARUP.

Protein hydrolysis in the determination of lysine in feeding stuffs. F. Kondo and T. Hatano (*Tohoku J. agric. Res.*, 1955, **5**, 243).—Comparison is made of the Kofrányi method (*Z. physiol. Chem.*, 1951, **287**, 170) and the conventional HCl method for protein hydrolysis prior to determining the NH_3-acid distribution. In the HCl process an increase in the period of hydrolysis from 12 to 24 hr. increased the breakdown of protein-N but also resulted in a decline in amino-N and an increase in the amount of NH_3 formed. The lysine content of proteins recorded by the HCl method exceeded that by Kofrányi's method; chromatographs of the hydrolysates showed the presence of valine and threonine in that by the former but not in that by the latter process. A. G. POLLARD.

Occurrence of histamine and tyramine in rumen ingesta of experimentally over-fed sheep. J. A. Dain, A. L. Neal and R. W. Dougherty (*J. Anim. Sci.*, 1955, **14**, 930—935).—Acute indigestion in over-fed rumen-fistulated sheep is associated with toxic levels of histamine in the rumen ingesta. Formation of histamine in the rumen increased at pH $<5{\cdot}0$ and at pH $<4{\cdot}5$ the content of the ingesta reached >70 μg. per ml. with fatal results. A. G. POLLARD.

Some relations among the major chemical components of the bovine body and their applications to nutritional investigations. J. T. Reid, G. H. Wellington and H. O. Dunn (*J. Dairy Sci.*, 1955, **38**, 1344—1359).—The mean %, with their standard deviations, of water, protein and ash in the fat-free whole empty body were $72{\cdot}91 \pm 2{\cdot}01$, $21{\cdot}64 \pm 1{\cdot}53$ and $5{\cdot}34 \pm 0{\cdot}95$, respectively; age was highly significantly correlated with % of water ($-0{\cdot}46$), protein ($0{\cdot}44$) and ash ($0{\cdot}43$). The fat content of the whole empty body can be derived from the water content. In the fat-free dry body, the % of protein and ash were $80{\cdot}3 \pm 1{\cdot}69$ and $19{\cdot}7 \pm 1{\cdot}69$, respectively; age was highly significantly correlated with % of protein ($-0{\cdot}42$) and ash ($0{\cdot}42$). Accurate estimates of the energy values of whole empty bodies of cattle, even under severe experimental conditions, can be made from these generalisations, and the mathematical relations derived, together with indirect measurements of body water contents, could be used to evaluate feeds and rations for cattle and certain nutritive qualities of meat. S. C. JOLLY.

Influence of dietary energy level on succinoxidase and lactic dehydrogenase of the heart of pregnant swine. R. L. Shirley, J. F. Easley, C. E. Haines, A. C. Warnick, H. D. Wallace and G. K. Davis (*J. agric. Food Chem.*, 1956, **4**, 68—70).—A ration adequate in dietary energy, fed to pregnant swine, resulted in greater heart wt. and succinoxidase activity in the left ventricles than did a ration having only about one-half of this energy. Tests made at two stages of gestation showed little difference in the results. The lactic dehydrogenase activity was lower than the corresponding succinoxidase activity and was unaffected by both diet and gestation stage. N. M. WALLER.

Hypomagnesæmia. R. Allcroft (*Agric. Rev.*, 1955, **1**, No. 7, 47—50).—A critical summary of recent work on the nature, possible causes and symptoms of "grass tetany" and of curative measures. A. G. POLLARD.

Effect of manganese on bone formation. H. E. Parker, F. N. Andrews, C. W. Carrick, R. D. Creek and S. M. Hauge (*Poultry Sci.*, 1955, **34**, 1154—1158).—Labelled Mn, Ca and P were used to study the effects of Mn deficiency on deposition of these elements in the bones of chicks. When Mn was supplied to Mn-deficient chicks there was a rapid deposition of Mn in the tibiæ. Mn was deposited in all parts of the tibiæ, the greatest concn. being found at the sites of active calcification. The deposition of Ca and P in the tibiæ were not affected by Mn level of the diet. A. H. CORNFIELD.

Chemical estimation of progesterone in the blood of cattle, sheep and goats. J. I. Raeside and C. W. Turner (*J. Dairy Sci.*, 1955, **38**, 1334—1343).—A method is described for the determination of progesterone (**I**) in blood based on extraction, partition between various solvents, paper partition chromatography and quantitative u.v. spectroscopy. The distribution of **I** in the blood of several large domestic animals is reported. Following the single subcutaneous injection of 1 g. of **I**, max. concn. in the blood occurred after 2 hr. After several successive daily injections, **I** appeared in the peripheral blood, and, in a young bull, levels of >1 μg. per ml. were maintained for 24 hr. daily. In dairy heifers, subcutaneous injection 100 mg. daily resulted in max. plasma levels in 1·5 hr., but no **I** was detectable after 4 hr.; lower max. but more prolonged levels were obtained when microcrystals suspended in water were injected. S. C. JOLLY.

Factors affecting experimental error in field trials in artificial insemination. E. L. Willett, J. I. Ohms and J. H. Torrie (*J. Dairy Sci.*, 1955, **38**, 1375—1384).—The effects are reported of antibacterial agents, no. of services per collection, infection with *Vibrio fœtus* and experimental design on the experimental errors in field trials in artificial insemination. S. C. JOLLY.

Field trials with semen containing several combinations of antibacterial agents. E. L. Willett and J. I. Ohms (*J. Dairy Sci.*, 1955, **38**, 1360—1368).—A more detailed account is given of the effects on non-return rates, already reported briefly (*ibid.*, 1954, **37**, 649), of the addition of streptomycin (**I**), sulphanilamide (**II**) and **I**, and penicillin (**III**) and **I** to yolk–citrate semen diluent, and of **I**, and **I** + **III** to yolk–citrate–**II** diluent. S. C. JOLLY.

Non-return rates and embryonic mortality from inseminations by bulls with *Vibrio fœtus*. E. L. Willett, J. I. Ohms, A. H. Frank, J. H. Bryner and D. E. Bartlett (*J, Dairy Sci.*, 1955, **38**, 1639—1374).—Embryonic mortality was markedly higher and non-return rates were lower among cows bred artificially to bulls infected with pathogenic *V. fœtus* when no antibacterial agents were added to the semen. When antibacterial agents were added to the diluent, result from these bulls were comparable to those from bulls which were not infected or infected with non-pathogenic vibrio (*V. bubulus*). Streptomycin alone was as effective as were combinations with sulphanilamide or penicillin. The ineffectiveness of *V. fœtus* was possibly reduced during storage at refrigerator temp. above freezing, even in the absence of antibiotics. S. C. JOLLY.

Parturient paresis in dairy cows. II. Determination of calcium ions in bovine serum. G. Carlström (*Acta Agric. scand.*, 1955, **5**, 357—374).—The determination is carried out spectrophotometrically with the use of the murexide reaction for the free Ca^{++} ion. The measurements are made on two portions (3·8 ml.) of the serum to one of which is added 0·2 ml. of aq. murexide (freshly prepared) and to the other 0·2 ml. of water (in order to compensate for the colour of the serum). By successive measurements (at intervals of 0·5 mμ.) within the range 490—525 mμ., the max. λ of the extinction curve is determined, first approx. and then accurately. A nomogram is given from which the Ca^{++} content can be found from the max. λ and the pH of the serum (accurately determined). Directions are given for avoiding errors due to the instability of the serum. With normal serum, the method is accurate within $\pm 0{\cdot}3$ mg. of Ca per 100 ml. The accuracy is not affected by the presence of Na^+, K^+, Mg^{++}, or the proteins of bovine serum. The normal ratio of total to free Ca is ~1·95. (28 references.) P. S. ARUP.

Value of animal fat in rations for milk production. O. H. Horton (*Dissert. Abstr.*, 1955, **15**, 1957—1958).—The investigations reported showed that the inclusion of hydrogenated animal fat in a dairy grain ration did not affect ration palatability, milk fat production, butterfat composition, or carotene and vitamin-A levels in the milk and blood plasma. O. M. WHITTON.

Utilisation of high-protein corn [maize] by beef cattle. J. Bond (*Dissert. Abstr.*, 1955, **15**, 1952).—Studies reported indicated that high-protein maize is equal to normal maize and soya-bean oil meal for fattening cattle. O. M. WHITTON.

Relationship between crude fibre content of food and milk production of cows in Indonesia. P. Schoorl (*Neth. J. agric. Sci.*, 1955, **3**, 35—39).—In spite of receiving adequate protein and starch equiv. in their diet, cows in Indonesia produce relatively poor yields of milk as compared with those in temperate climates. This was traced to the relatively high crude fibre content of the tropical grasses. Manuring pastures with inorg. N and K fertilisers increased the protein and reduced the fibre content of grasses. Cows fed with these grasses produced relatively high yields of milk.
A. H. CORNFIELD.

Response of dairy calves to aureomycin fed with a liberal milk and grain ration. E. W. Swanson, S. A. Hinton and J. B. McLaren (*J. Dairy Sci.*, 1955, **38**, 1385—1389).—Growth stimulation due to supplementary aureomycin is not attained consistently in young calves on a liberal milk feeding regime (15—20% of body wt. of milk and milk-replacement mixture daily with liberal starter ration and good quality hay). S. C. JOLLY.

Apparent selective liberation of butyric acid from milk fat by the action of various lipase systems. W. J. Harper (*J. Dairy Sci.*, 1955, **38**, 1391).—Butyric acid was apparently liberated selectively from milk fat by glandular lipases from calves, kids and lambs, but not by pancreatic lipase or milk lipase. S. C. JOLLY.

Dwarfism in beef cattle. O. F. Pahnish, E. B. Stanley, C. E. Safley and C. B. Roubicek (*Ariz. agric. Exp. Sta.*, 1955, *Bull.* 268, 19 pp.).—Dwarfism is described and possible causes and methods of control are discussed. A. H. CORNFIELD.

Uptake of phosphorus by sheep. I. Excretion of injected radiophosphorus. II. Availability of phosphorus of a diet of hay and concentrates. Evan Wright (*N.Z. J. Sci. Tech.*, 1955, **37**, 332—348).—I. There is a variable time lag between fæcal and urinary excretion of P and a daily rhythm of excretion. The specific activity of the urine may be used as an estimate of the endogenous fæcal specific activity.

II. The absorption of P in the diet varied widely from day to day, and from sheep to sheep, with a max. variation of 100%. The only significant correlations between intakes and excretions are between absorption of P and P balance, giving a regression coefficient of approx. 1. The state of PO_4''' balance is determined not by excretion but by control of absorption by unspecified factors. (31 references.) R. H. HURST.

Effect of stilbœstrol, progesterone–œstradiol implants and oral administration of stilbœstrol on fattening lambs. P. S. Jordan, R. M. Jordan and H. G. Croom (*J. Anim. Sci.*, 1955, **14**, 936—940).—Implants of a mixture of progesterone (250 mg.) and œstradiol (10 mg.) or of stilbœstrol (12 mg.) accelerated the growth of fattening lambs. The latter, but not the former, implant lowered the carcass grade and carcass yield (% of live wt.). Oral administration of stilbœstrol (0·1—1·5 mg. per head) did not affect growth rates but at the 0·1 or 0·05 levels slightly improved carcass grading.
A. G. POLLARD.

Response of lambs fed varied levels of diethylstilbœstrol. W. H. Hale, P. G. Homeyer, C. C. Culbertson and W. Burroughs (*J. Anim. Sci.*, 1955, **14**, 909—918).—Incorporation of diethylstilbœstrol (**I**) (approx. 2 mg. per head daily) to a fattening ration raised the rate of increase in live-wt. (>20%) without consistent increase in food consumption or ill-effects on carcass quality. Larger doses of **I** were less effective in accelerating growth, were detrimental to carcass quality and produced symptoms of toxicity.
A. G. POLLARD.

Value of several non-protein-nitrogen compounds as protein substitutes in lamb fattening rations. W. W. Repp, W. H. Hale and W. Burroughs (*J. Anim. Sci.*, 1955, **14**, 901—908).—In feeding trials, urea, NH_4 acetate, NH_4 propionate, NH_4 formate, formamide and propionamide were compared as substitutes for 15, 30 or 50% of the conventional protein-N in the ration. The non-protein sources of N (except formamide) were of similar value as measured by increases in live-wt. and at protein replacement levels of 15 and 30% were as effective as protein after a period of 2—3 weeks. In this period rumen organisms, in *in-vitro* experiments, became adapted to the different N sources. A. G. POLLARD.

Influence of amino-acids and other dietary factors upon nitrogen utilisation by growing swine. R. J. Meade (*Dissert. Abstr.*, 1955, **15**, 1958—1959).—The influence of aureomycin and vitamin B_{12}, alone and in combination, on N utilisation by growing swine fed a 14·1% protein diet at approx. 2·90, 3·52 and 4·60% of their body wt. was studied. Diets containing approx. 14% of crude protein and >0·13, 0·30, 0·62—0·69, 0·63 and 0·54% of tryptophan, methionine, lysine, *iso*leucine and threonine, respectively, were adequate to promote a satisfactory N balance of growing pigs. O. M. WHITTON.

Effect of products obtained from *Streptomyces aureofaciens* fermentation on the growth and reproduction of swine. E. G. Hill and N. L. Larson (*A. R. Hormel Inst.*, 1954—5, 69—73).—A decrease in the no. of clostridia in the ileum was the only marked effect of aureomycin (**I**) on the microflora of young pigs. Feed supplementation with **I** significantly increased average daily wt. gains from 0—56 days of age and generally increased feed utilisation. The presence of **I** in ileum samples decreased the metabolic rate of the samples.
S. C. JOLLY.

Avian respiratory quotient. W. J. Mellen and F. W. Hill (*Poultry Sci.*, 1955, **34**, 1085—1089).—The respiratory quotient of protein for chickens was well below 0·70 for many birds after a fast of one or more days. Respiratory quotient was independent of age (2·5 to 7·5 weeks) or duration of fast (24 to 54 hours).
A. H. CORNFIELD.

Method of reporting random sample broiler tests. N. R. Gyles, J. C. Gilbreath and R. M. Smith (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 558, 12 pp.).—The method is described.
A. H. CORNFIELD.

" Performance index " of growing chickens. H. R. Bird (*Poultry Sci.*, 1955, **34**, 1163—1164).—A discussion of methods of calculating the " performance index " of chickens, whereby wt. gains and feed efficiency can be expressed as a single value.
A. H. CORNFIELD.

Preference by chicks for fat-supplemented diets. R. W. Lewis, D. J. Bray and P. E. Sanford (*Poultry Sci.*, 1955, **34**, 1165—1167).—When given a free choice chicks consumed more of the basal diet containing 2% lard or maize oil than of the basal diet itself. There was no difference in preference between the lard- and maize-oil-supplemented diets. A. H. CORNFIELD.

Storage of vitamin A in chick livers as a criterion of stability, availability and dietary level. R. H. Harms, B. L. Reid and J. R. Couch (*Poultry Sci.*, 1955, **34**, 1125—1133).—Growth of chicks was better and the vitamin A content of their livers was higher where vitamin A was supplied as a stabilised concentrate than when supplied as fish oil. The vitamin A content of the liver of birds increased with the amount of vitamin supplied (500 to 240,000 i.u. per lb. of feed). Of the vitamin A ingested the % which was stored in the liver increased with the level of A supplied. Measurement of the vitamin A content of the liver of chicks is a satisfactory method of assessing the stability, availability and utilisation of the vitamin from various sources. A. H. CORNFIELD.

Effect of incorporating diphenyl-*p*-phenylenediamine into a ration containing various levels of vitamin A from fish oils. L. D. Matterson, R. H. Bunnell, L. D. Stinson, E. P. Singsen and L. M. Potter (*Poultry Sci.*, 1955, **34**, 1080—1084).—Max. growth response of chicks to eight weeks of age was obtained with 1·635 i.u. of vitamin A per lb. of feed when 0·0125% of diphenyl-*p*-phenylenediamine (**I**) was added to the ration and with 2445 i.u. of vitamin when **I** was not added. The vitamin A concn. in the liver was increased to a fair extent, whilst the vitamin A level of the plasma was increased somewhat, by addition of **I** to the diet. A. H. CORNFIELD.

Blood clotting in dams and chicks as related to the composition of the breeder diet. B. E. March, J. Biely and S. P. Touchburn (*Poultry Sci.*, 1955, **34**, 1097—1100).—The prothrombin time of blood from hens was not affected by addition of 5—10% of dehydrated cereal grass or dehydrated lucerne to the birds' diet from birth to two years of age. The prothrombin time of blood from day-old chicks was reduced where their dams received the green feed supplement. A. H. CORNFIELD.

Effect of low dosage of *X*-ray irradiation on reproduction in chickens. S. Lesher, G. E. Cottral and N. F. Waters (*Poultry Sci.*, 1955, **34**, 1089—1092).—Subjecting hens to *X*-rays (50—300 r. at a rate of 5 r. per min.)either before or after laying had commenced had no effect on egg production or on fertility or hatchability of eggs. A. H. CORNFIELD.

Prevention of premature oviposition and shell-less eggs with ephedrine. D. Polin and P. D. Sturkie (*Poultry Sci.*, 1955, **34**, 1169—1170).—Subcutaneous injections of ephedrine sulphate (0·075—0·100 g.) retarded egg-laying by 10—20 hr. in a bird which had consistently laid eggs without shells. The treatment resulted in a certain amount of shell being formed, although the wt. of shell was below normal for the breed. A. H. CORNFIELD.

Riboflavin and thiamine content of eggs from New Hampshire and White Leghorn hens fed diets containing condensed fish or dried whale solubles. H. L. Mayfield, R. R. Roehm and A. F. Beeckler (*Poultry Sci.*, 1955, **34**, 1106—1111).—Addition of 1% of dried whale solubles or 3% of condensed fish solubles to the diet of both breeds had no effect on the % of riboflavin in the eggs. White Leghorn eggs had a somewhat higher % of riboflavin than had New Hampshire eggs. Neither supplement had any effect on the % of thiamine in the eggs from New Hampshires, but both supplements increased slightly the % of thiamine in eggs from White Leghorns.
A. H. CORNFIELD.

Restriction of ooporphyrin deposition on egg shells by feeding hens with nicarbazin. C. F. McClary (*Poultry Sci.*, 1955, **34**, 1164—1165).—The colour (normally medium-brown) of egg shells from White Plymouth Rock hens became almost pure white within two days of adding 0·0125% nicarbazin (4 : 4′-dinitrocarbanilide, 2-hydroxy-4 : 6-dimethylpyrimidine) to the hens' diet. The colour of the egg shells remained white while the drug was supplied (seven days) but returned to normal within 1—2 days of discontinuing the administration of the drug. A. H. CORNFIELD.

Association between lysozyme level and quality of egg white. F. H. Wilcox, jun. (*Poultry Sci.*, 1955, **34**, 1170—1172).—There was a significant positive correlation between egg white quality and lysozyme concn. for eggs selected at random from White Leghorn pullets as well as for eggs from second and third generations of lines bred specifically for high and low lysozyme level within each of two strains. A. H. CORNFIELD.

Effect of strain, sex and diet on dressing percentage and on cooked meat yield of 10-week-old broilers. H. L. Orr (*Poultry Sci.*, 1955, **34**, 1093—1097).—The effect of two diets (one free from and one containing 5% of stabilised animal fat) on the dressing % and meat yields of 10 strains and crosses of broilers was studied. There were no significant differences due to strain, sex or diet on chilled dressed wt. as % of live wt. There were significant differences due to strain and sex on ready-to-cook wt. as % of live wt. Yields of cooked edible meat did not differ significantly with sex or diet but did differ among strains. A. H. CORNFIELD.

The œstrogenic activity of residues obtained from chickens treated with pellets of diethylstilbœstrol. P. C. Merker, L. D. Edwards, F. N. Andrews and J. E. Christian (*Poultry Sci.*, 1955, **34**, 1118—1125).—The free and conjugated phenolic residues from birds receiving implants of 0·012 g. of diethylstilbœstrol did not show significantly different œstrogenic activity from those from control birds. A. H. CORNFIELD.

Effect of feeding various levels of sodium fluoride to growing turkeys. J. O. Anderson, J. S. Hurst, D. C. Strong, H. Nielsen, D. A. Greenwood, W. Robinson, J. L. Shupe, W. Binns, R. A. Bagley and C. I. Draper (*Poultry Sci.*, 1955, **34**, 1147—1153).—Performance of turkeys from 10 to 26 weeks of age was not affected by increasing the F, content of the ration to 100 p.p.m. (control ration contained 43 p.p.m. F). Wt. gains of male turkeys were reduced when 200 p.p.m. F was present in the ration. With increasing levels of F, wt. gains of both males and females were reduced further, feed consumption and feed efficiency decreased and the F content of the soft tissues of the birds increased. The F content of the bones increased with F content of the ration and also with length of time the ration was supplied. A. H. CORNFIELD.

Thyroxine secretion rate of growing turkey poults. H. V. Biellier and C. W. Turner (*Poultry Sci.*, 1955, **34**, 1158—1162).—At three weeks of age the rate of secretion of DL-thyroxine was for Broad Breasted Bronze males 2·28 μg. and for females 2·66 μg. per 100 g. body wt.; for Beltsville White males 2·31 μg. and for females 2·55 μg. per 100 g. body wt. At six weeks of age the secretion rate for Beltsville White males was 1·93 μg. and for females 2·30 μg. At 10 weeks of age the rate was 1·52 μg. for males and 1·67 μg. for females. A. H. CORNFIELD.

Lymphomatosis in chicks immunised against a transplantable lymphoma. G. R. Sharpless and R. Love (*Poultry Sci.*, 1955, **34**, 1111—1113).—Over a period of 15—20 months, the incidence of lymphamotosis in chickens was not significantly affected by immunisation against the transplantable RPL-12 lymphoma through inoculation with the tumour and subsequent infection with St. Louis encephalitis virus. A. H. CORNFIELD.

Lymphomatosis in chickens. B. Winton, B. R. Burmester, E. M. Denington, A. M. Lucas, S. W. Lesher and N. F. Waters (*U.S. Dep. Agric.*, 1955, *Circ.* 970, 17 pp.).—Distribution and economic importance, manifestations, associated diseases, causative agents, spread, resistance factors, and control measures by selective breeding and isolation, are discussed for visceral, neural and ocular lymphomatosis. (40 references.) E. G. BRICKELL.

Encephalomalacia in the chick. III. Influence of feeding or injecting various tocopherols and other antioxidants on the incidence of encephalomalacia. R. H. Bunnell, L. D. Matterson, E. P. Singsen, L. M. Potter, A. Kozeff and E. L. Jungherr (*Poultry Sci.*, 1955, **34**, 1068—1075).—When added to the diet at the 0·0125—0·0250% level the following compounds were effective in preventing encephalomalacia in chicks: diphenyl-*p*-phenylenediamine (**I**), 2 : 6-di-*tert.*-butyl-4-methoxyphenol, dibutyl- and diamyl-hydroquinones, di-*sec.*-butyl-*p*-phenylenediamine, and 6-ethoxy-2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline. When injected, **I** was not as effective as was vitamin E on an equimol. basis, but was as effective on a wt. basis, in preventing encephalomalacia. When supplied in the feed D- and DL-α-tocopheryl acetate were fairly effective, whilst D-α-tocopherol was ineffective in preventing encephalomalacia. When injected, D-α- and D-γ-tocopherol were effective, whilst D-δ-tocopherol was ineffective. A. H. CORNFIELD.

Encephalomalacia in the chick. IV. Influence of oil in fish meal. oils from various species of fish, and animal fats on the incidence of encephalomalacia. E. P. Singsen, L. M. Potter, L. D. Matterson, R. H. Bunnell, A. Kozeff and E. L. Jungherr (*Poultry Sci.*, 1955, **34**, 1075—1079).—When oil from a no. of species of fish was added to the diet of vitamin E-deficient chicks at a 2% level both % mortality and incidence of encephalomalacia were correlated with the I values of the oils. Menhaden fish meal added in amount ≡1—2% of menhaden oil was as effective as was the addition of the oil itself in producing encephalomalacia in vitamin E-deficient chicks. Encephalomalacia increased in vitamin E-deficient chicks with the level of vitamin A and D feeding oil added (0·5—2·0%). The fat in meat and bone scrap and in unstabilised yellow grease did not cause encephalomalacia when added to the diets of vitamin E-deficient chicks. A. H. CORNFIELD.

Morphological changes in young chickens and reproduction performance of adult chickens fed furazolidone or nitrofurazone. D. W. Francis (*Dissert. Abstr.*, 1955, **15**, 1955—1956).—The history and physiological properties relative to the safety of several drugs used for the prevention or control of coccidiosis and blackhead in normal chicks are discussed. The morphological changes in young chickens and reproductive performance of adult chickens fed with furazolidone (**II**) or nitrofurazone (**II**) with or without Enheptin or thiouracil were investigated. Hatchability of all eggs set, egg production and shell quality were unaffected when **I** or **II** were present in concn. 0·011% in the ration of laying pullets for a 10-week period. O. M. WHITTON.

Response of young rabbits to infectious bronchitis virus (Wachtel strain). R. L. Reagan, F. Yancey and A. L. Brueckner (*Poultry Sci.*, 1955, **34**, 1173—1174).—Young rabbits cannot be used as test animals for studying the Wachtel strain of infectious bronchitis, since they could not be infected with the disease by any of the various routes tested. A. H. CORNFIELD.

Solubility of sulphonamide mixtures in solutions of caustic soda. E. Holz, A. García Onandía and S. Holz (*Acta cienc. venez.*, 1955, **6**, 68—73).—Min. quantities necessary for dissolution of 1 g. of sulphadiazine are 0·168 g. of NaOH and 1·1 c.c. of water (≡3·8N); of 1 g. of sulphathiazole are 0·161 g. of NaOH and 2·3 c.c of water (≡1·75N.); and of 1 g. of sulphamerazine are 0·159 g. of NaOH and 3·4 c.c. of water (≡1·17N.). The same weights of NaOH are required when dissolving the sulphonamides in 1N-NaOH, both separately and in combination. D. LEIGHTON.

Soil regeneration. H. Coanda (B.P. 736,785, 7.4.52. Fr., 12.4.51) —A soil regenerant or fertiliser is produced as follows: the solid and liquid fractions obtained by pressing separately the paunches of ruminant animals and vegetable matter are mixed, after optional addition of phosphate, K salts, chopped vegetable matter, dry earth and starch; liquid manure or fæcal matter is added, and the mass which heats up to 68—85° is cooled to 30—38°, and is inoculated with a bacterial culture (*Azotobacter, Clostridia*), an enzyme oxidiser of NH_3, a cellulolytic ferment, and a chemical compound of, e.g., B, Fe, Cl, Ca, Co etc. Earthworms or their eggs may also be incorporated. F. R. BASFORD.

Improvement of soil structure. Monsanto Chemical Co. (B.P. 735,391. 18.5.53. U.S., 16.5.52).—Soil structure is improved by incorporation of 0·001—2 wt.-% (on tillable top soil) of a water-sol. polymer mol. wt. ≮10,000 (30,000—100,000) of $(OH)_m{\cdot}C_nH_{2n+1-m}{\cdot}CO_2{\cdot}CH{:}CH_2$ (*m* is ≯*n*, *n* is 1—5), e.g., vinyl glycollate or lactate, or a copolymer thereof, with, e.g., vinyl acetate or chloride. F. R. BASFORD.

Production of a citrate-soluble fertiliser containing mainly secondary calcium phosphate. Österreichische Stickstoffwerke A.-G. (B.P. 735,086, 17.8.53. Austria, 16.8.52).—In the production of citrate-sol. fertiliser (from raw phosphate and mineral acid), material of good filterability and citrate-solubility is obtained by initiating the pptn. (of secondary Ca phosphate) at moderate temp. (20—50°), heating (to ≮75°), cooling (to 20—50°), and completing pptn. thereat. F. R. BASFORD.

Manufacture of phosphated fertilisers. Potasse et Engrais Chimiques (B.P. 734,887, 24.4.53. Fr. 8.5.52).—Natural phosphate is digested with mineral acid, then Mn^{II} is added (≮20 at. per mol. of P_2O_5), followed by a neutralising agent to give a stable Ca phos-

phate completely sol. in NH_4 citrate (**I**). Thus, natural Morocco phosphate (34·2% of P_2O_5) is stirred (1000) with 32% aq. HCl 1450 l. for 2 hr., then $MnCO_3$ (60) is added followed by $Ca(OH)_2$ (280 kg.), to give $CaHPO_4$ (34·5% of P_2O_5), 99·6% sol. in **I**. F. R. BASFORD.

Manufacture of phosphated fertilisers. Potasse & Engrais Chimiques (B.P. 735,308, 20.6.52. Fr., 31.8.51).—Natural phosphate is treated with mineral acid, then Al^{III} is incorporated, and the product is neutralised, e.g., with aq. NH_3 (while simultaneously adding SO_4''), to give citrate-sol. Ca phosphate. Thus, Moroccan natural phosphate (P_2O_5, 34·2%) is decomposed (1000) with 32% aq. HCl 1450 l. during 2 hr., then $Al(OH)_3$ (40) is added, followed by $Ca(OH)_2$ (280) (as lime wash), with pptn. of $CaHPO_4$ (980 kg.), 99·6% sol. in NH_4 citrate. F. R. BASFORD.

Phosphate fertilisers. Imperial Chemical Industries, Ltd. (Inventors: J. W. R. Rayner and J. H. Hudson) (B.P. 735,293, 23.1.52—In the production of phosphate fertiliser as in BP.. 697,019 or 702,860, a water-sol. phosphate (conc. mixed fertiliser, optionally containing NH_4 sulphate and/or KCl) is added after treatment with NH_3 to give a product of improved solubility (e.g., 30—60 wt.-% of water-sol. P_2O_5). F. R. BASFORD.

Preparation of (chlorotoloxy)ethyl phosphates. Dow Chemical Co. (B.P. 734,824, 8.9.53. U.S., 3.11.52).—Alkali metal, alkaline-earth metal, and Mg salts of 2-(*p-chloro-o-toloxy)ethyl* H_2 *phosphate* (**I**) are claimed as selective weed killers. $POCl_3$ (122) is added rapidly to a warm solution of 2-(*p*-chloro-*o*-toloxy)ethanol (37·2), CCl_4 200 c.c., and a few crystals of anhyd. $MgCl_2$, then after 2 hr. at boiling, the mixture is cooled and air blown to remove HCl (7·28). Distillation of volatile constituents affords a residue of 2-(p-*chloro-o-toloxy)ethyl phosphoric dichloride*, m.p. 90—92° which (10) is hydrolysed during 30 min. with hot water (30); the resulting oily layer is separated, washed with water and treated with aq. NaOH to give the *Na salt* of **I**. F. R. BASFORD.

[Preparation of] chlorotoloxyethyl sulphates. Dow Chemical Co. (B.P. 735,408, 7.9.53. U.S., 3.11.52).—2-(*p*-Chloro-*o*-toloxy)ethanol (**I**) is treated with $ClSO_3H$, and the resulting acid sulphate is converted into alkali metal, alkaline-earth metal, or Mg salt, for use as selective weed killer. Thus, $ClSO_3H$ (29·2) is added to a solution of technical (**I**) (48) in CCl_4 300 c.c. at 15°, during 15 min., while keeping at 10—18°, then the mixture is air-blown and treated with 50% aq. NaOH (26 g.) to give *Na* (2-p-*chloro-o-toloxy)ethyl sulphate*. The crude product may be purified by washing the filtered solid with CCl_4 and recrystallising from 65 : 110 MeOH or water. F. R. BASFORD.

Maleamic esters. Ethyl Corp. (B.P. 735,302, 1.5.52. U.S., 8.11.51).—Esters of *N*-(substituted phenyl) maleamic esters, useful as fungicides, have the formula $RO_2{\cdot}CY{:}CX{\cdot}CO{\cdot}NH{\cdot}C_6H_{4-n}{\cdot}Z_n$ where R is alkyl (especially C_1—C_8), aralkyl, alkanyl, or a halogen-, S-, or N-substituted deriv. thereof, n is an integer 1—5, X and Y are H or halogen, and Z is an org. radical or a negative group not reactive with an aliphatic alcohol. They are made by esterification of the alcohol ROH with the appropriate acid. Among many esters described are *Me* N-o-*diphenylylmaleamate*, m.p. 137—138° and the Pr^n, Pr^i and *Et* esters of N-(p-*nitrophenyl)-chloromaleamic acid*. The materials are used as aq. dispersions containing a surface-active agent, as solutions in an org. solvent, or as dusts compounded with Fullers' Earth or Filtrol. H. L. WHITEHEAD.

2.—FOODS

Carbohydrates of the Gramineæ. VI. Nature of the water-soluble polysaccharides of the flour of wheat (*Triticum vulgare*). K. A. Gilles and F. Smith (*Cereal Chem.*, 1956, **33**, 29—37).—Wheat gums extracted from the flour of spring and winter wheat by either water or aq. $(NH_4)_2SO_4$ contained arabinose, xylose and glucose; those extracted with the salt solution had the higher pentosan content. The gums probably consist of a mixture of two polysaccharides (one composed of arabinose and xylose and the other of glucose), which were not separable by fractional pptn. from aq. solutions by methanol. (19 references.) S. C. JOLLY.

Cereal proteins. A. Bourdet (*Rev. Ferment. Industr. aliment*, 1955, **10**, 235—244).—Current knowledge of cereal proteins is reviewed, dealing with content and method of determination, a discussion of the proteins and their physico-chemical properties, amino-acid composition of proteins, proteins of wheat and flour and their baking value. Data are presented in four tables, on (*a*) proteins of cereal grains, wheat, barley, oats, rye, maize, rice, and their derivatives, (*b*) a comparison of the contents of wheat and maize (Hinton 1953), (*c*) % composition of proteins of grains of cereals (Osborne), (*d*) % of total proteins in wheat, barley, rye, rice, oats, maize. E. M. J.

Extraction of rice proteins. R. T. McIntyre and K. Kymal (*Cereal Chem.*, 1956, **33**, 38—44).—Almost complete removal of proteins from rice (in 100-mesh powder) can be effected by extraction for 2, 4 or 9 hr. with a 4% solution of an alkylarylsulphonate-type of detergent (Santomerse No. 3) containing 2% of Na_2CO_3 and 0·2% of Na bisulphite. Extraction was slightly less efficient with a 1% detergent solution. Most of the 25% of protein left undispersed by the usual methods of extraction using successively water, 5% NaCl solution, alcohol (70%) and 0·2% NaOH solution can be dissolved by a detergent solution. S. C. JOLLY.

Variation in amino-acid content of rice varieties. P. K. Kymal (*Dissert. Abstr.*, 1955, **15**, 1999).—The content of lysine, methionine, phenylalanine, threonine, *iso*leucine, leucine, valine and tryptophan was determined by standard microbiological procedures in 32 samples of rice covering four varieties and four stations. Tryptophan was liberated from ground fat-free rice by enzymic digestion at 32° for 32 hr. with pancreatin and a hog mucosa preparation. The other amino-acids were liberated by separate hydrolysis of the fat-free samples with 2·5N-HCl for 10 hr. at 15 lb. pressure. The N and moisture content of the samples were also determined. Considerable variations in amino-acid composition were found due to varietal and environmental factors. Milling reduced the N and the essential amino-N contents. The low N-content rice showed a higher incidence of essential amino-acids in proportion to the total N content than did the high-N-content samples. O. M. WHITTON.

Sulphiting sweet maize with an aqueous salt solution prior to dehydration. R. E. Hayes, A. I. Nelson and M. P. Steinberg (*Food Technol.*, 1956, **10**, 18—22).—The mechanism of sulphite absorption from an aqueous salt solution by sweet maize which had been cut from the cob and blanched was studied. By dipping in a 0·5 or 1% solution, most of the sulphite is absorbed in the first 10 sec., greatest uptake being from a solution of pH 5. Immature sweet maize takes up more sulphite than does the mature product. About two to three times more sulphite is taken up through the tip cap end than from the crown section of the sweet maize kernel; the hulls reduce penetration but tend to strongly hold sulphite. E. M. J.

Cœliac disease. V. Experiments on cause of harmful effect of wheat gliadin (preliminary communication). J. H. van de Kamer and H. A. Weijers (*Acta pædiat.*, 1955, **44**, 465—469; cf. *ibid.*, 1953, **42**, 223).—The deleterious effects on cœliac patients of gliadin (which contains ~43% of combined glutamine) can be eliminated by boiling the gliadin for a short time with N-HCl, whereby the glutamine is liberated and converted into glutamic acid, without serious interference with the peptide linkings. Since glutamine by itself is harmless, the deleterious effects are probably due to the combined glutamine. A ratio of amino-N : non-amino-N (determined for 10 foodstuffs) greatly exceeding 11 is probably an unfavourable factor. P. S. ARUP.

Intrinsic viscosities of the water-soluble components of wheat flour. D. C. Udy (*Cereal Chem.*, 1956, **33**, 67—74).—Polysaccharides are responsible for ~95% of the intrinsic η, [lim. $c \rightarrow 0$ $(\ln \eta_r)/c$, where $\ln \eta_r$ = natural log of relative η and c = concn. of solute in g. per 100 ml. of solution] of aq. extracts of several wheat flours; sol. proteins contribute the remainder of the η. Polysaccharides and proteins are present in approx. equal amounts and form ~40% of the total solids; the remaining solids are low-mol.-wt. constituents that contribute little if at all to the η of the extracts. Both size and amounts of sol. polysaccharides vary considerably among pure wheat varieties of widely differing protein contents and growth environment. Single varieties were fairly consistent in these properties, which correlate to a certain extent with cookie diameters used in quality testing. S. C. JOLLY.

Relations between wheat protein content, loaf volume, expansion volume and sedimentation value. I. Plant breeders' samples. R. H. Harris and L. D. Sibbitt (*Cereal Chem.*, 1956, **33**, 74—78).—Correlations are reported between protein content, expansion vol., sedimenation value and loaf vol. for wheat hybrids differing widely in protein content and baking strength and grown in Mexico and N. Dakota. Expansion vol. and especially sedimentation value may be of some use for screening promising materials from hybrid lines of widely varying genetic origin. S. C. JOLLY.

Daily bread in America. III. Bulk transport of flour and meal. H. M. R. Hintzer and G. J. Langenberg (*Bakkerswereld*, 1955/56 **16**, No. 10, 11, 12, Repr. 15 pp.; cf. *ibid*,. 1954/55, **15**, No. 27).—A review covering the principal systems in use. P. S. ARUP.

Alcohol acidity as a measure of the soundness of *ata* **(whole meal flour).** S. N. Mitra and R. K. Chatterji (*J. Indian chem. Soc., Industr. Edn*, 1955, **18**, 139—142).—Deterioration of *ata*, particularly in the incipient stage, may be detected by determining the acidity of an alcoholic extract. An upper limit of acidity of 220 mg. of NaOH per 100 g. of sample is suggested for sound *ata*. S. C. JOLLY.

Properties of certain protease systems used in breadmaking. John A. Johnson, Byron S. Miller, P. D. Boyer and W. F. Geddes (*Cereal Chem.*, 1956, **33**, 1—17).—The proteases of malted wheat flour (*M*) and of *Aspergillus niger* (*A*) hydrolyse undenatured gluten less readily than hæmoglobin; denatured gluten is even less readily attacked, because of its low solubility. "Apparent" activation energies for several enzyme systems acting on gluten or hæmoglobin have been calculated. The pH optima for proteases of *M* and *A* are 3·0—4·0 for gluten and hæmoglobin, 5·5—6·0 for casein and 7·0 for gelatin; and for trypsin 7·0—7·5 for all substrates. The pH optima for hydrolysis of complex substrates are apparently mainly a function of solubility and subsequent availability of the linkages to attack. *M* and *A* contained enzymes with trypsin-like and dipeptidase-like activity, but no pepsin-like or carboxypeptidase-like activity. Dipeptidase activity of *A* was destroyed by acid and heat, but trypsin activity was unaffected. Many other specific peptide linkages are possibly hydrolysed by protease systems of cereal and fungal supplements. (40 references.) S. C. JOLLY.

Effect of fermentation time on certain chemical constituents of pre-ferments used in breadmaking. J. A. Johnson, Byron S. Miller, F. Y. Refai and Donald Miller (*J. agric. Food Chem.*, 1956, **4**, 82—84).—The chemical changes occurring in three different pre-ferments used in breadmaking are examined. One ferment comprises water, sugars, malt, salt, yeast and a mineral yeast food and the others have in addition either dried milk or flour. The presence of milk causes greater rates of gas production and prevents large decreases in pH. The utilisation of sugars is slightly retarded in the presence of flour. Dextrose is utilised more quickly than sucrose, but at the end of 5 hr. fermentation at 30° only 5—17% of the sugars remain unfermented. N. M. WALLER.

Investigations on [materials for] bread-baking tins. Anon. (*Bakkerswereld*, 1954/55, **15**, No. 44, Repr. 7 pp.).—The shortcomings of cold-rolled tinplate are demonstrated, and current work on experimental treatments for the improvement of this material is outlined. The optimum thickness of the tinplate is 0·65—0·75 mm. Promising results have been obtained with the use of Al-sheet of thickness ⩽0·75 mm. P. S. ARUP.

Moisture distribution in fresh, frozen and frozen-defrosted bread. J. W. Pence, N. N. Standridge, D. K. Mecham, T. M. Lubisich and H. S. Olcott (*Food Technol.*, 1956, **10**, 76—79).—The moisture distribution in frozen freshly baked bread remained essentially like that of unfrozen freshly baked bread for at least seven weeks of storage at 0°F. The distribution of moisture in frozen-and-defrosted bread was likewise essentially like that of unfrozen freshly baked bread. No change occurred in the moisture distribution of bread stored at 0° for seven weeks before defrosting. E. M. J.

Tripolyphosphate and trimetaphosphate in yeast extracts. S. R. Kornberg (*J. biol. Chem.*, 1956, **218**, 23—31).—Hot water and trichloroacetic acid extracts of bakers' yeast contain tripolyphosphate (a linear triphosphate) and trimetaphosphate (a cyclic triphosphate); the amounts of these in the extract are ~10—20 and 3—4%, respectively. Tripolyphosphate is produced by the action of yeast trimetaphosphatase on trimetaphosphate. J. N. ASHLEY.

Continuous extraction of sugar from beets in the B.M.A. [Braunschweigische Machinenbauanstalt] diffusion tower. S. Boettger (*Industr. aliment. agric.*, 1955, **72**, 657—664).—The construction of the apparatus which is described in detail is based on the two-column Hildebrandt system. The method of working is discussed including pH of the juice which remains paractically constant, between 5·9 and 6·1 during the extraction process; no. of bacteria, the lack of formation of invert sugar. The diffusion constant and formula of Oplatka are used. Diffusion losses are influenced chiefly by the thickness of the cossettes. Data are presented including yields of towers of diameter 2—4·5 m. E. M. J.

Activity of micro-organisms in raw juice production. M. von Lillienskiold and D. Becker (*Zucker*, 1955, **8**, 411—414).—Examinations of the micro-organisms present in raw beet juice from a diffusion battery indicated the presence chiefly of aërobic spore-formers, e.g., *Bacillus subtilis*, *B. pumilus* and *B. megatherium*. The principle micro-organisms in raw juice from a BMA diffusion tower were cocci such as *Leuconostoc* and *Streptococcus fæcalis*, although the bacteria in the battery juice were also present. The pH values were lower at the end of the season when beet quality fell off. Disinfection by formalin alone was not sufficient and needs to be alternated with the use of, e.g., Cl. The application of SO_2 to beets before slicing produces almost complete sterility, but the acidity from adsorbed SO_2 is difficult to control and may produce corrosion. SUG. IND. ABSTR. (E. M. J.).

Bacteriological activity in juice extraction. E. Andersen (*Socker Handl. I*, 1955, **11**, 33—40).—The relationship between bacteriological activity, temp. and pH is discussed; methods of measuring the pH or the redox potential change in diffusion juice as an indication of the activity are described. The sources of infection of the diffusion system are mentioned. Investigations concerned with thermophilic infection are recorded; experiments on the disinfection of waste water with Cl, SO_2 and formalin indicate that Cl and formalin treatments are effective but that the latter is cheaper. The most effective method of keeping down mesophilic activity was the scalding of cossettes. Further work on mesophilic infection is recommended. SUG. IND. ABSTR. (E. M. J.).

Preliminary studies on plant gums as flocculating agents for cane juice clarification. G. P. Mather and S. Mukherjee (*Indian Sugar*, 1955, **5**, 279, 281—283, 285).—The literature is reviewed. Results of experiments comparing the effect on the settling rate of calcium phosphate ppt. of 10 p.p.m. of Lytron X-886, jeolic acid, from jeol gum, kethic acid, from ketha gum, or sodium alginate show that jeolic acid is nearly as effective as Lytron. Analyses of these substances together with these results indicate that plant gums and mucilages having galacturonic acid polymers influence the settling rate more than do those having glucuronic acid. Experiments to determine the optimum concentration of jeolic acid for cane sugar clarification are described; at neutral pH, 2 p.p.m. of jeolic acid was the optimum. Factory trials of this clarificant are recommended as it is abundantly available in Bihar and Bengal and can be purified at small cost. SUG. IND. ABSTR. (E. M. J.).

Dicalcium phosphate for clarification of cane juice. S. N. Gundu Rao and B. H. Hoshing (*Proc. 12th Ann. Conv. Deccan Sugar Technol. Assoc.*, 1955, Pt. I, 52—56).—The solubility of dicalcium phosphate in buffer solutions was investigated; SO_2 gas was passed through a slurry of 15 g. of dicalcium phosphate in 100 c.c. of water for 20 min.; the phosphate concentration in the resulting solution was 4·63%. The good results of the laboratory experiments, which are described, to test the use of this dicalcium phosphate solution to replace triple superphosphate in the clarification process prompted factory trials. Improved sugar quality, low mud vol. and clear, brilliant juices were obtained and the process was continued until the close of the season. SUG. IND. ABSTR. (E. M. J.).

Double clarification of cane juice. R. P. Chitale (*Proc. 12th Ann. Conv. Deccan Sugar Technol. Assoc.*, 1955, Pt. I, 28—30).—Experiments are described in which raw juice samples were limed with 2·5%, 2·0% and 1·5% milk of lime of 15° Brix at room temp. and then centrifuged through a milk-cream separator or Super centrifuge. The alkaline clear juice was brought to pH 7·4 by treatment with a 10° Brix solution of triple super-phosphate; the mixture was boiled, settled and passed through a vacuum filter. Liming with 2·5% or 2% of milk of lime gave 1·8° rise in purity from raw juice to final clear juice; 1·5% of lime gave a lower rise in purity. SUG. IND. ABSTR. (E. M. J.).

Quantitative determination of the amino-acids of sugar cane juice. E. J. Roberts and L. F. Martin (*Sugar, N.Y.*, 1956, **51**, No. 1, 32—33).—Recent work on the determination of amino-acids in sugar cane juices is reviewed. Paper chromatography requires the preliminary separation and concentration of the ionic material containing the amino-acids by collection on, and elution from, an ion-exchange resin. Another method applies a sample of whole juice solids directly to a column of ion-exchange resin from which the amino-acids are then individually eluted. Threonine, proline and phenylalanine have now been isolated from cane juices by this procedure. (20 references.) J. S. C.

***X*-Ray diffractometer and microscopical investigation of crystallisation of amorphous sucrose.** K. J. Palmer, W. B. Dye and D. Black (*J. agric. Food Chem.*, 1956 **4**, 77—81).—An *X*-ray diffractometer method for determining the crystalline to amorphous ratio in spray-dried sucrose samples is described and applied to samples stored at 30·0 and 32·5% R.H. Time for complete crystallisation to occur decreases from 28 days at 30·0% R.H. to 4 days at 32·5% R.H. Seeding of the amorphous powder with 5% by weight of finely-ground cryst. sucrose speeds up the commencement and completion of crystallisation. Observations made with a polarising microscope are used to postulate a mechanism for the crystallisation process under the experimental conditions used. N. M. WALLER.

Equilibrium moisture content and crystallisation of amorphous sucrose and glucose. B. Makower and W. B. Dye (*J. agric. Food Chem.*, 1956, **4**, 72—77).—The conditions governing transformation of sugars from the amorphous to the cryst. state are examined with respect to the prep. of free-flowing powders from fruit juices and purees. Amorphous sucrose and glucose were exposed to R.H. conditions ranging from 4·6 to 33·6% at 25°. At humidities <12% for sucrose and <5% for glucose practically no crystallisation occurred over a period of three years. At higher humidities the absorbed water initiated crystallisation with subsequent release of moisture to yield anhyd. material. The rate of crystallisation of

amorphous sucrose follows an exponential law with respect to time, after an initial induction period during which a build-up of sufficient nuclei to initiate an appreciable rate of crystallisation occurs. N. M. Waller.

Chromatography of glucose on paper. III. Chemical hydrolysis of starch. J. Moreno Calvo (*Ann. Bromatologia*, 1955, **7**, 117—126).—A starch solution (13·3 mg. per ml.) is hydrolysed with 0·33N-HCl for 8 hr. at 90°. The hydrolysate is examined from time to time by the technique described in *ibid.*, p. 95, 107 (cf. J.S.F.A. Abstr., 1956, i, 37) and it is shown that for the first 50 min. no sugars are detectable, but that the glucose content of the solution rises thereafter, reaching its limiting value in about 4 hr. L. G. L. Unstead-Joss.

Paper chromatography of glucose polymers. I. Correlation of colour reaction with chemical structure. II. Correlation of R_F value with chemical structure. K. Aso and F. Yamauchi (*Tohoku J. agric. Res.*, 1955, **5**, 305—310, 310—316).—Techniques for the chromatographic separation of gluco-bioses and certain more complex glucose polymers are examined. The position of the linkage is of greater significance for this purpose than is the α- or β-configuration. A. G. Pollard.

The unfermentable sugars. IX. Ionophoresis of sugars. K. Aso and S. Hamada (*Tohoku J. agric. Res.*, 1955, **5**, 317—321).—Using the technique described gluco-bioses may be classified in three groups, (i) those with 1 : 3 and 1 : 6 linkages, (ii) those with 1 : 2 and 1 : 4 linkages and (iii) those with 1 : 1 linkages. A. G. Pollard.

Volatile flavour of strawberry essence. I. Identification of the carbonyls and certain low-boiling substances. K. P. Dimick and B. Makower (*Food Technol.*, 1956, **10**, 73—75).—In aq. distillates of strawberry puree, aldehyde, acetone, 2-hexenal, diacetyl, methanol, ethanol, and esters containing acetic and *n*-butyric acids were identified. An oil fraction obtained on further distillation amounting to ~13% of the total essence was about ⅓ free fatty acids, *n*-caproic, *n*-valeric, *n*-butyric, *iso*butyric and acetic. The characteristic aroma seemed to be in the fatty-acid-free oil fraction. The amount of carbonyls and the total amount of essence as measured by C analysis were not correlated with the flavour potency of the essence as judged by a taste panel. E. M. J.

Effect of oxygen and hydrogen-ion concentration on colour changes in processed beets, strawberries and raspberries. A. T. Habid and H. D. Brown (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 29—30).—Colour changes were due chiefly to a reduction in red anthocyanin content and these changes were greatest when O_2 was present in the headspace of the can. Some change from red to blue also occurred. L. G. G. Warne.

Refrigeration and fumigation of blueberries. D. H. Dewey (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 12).—Commercially packed blueberries stored at 0°, 4·4° and 12·8° for 2—5 days and then kept at 23·9° developed less mould if treated for 20 min. at room temp. with SO_2 (0·25 or 0·50%) : 1% SO_2 was injurious. L. G. G. Warne.

Influence of ripeness on the organic acids, sugars and pectin of canned Bartlett pears. C. Dame, jun., S. J. Leonard, B. S. Luh and G. L. Marsh (*Food Technol.*, 1956, **10**, 28—33).—Analyses by silica gel column and paper chromatography of Bartlett pears, ripened to different pressure tests and canned according to commercial procedures, indicated that malic and citric acids were the chief acids present. Ripening at 68°F. caused rapid decrease in malic acid, and decrease in citric acid. Other acids, e.g., chlorogenic, pyruvic etc. were present in very small quant. Glucose, fructose and sucrose were identified by chromatography. During ripening there was increase in sol. solids and reducing value, glycosidic hydrolysis of the polygalacturonide chain, and de-esterification of the Me ester groups in the pectin mol. (35 references.) E. M. J.

Routine determination for control of sulphur dioxide content in dipping solutions [for sliced apples prior to drying]. A. Meijer and H. Zonnefeld (*Conserva*, 1956, **4**, 212—214).—The necessity for standardising such solutions is pointed out. The method described depends on the expulsion of the SO_2 from a given vol. of the diluted acidified solution (≡0·5 ml. of the original solution) by gentle distillation, the absorption of the SO_2 by aq. NaOH contained in the receiver, and the testing of the latter solution with 0·0474% $KMnO_4$ (20 ml.). If the $KMnO_4$ is not completely decolorised, a content of SO_2 in the original solution of ⩾16 g. per l. is indicated. P. S. Arup.

Carbon dioxide injury of Jonathan apples in controlled atmosphere storage. W. E. Ballinger and D. W. Dewey (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 48—49).—Jonathan apples were stored at 0°, 2·2° and 4·4° in atm. with 0·5, 2·5 and 5·0)% of CO_2 with 3% of O_2 and in normal air. CO_2 injury occurred mainly at 4·4° but no injury occurred at any CO_2 concn. at 0°. Jonathan spot did not develop with CO_2 concn. of 2·5% and over. Apples in ordinary air developed scald at 0° but those in the controlled atm. remained free of scald. L. G. G. Warne.

Polyethylene film box liners for reducing weight loss and shrivelling of Golden Delicious apples in storage. R. E. Hardenburg (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 13).—Polyethylene 150-gauge box linings reduced wt. losses and prevented shrivelling of Golden Delicious apples stored at −0·6°. Non-sealed were as efficient as sealed linings. L. G. G. Warne.

Further studies with sealed film liners for Watsonville Yellow Newtown apples. A. L. Ryall and M. Uota (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 13).—Yellow Newtown apples stored in boxes with sealed linings developed less internal browning at 4·4° and 7·2° than at 0° and at all temp. the fruit was greener and had less scald than when in non-lined boxes. Both with and without box linings more scald and decay and quicker ripening occurred at 7·2° than at 4·4°. L. G. G. Warne.

Prepackaging Florida and California oranges in open mesh and polyethylene film bags. J. Kaufman, R. E. Hardenburg and J. M. Lutz (*Amer. Soc. hort. Sci., 52nd Annu. Meet., East Lansing*, Sept. 1955, 13).—Less decay developed in oranges stored for one week at 21·1° in open mesh bags than in polyethylene bags with various perforations. The open mesh bag gave the greatest loss in weight and loss of firmness. L. G. G. Warne.

Filth test in industrial fruits and fruit pulps treated with sulphur dioxide. G. P. Peeters (*Rev. Ferment. Industr. aliment.*, 1955, **10**, 245—261).—Fresh fruit and fruit pulp (211 samples) were examined for insect and rodent fragments etc. by digestion with HCl, separating and collecting the fragments on filter paper. In fresh raspberries the no. of fragments per 100 g. sample varied from 8—114, in pulp, 18—122; in fresh strawberries 0—40; in pulp, 2—8, in some samples 0. The practice of gathering raspberries and sending them to market in uncovered containers gives a further source of contamination. The washing of strawberries to free them from sand diminishes the no. of fragments. Photographs (50) of microscopical specimens are appended. E. M. J.

Stability of frozen concentrated orange juice. I. Effect of heat treatment on enzyme inactivation and cloud stability of frozen concentrate made from Pineapple and Valencia oranges. R. B. Guyer, W. M. Miller, O. W. Bissett and M. K. Veldhuis (*Food Technol.*, 1956, **10**, 10—16).—Temp. of 150°F. and above, except for several of the shorter holding times, reduced the pectinase activity in the final product to 25% or less of the original activity in frozen orange concentrate made from Pineapple and Valencia oranges. There was an increase in cloud stability in the temp. range 170—180°F. without a corresponding change in enzyme activity, indicating that there is some factor other than the enzyme pectinesterase which is affected by heat treatment and which inhibits separation and gelation. (13 references.) E. M. J.

Evolution of desulphitation techniques and production of flavoured juices. M. Flanzy and P. André (*C. R. Acad. Agric. Fr.*, 1955, **41**, 738—740).—Techniques employed in desulphitation of grape juice are discussed including the principles involved in discontinuous and continuous processes, with special reference to the development of a continuous process. An apparatus is described in which the juice boils at 80° at a pressure of 450 mm. Hg., temp. of juice at bottling is 70° and time taken to transfer is <2 min. The residual SO_2 is in inverse relation with the acidity. Grapes for juice should be harvested before maturity, that is, before those to be used for wine making. In this way the very sweet insipid flavour of grape juice may be improved, helped by maceration of the fruit, and still further improved by mixing with a very small proportion of the juice of pine-apple, or lemon or orange. The production of grape juice should be considered separately from the production and treatment of wines. E. M. J.

Utilisation of grape juice. IV. Production of grape juice for drinking. T. Nakayama, A. Sato, N. Oki and K. Aso (*Tohoku J. agric. Res.*, 1955, **5**, 323—343).—The quality (acidity, tannin, colour, aroma, flavour) of grape juices are examined in relation to details of processing. A. G. Pollard.

Quantities of total sulphur dioxide and of sulphate ion in organic liquids. Application to wines, to grape juice and to solutions of crystallised sugar. L. Deibner and P. Benard (*Industr. aliment. agric.*, 1955, **72**, 673—676; cf. J.S.F.A. Abstr., 1954, ii, 240).—The techniques described were developed from those discussed by the authors, *ibid.*, 1948, **25**, No. 1—3. A special distillation apparatus is used by means of which complete separation of the SO_2, and its absorption into moderately strong acids or strong alkalis may be effected. SO_2 combined with aldehyde may also be determined quantitatively. Improvement in the quant. determination of sulphate ion in wines is reported and the successful application

of the technique to evaluation of small quant. of SO_2 in crystalline sugars. (24 references.) E. M. J.

Incorporation of natural fruit flavours into fruit juice powders. I. Locking of citrus oils in sucrose and dextrose. T. H. Schultz, K. P. Dimick and B. Makower (*Food Technol.*, 1956, **10,** 57—60).—The flavouring oil is emulsified in a molten carrier, glucose or sucrose, and the mixture is cooled, giving a dispersion of oil within the resulting solid which is ground to granular form. Maize syrup solids in small proportion are included to inhibit crystallisation. This product added to reconstituted orange juice powder gives good flavour, even after storage for six months at 100° F. (14 references.) E. M. J.

Changes in pectic substances of tomatoes during storage. E. F. Stier, C. O. Ball and W. A. Maclinn (*Food Technol.*, 1956, **10,** 39—43).—During a storage period of 21 days protopectin decreased and pectin increased in tomatoes harvested at the red-ripe stage. A definite relationship existed between the fate of the pectic constituents of tomatoes and the time interval of harvest. E. M. J.

Factors influencing the degree of settling in tomato juice. W. B. Robinson, L. B. Kimball, J. R. Ransford, J. C. Moyer and D. B. Hand (*Food Technol.*, 1956, **10,** 109—112).—In tomato juice the particles appear to be in contact and settling depends on packing of the particles; it is not a simple sedimentation process. There is an inverse relationship between the degree of settling and the gross viscosity of tomato juice; the amount of pectin does not directly affect the degree of settling. (14 references.) E. M. J.

Effect of temperature and moisture on storage stability of vacuum-dried tomato juice powder. Francis F. Wong, W. C. Dietrich, J. G. Harris and F. E. Lindquist (*Food Technol.*, 1956, **10,** 96—100).—Vac.-dried tomato-juice powder, when suitably packed can be stored at a temp. of 90°F. for 12 months; at 100°F. off-flavours were produced. Moisture contents of ~2·5% were tolerated at storage temp. of 70°F., but at 90° and 100°F. in addition to storing in an inert atm., the moisture content should be lowered. An in-package desiccant was used to prevent untoward changes in flavour and ascorbic acid content and to repress non-enzymic browning. (15 references.) E. M. J.

Effect of herbicide Karmex-W on the flavour of canned and frozen asparagus. E. F. Stier and W. A. Maclinn (*Food Technol.*, 1956, **10,** 26—27).—Tests were made to find whether Karmex-W (3-*p*-chlorophenyl-1 : 1-dimethyl urea) produced a flavour effect in canned and frozen asparagus. After storage for five months flavour differences were found in only two samples of frozen asparagus; and after nine months of storage commercially canned asparagus samples had detectable flavour differences. E. M. J.

Dehydration of lima beans. A. I. Nelson, M. P. Steinberg, H. W. Norton, C. C. Cleven and H. W. Fritzsche (*Food Technol.*, 1956, **10,** 91—95).—A procedure is described for the prep., dehydration and packaging of dehydrated lima beans that would yield an acceptable product after six months' storage at 100°F. It is recommended that shelled lima beans should be thoroughly cleaned and washed, blanched 3 min. in water at 210°F., treated with 1·5% sulphite solution, initially dehydrated in a through-flow atmospheric drier using the high-temp. dehydration schedule to a T value of 0·5 (T = lb. of moisture per lb. of bone-dry lima-bean solids), finish-dried to a moisture content of ~5% and the product vac. packed in plain tin cans. E. M. J.

Chemical and physical changes as related to maturity of raw and processed sweet peas. N. E. Elehwany (*Dissert. Abstr.*, 1955, **15,** 2156).—Objective methods were developed for measuring maturity of raw and processed peas, based on physical and chemical changes during development. The tests were evaluated in relation to organoleptic response. Maturity of individual varieties of raw peas was measured satisfactorily by a tenderometer, although readings overlapped with different varieties. A di-metric method, including alcohol-insol. solids, viscosity and seedcoat determinations was developed from which an equation was deducted for predicting maturity of raw peas. Maturity of canned peas was satisfactorily predicted from the viscosity of a blended sample. O. M. Whitton.

Relationship of mealiness in cooked potatoes to certain microscopical observations of the raw and cooked product. A. L. Shewfelt, D. R. Brown and K. D. Troop (*Canad. J. agric. Sci.*, 1955, **35,** 513—517).—Significant positive correlations ($r = 0{\cdot}45$—$0{\cdot}7$) are found between texture ratings (mealiness) of the cooked potatoes on the one hand, and diameter of the raw granules and cell-condition and -fragmentation (amount of extraneous starch in the cooked potatoes) on the other. A coeff. of $-0{\cdot}7$ is found between texture and cell-wall thickness. Considerable varietal and environmental variations in the above factors are found for five varieties of potatoes. P. S. Arup.

Prepeeled carrots. F. J. Francis (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing.* Sept. 1955, 12).—Mould develops less on prepeeled carrots if they are soaked after peeling in 9·2% aq. sorbic acid and 0·1% Tween-20 in 2% orthophosphoric acid for 5 min. Carrots so treated will keep for 8—10 days if refrigerated at night and kept at room temp. by day. For peeling a 20-sec. dip in 25% boiling lye was adequate. Longer immersion caused exudation of liquid from the peeled carrots. L. G. G. Warne.

Storage conditions for lettuce used by Navy personnel at distant points. C. Parsons (*Amer. Soc. hort. Sci.*, 52*nd Annu. Meet., East Lansing*, Sept. 1955, 11).—Lettuce store better at 0° than at 3·3° and the temp. effect is greater after six than after two weeks' storage. Trimming in the field increased the storage life. Lining of boxes with polyethylene or wrapping in polyethylene or Cellophane improves the retention of green colour and turgidity. L. G. G. Warne.

Biological assay of insecticides in processed vegetables. G. D. Gernon, jun. (*Dissert. Abstr.*, 1955, **15,** 2157).—Six insecticides Malathion (**I**), Demeton (**II**), Perthane (**III**), Strobane (**IV**), Dieldrin (**V**) and Endrin (**VI**) were evaluated by the modified Sun method, with *Drosophila melanogaster* as the assay organism. **I** and **II** had to be eliminated because of variation between results. **V** and **VI** were assayed satisfactorily by the direct-contact macerated-tissue technique, and they were assayed in canned and frozen snap beans by the modified Sun method. Dosage–mortality curves were plotted by the simplified method of Litchfield and Wilcoxon. A preliminary study was made of the Culture Tube method, using **V** and **VI**. O. M. Whitton.

Studies on English (Persian) walnuts, *Juglans regia*. I. Evaluation of skin colour in shelled walnuts. L. B. Rockland, P. C. Slodowski and E. B. Luchsinger (*Food Technol.*, 1956, **10,** 113—116).—Darkening of walnut skins during storage appears to be associated with development of rancidity, although edible tree-ripe walnut meats may vary in colour from light tan to brown-black. A solvent extraction technique for 30 min. with hot aq. methanol (65%) and photometric determination of the solution at 400 mμ. was developed for obtaining numerical values for skin colour of walnut kernels and pieces, and colour changes associated with the development of staling and rancidity. Data are presented to indicate the reproducibility and sensitivity of the procedure. E. M. J.

Clarification and stabilisation of wines. J. Ribereau-Gayon (*Rev. Ferment. Industr. aliment.*, 1955, **10,** 206—213).—The clarification of wines with protein, e.g., albumin, etc., or gelatin, the rôle of tannin, and the sedimentation and filtration are discussed, the choice of method depending on the quality of the wine. The problems associated with the stabilisation particularly of white wine are discussed. A synopsis is presented of procedures for detecting metals Cu and Fe which are naturally occurring as traces, or present in larger quantities derived from Cu boilers or material, during fermentation. E. M. J.

Pantothenic acid in grapes and in Bordeaux wines. E. Peynaud and S. Lafourcade (*Industr. aliment. agric.*, 1955, **72,** 665—670).—A technique was developed using a strain of *Saccharomyces ellipsoideus* of which the rate of multiplication is between certain limits, a function of the quantity of pantothenic acid, to determine the pantothenic acid content in 25 white and 51 red wines. Amounts of pantothenic acid found were: in white wines 0·55—1·24 mg. with a mean of 0·81 mg. per l., and in red wines 0·47—1·87 mg. with a mean of 0·98 mg. per l. (25 references.) E. M. J.

Effect of heat treatment of musts on the colour characteristics of red wine. H. W. Berg and G. L. Marsh (*Food Technol.*, 1956, **10,** 4—9).—High temp., short time processing treatments were applied to six lots of wine produced during the period 1949—51. Changes in the organoleptic characteristics of the wines, especially colour stability were studied during ageing for periods of 16 to 55 months. Heat treatment of musts fermented on the skins slightly increases the red hue, increases the saturation, and markedly decreases the brightness of red wines. Ageing resulted in a more or less marked decrease in the red hue as well as in the colour density. Fermentation on the skins of heat-treated musts produced wines of inferior quality. E. M. J.

Science of brewing. A. H. Cook (*J. roy. Soc. Arts.*, 1956, **104,** 243—286).—(Cantor Lectures.) The brewing process, the materials and reactions involved, and the research associated with it, are reviewed systematically and in considerable detail. (58 references.) J. S. C.

Transformation of carbohydrates in the course of malting, brewing and alcoholic fermentation. R. H. Hopkins (*Rev. Ferment. Industr. aliment.*, 1955, **10,** 199—202).—The changes taking place in starch and the products formed by the breakdown of the starch molecule are discussed. E. M. J.

Amylases. R. H. Hopkins (*Rev. Ferment. Industr. aliment.*, 1955, **10**, 262—264).—The following are discussed: The structure of amylose and of amylopectin ; the actions of β-amylase, (*a*) attacking the glucosidic chains cutting off mol. of maltose (mechanism of the single chain), (*b*) under other conditions of raised or lowered temp. taking its activity from one chain to another, the formation of each mol. of maltose constituting a complete reaction (mechanism of multiple chains), this continuing until about 70% of maltose is formed ; the action of the α-amylases of saliva, of malt and of bacteria ; the action of glucamylase found in *Rhizopus*, and probably in *Aspergillus*, the action corresponding to that of β-amylase. E. M. J.

Factors involved in the determination of barley amylase. L. L. Zoch and A. D. Dickson (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 5—10).—Wiley mill grinding of barley at room temp. may reduce β-amylase activity by 5—10% and grinding in high-speed rotor type mills, which may heat the sample by friction, may reduce β-amylase by 25—30%). The causes of inactivation of the enzyme during grinding appear to be complex. Temp. and oxidation have approx. equal effects and other undetermined factors also operate, as evidenced, e.g., by a substantially greater reduction in 6-row as compared with 2-row barley. It is shown that cysteine is as effective as an activator of β-amylase as papain. The use of 1 g. cysteine/5 g. barley and a 5-hr. extraction at 40° gave values almost as high as with papain or cysteine in the longer (20—22 hr. at 20°) extractions. J. S. C.

Cytolytic enzymes in germinating barley : a review of current research. E. J. Bass and W. O. S. Meredith (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 11—17).—The progress made in characterising cytolytic enzymes of germinating barley and in developing a practical test of cytolytic activity as an additional criterion of malting quality, is reviewed (cf. Bass *et al.*, Brit. Abstr., BIII, 1953, 141 ; Enebo *et al., ibid.*, 1953, 383 ; Gilles *et al., ibid.*, AII, 1953, 468 ; Preece and Mackenzie, *ibid.*, BIII, 1953, 91 ; Sandegren and Enebo, *ibid.*, BIII, 1952, 538). (15 references.) J. S. C.

Statistical methods find hidden relationships in plant data. A. P. Van der Kloot and R. I. Tenney (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 18—23).—The application of Regression Analysis to control-test data in brewing is illustrated in detail, using the standard test for fermentable extract of a wort to predict the value of the final Balling. J. S. C.

Use of antibiotics in the preparation of pure yeast cultures to be used in a plant propagator. E. L. Van Engel and H. T. Czarnecki (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 29—35).—Two members of the genus *Acetobacter* persisted in a pitching yeast treated with an acid wash to keep the no. of these organisms to a min. of $< 1/10^6$ yeast cells. Various antibiotics were evaluated in respect of their efficacy as controlling agents against these *Acetobacter* sp. Those found to be effective were aureomycin (40 p.p.m.) and Terramycin (80 p.p.m.). The use of aureomycin enabled a pure culture yeast to be produced from yeast taken directly from a plant fermenter and this was used to inoculate a plant propagator. The procedure recommended for this technique is : (1) isolate the yeast contaminants ; (2) screen the isolates with antibiotic sensitivity discs ; (3) use one or more of the effective antibiotics to prepare the pure yeast culture. (11 references.) J. S. C.

Nutritional requirements of brewing micro-organisms. I. Nutritional requirements of *Flavobacterium proteus*. F. B. Strandskov and J. B. Bockelmann (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 36—42).—The rate of growth of *F. proteus* in a synthetic medium is dependent on the presence of a number of amino-acids together with uracil and adenine. The organism will not grow in a medium containing only ammonia, glucose and inorg. salts. The addition of the amino-acids, uracil and adenine to a fermentation contaminated with *F. proteus* did not increase its growth-rate as much as might be expected. This is attributed to breakdown of the amino-acids by yeast. (13 references.) J. S. C.

Influence of antibiotics on some biological contaminants in the brewery. G. J. Haas (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 43—55).—The effects of various antibiotics on strains of *Pediococcus cerevisiæ* (**I**) and of *Lactobacillus pastorianus* (**II**) were investigated. Both organisms were found to be sensitive to several antibiotics. **I** was inhibited but not killed by polymixin. The most effective agent against **II** was chloromycetin. Polymixin is adsorbed by filtration media used in breweries if passed through in water but it was found that very little is actually adsorbed from beer itself. The results are discussed from the point of view of the possibility of using antibiotic washes to reduce the bacterial count of brewery yeast but it is concluded that a great deal more research is required before this can be regarded as safe. (14 references.) J. S. C.

Recent developments in the field of industrial microbiology and their possible impact on brewing technology. C. G. Dunn (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 65—79).—Recent developments reviewed include : the use of inhibitors, including particularly antibiotics, for preventing the growth of spoilage micro-organisms in fermentation processes, the use of ionising radiation for stabilisation of ground malt and beers, the membrane filter technique for examination of the bacterial content of brewing liquors, yeast genetics, continuous brewing processes, the *in situ* cleaning of pipelines, use of chromatography, spectrophotographic techniques and the ultra-centrifuge in brewing analysis. (76 references.) J. S. C.

Comparison of methylene-blue and acridine-orange methods with culture method as proof of survival or death of various yeasts after injury by various methods. I. H. Ketterer (*Brauwissenschaft*, 1956, **9**, 14—19).—Both staining media (in 0·01% concn.) are toxic to yeasts ; the sensitivity of different strains of *Saccharomyces cerevisiæ* varies widely. In comparison with the micro-culture method, both staining methods underestimate the % of dead cells in yeast cultures. In experiments in which yeast-suspensions have been exposed to heat (at 44° or 48° for various periods) or to u.v. radiation, the results of the staining methods show neither mutual agreement nor agreement with those of the culture method. For the staining methods to take full effect, the requisite degree of protein-denaturation is higher than that associated with loss of viability. The biochemical implications of these and other findings are considered. P. S. Arup.

Sanitation control in the food processing industry. V. S. Troy (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 80—85).—The more common sources of bacterial contamination in food processing and in brewing, together with preventive and remedial methods relevant to each are discussed. A sanitation programme for beer handling equipment is outlined. J. S. C.

Brewing water in relation to biological aspects of beer production. M. Burger, P. R. Glenister and K. Becker (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 86—100).—Slimes in brewery water systems may cause contamination of wort and beer. The organisms which appear to be most dangerous are *Aerobacter* and *Pichia* spp., which can grow in wort at a pH as low as 4·7, in CO_2, and in the presence of 4% ethanol. Routine microbiological examination of brewery water systems is advised and should include plate counts on nutrient agar (**I**) and on acidified potato dextrose agar (**II**), or **I** and the Schlesinger test, or indicated number coliform test and **II**. Cleaning of brewery water systems and chlorination of the waters to a residual Cl content of 0·5 p.p.m. will remove slimes and inhibit their recurrence, and thus remove any biological " off-tastes " in the beer due to this cause. (19 references.) J. S. C.

Review of differential techniques in brewing microbiology. Samuel R. Green (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 107—119). —Recent progress in the detection and enumeration of bacteria in the presence of yeast by means of actidione and other antibiotics, and the differentiation of yeast genera and strains by antifungal antibiotics (e.g., actidione, clavatin), carbohydrates (e.g., maltotriose), amino-acids, giant colony morphology, vitamins or " bios " requirements, and sporulation characteristics, is reviewed. (22 references.) J. S. C.

Rôle of chlorine germicides. A. L. Sotier (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 120—124).—The germicidal use of Cl is reviewed historically including the use of Cl-liberating org. compounds. The potent agent is HClO which is more effective in the un-ionised state. The use of a formulated mixture containing 25% (min.) of 1 : 3-dichloro-5 : 5-dimethylhydantoin, a stable wetting agent, inorg. salts and a compatible acidic ingredient, is described. J. S. C.

Determination of volatile sulphur compounds. IV. Further notes on mercaptans. M. W. Brenner, J. L. Owades and T. Fazio (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 125—132).—An olfactory test, based on the screening of the odour of both H_2S and mercaptans by $CuSO_4$ and of H_2S, but not of mercaptans, by $CdSO_4$, is described to enable the influence of mercaptans and H_2S in the odour of beers to be assessed. A simplified method for the quant. determination of mercaptans is described. The sample is distilled with a little Cd acetate, the buffered distillate is warmed and N_2 swept through it and then into a solution of Zn acetate, *p*-aminodimethylaniline sulphate, H_2SO_4 and $FeCl_3$, which is examined by spectrophotometer or colorimeter. The mercaptan contents of various brewing materials and beers are reported and the reactions involved in the formation of mercaptans and/or other volatile I compounds in beer are discussed. (13 references.) J. S. C.

Determination of volatile sulphur compounds. V. Sulphur dioxide. M. W. Brenner, J. L. Owades and T. Fazio (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 133—144).—SO_2 is determined in beer by

reduction with $SnCl_2$ to H_2S which is then determined colorimetrically after conversion to methylene blue by absorption in Zn acetate solution and reaction with *p*-aminodimethylaniline and $FeCl_3$ (cf. preceding abstract). The procedure is effected by passing a stream of N through a series of wash bottles containing, firstly, the sample and $SnCl_2$, then a pH 7 phosphate buffer, and, finally, 2% aq. Zn acetate. The SO_2 contents of various brewing materials and beers are reported and it is shown that SO_2 is formed during fermentation. The relationship between SO_2 content and various S compounds in beers and the concept of " free " and " bound " SO_2 are discussed. Results obtained by the procedure described are generally lower than those obtained by the Monier-Williams method, which is considered to be subject to appreciable positive errors. At <20 p.p.m. SO_2, the effects on the odours of beers are undetectable. (20 references.)
J. S. C.

Traces of nickel in beers and brewing. I. Stone and Philip P. Gray (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 45—158).—A precise colorimetric method for determining traces of Ni in malt beverages is described (cf. Kenigsberg and Stone, J.S.F.A. Abstr., 1956, i, 42) and results obtained with brewing raw materials, commercial beers and on the distribution of Ni in the various steps of processing beer, are reported and discussed. Beers normally have a Ni content of $<0{\cdot}05$ p.p.m. A considerable proportion of Ni in wort is separated with the yeast. In pilot brewery tests high Ni levels in the yeast caused only moderate retardation of fermentation. The presence of high levels of Ni in beer appears to promote wildness.
J. S. C.

Effect of time upon iron content of canned beer. R. I. Tenney (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 159—166).—The Fe content of canned beers was examined with reference to variation with storage time and variability of result between different cans and the analytical results statistically examined with the object of evolving a method for predicting shelf life of beer packaged in cans, based on an " accelerated ageing " procedure. J. S. C.

Determination of fermentable sugars in beer by paper chromatography. H. R. Held, R. H. Garratt and W. D. McFarlane (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 167—173).—The chromatographic procedure previously described for quant. estimation of carbohydrates and of total fermentable sugars in wort (McFarlane and Held, *ibid.*, 1953, 67; cf. also J.S.F.A. Abstr., 1955, i, 321) has been modified so that it can be used with beer. The beer sugars are collected on a small area of the papergram so that direct colorimetric analysis can be made. The fermentable sugar content of a series of beers varied from 0·24 to 0·86 g./100 ml., expressed as glucose. J. S. C.

Separation of the aromatic constituents of hops. F. L. Rigby and J. L. Bethune (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 174—183).—Some preliminary results of a study of the constituents of hop oil are described. The chromatographic technique of Kirchener, Miller and Keller was used (cf. Brit. Abstr., C, 1951, 316; 1953, 473). The volatile oil of hops includes at least 26 constituents, which include humulene, myrcene, β- and γ-caryophyllene, linalool, methyl nonyl ketone and either geraniol or nerol; others remain to be identified. Various differences in composition among different varieties of hop oils were found but their significance in brewing has not been established. (14 references.) J. S. C.

Evaluation of bitter substances of hops in the manufacture of beer. P. Kolbach (*Brass. et Malt. Belge.*, 1955, **5**, 403—411).—Extensive data on 38 experimental brewings carried out in 12 different breweries are presented, comprising: quantities of hops used and conditions of boiling; analyses of bitter substances in hops; conditions of the wort and fermented liquor, pH, and cold haze; nitrogenous matters, coloration and viscosity. These findings are discussed. E. M. J.

Potentiometric determinations in malt wort. K. Raible (*Brauwissenschaft*, 1956, **9**, 8—14).—The measurements are carried out on filtered, de-aërated worts as in previously described analogous experiments with beer (cf. J.S.F.A. Abstr., 1955, ii, 183). As with beer, the rH values of different types of wort tend to reach a max. value of ~9. The rate of change in rH depends directly on the pH and temp. Possible factors (including the formation of new reductones through the melanoidin reaction, and the irreversibility of dehydrone reactions) operative in the attainment of the constant rH value are considered. (22 references.) P. S. Arup.

Solubility of carbon dioxide, oxygen and nitrogen in beer and water. I. C. Enders, W. Kleber and E. Paukner (*Brauwissenschaft*, 1956, **9**, 2—8).—Shortcomings of the available manometric methods for determining the gases in beer are pointed out. Fundamental solubility investigations at different temp. and pressures are necessary in order to place such determinations on a satisfactory basis. A preliminary account of the investigations includes theoretical considerations and descriptions of the construction and operation of apparatus for determining the pressure in beer bottles and for the evacuation and analysis of the gases from beer. P. S. Arup.

Production of diacetyl by *Streptococcus citrophilus*-209. S. N. Anantharamiah, H. Laxminarayana and K. K. Iya (*Indian J. Dairy Sci.*, 1955, **8**, 146—157).—Among the organisms examined, *S. citrophilus*-209 produced the highest amounts of volatile acid (25·7 ml. of 0·1N. acid per 250 g.) as well as diacetyl (24·6 mg. per 100 g.) in milk cultures; *S. liquefaciens*-108 and *Lactobacillus plantarum*-89 produced 12·0 and 10·1 mg. per 200 g. of diacetyl respectively. When citrate was added to the medium diacetyl production was increased to 56·9 mg. in the case of *S. citrophilus* and to 34·4 and 14·8 mg. respectively in the case of the other two organisms. A medium was developed containing citric acid 1% and yeast extract 0·5% in which *S. citrophilus* produced diacetyl at the rate of ~900 mg. per 1000 g. of culture medium. (20 references.)
E. M. J.

Physical properties of milk. I. Density. W. D. Rutz, C. H. Whitnah and G. D. Baetz (*J. Dairy Sci.*, 1955, **38**, 1312—1318).—The *d* of milk is not a max. at 4°, but apparently undergoes an irregular change at this temp. Between 18° and 44°, *d* is, within 0·0005 g. per ml., a linear function of temp. with a calc. temp. coeff. of 0·00038. Increasing homogenisation pressure up to 300 lb. per sq. in. causes highly significant increases in *d*, but pressures of 500—3000 lb. per sq. in. have no significant effect.
S. C. Jolly.

Comparison of the rates of *in-vitro* proteolysis in human milk, cows' milk and cows' milk preparations by human gastric and duodenal juices. J. G. Kennedy, E. R. Spence and F. W. Bernhart. (*J. Dairy Sci.*, 1955, **38**, 1307—1311).—The *in-vitro* proteolysis of human milk during digestion by unpurified human gastric juice and subsequently by unpurified human pancreatic juice is slower than is that of raw cows' milk or sterilised and spray-dried milk products. The proteolysis rates of pasteurised and unheated cows' milk are essentially the same as those of heat-sterilised and spray-dried milk products. S. C. Jolly.

Elimination of dec-9-enoic acid as a precursor of δ-decalactone in milk fat. P. G. Keeney and S. Patton (*J. Dairy Sci.*, 1955, **38**, 1390).—The prep. of dec-9-enoic acid by a Barbier–Wieland degradation of hendec-10-enoic acid is described. The characteristic coconut-like flavour due to δ-decalactone that develops in certain fat-containing dairy products could not be produced from dec-9-enoic acid by subjecting it to conditions (heat, storage and moisture) known to accelerate this defect. S. C. Jolly.

Influence of certain vitamin K compounds on lactic acid development in milk. H. H. Wilkowske, W. A. Krienke, L. R. Arrington and E. L. Fouts (*J. Dairy Sci.*, 1955, **38**, 1077—1082).—The rate of lactic acid development (*R*) was not reduced in milk from cows fed >600 mg. of Menadione (**I**) or 10 mg. of **I** diphosphate daily for >45 days. *R* was reduced by the direct addition of 3 p.p.m. of **I** to milk inoculated with commercial dairy starter. To inhibit lactic acid production for 24 hr. at 30°, 100 p.p.m. of **I** were necessary, but such concn. adversely affected the colour and flavour of the milk. S. C. Jolly.

Vitamin D in milk. C. Engel (*Neth. Milk Dairy J.*, 1955, **9**, 139—145).—Various methods of fortifying milk with vitamin D are reviewed. Vitamin D assay results in condensed, irradiated milk reported in the literature are summarised: the vitamin D content, (of non-condensed milk) was between 160 and 200 i.u. per l. It is therefore concluded that the Scholl–Scheer–Steinbeil irradiation process is as effective as fortification with vitamin D. (11 references.)
J. S. C.

Tocopherol content of the fat of dairy products as an index of adulteration. J. H. Mahon, C. Anglin and R. A. Chapman (*J. Dairy Sci.*, 1955, **38**, 1089—1095).—Adulteration of evaporated milk, condensed milk, whole milk powder, ice cream and cheese with vegetable fats can be detected by the method of Mahon and Chapman (*Analyt. Chem.*, 1954, **26**, 1195), based on the tocopherol content of the fat, by using a slight modification of the method of Sager and Sanders (Milk Ind. Foundation, *Convention Proc., Lab. sect.*, Sept., 1952, 1—14) for isolation of the fat. The method will not detect added lard, tallow or coconut oil, and it cannot be used for chocolate ice cream or for processed cheeses containing colouring matters other than annatto, Oil Yellow AB (F.D. & C. Yellow No. 3), or Oil Yellow OB (F.D. & C. Yellow No. 4).
S. C. Jolly.

Leucine metabolism of *Streptococcus lactis* var. *maltigenes*. I. Conversion of α-keto*iso*caproic acid to leucine and 3-methylbutanal. P. MacLeod and M. E. Morgan (*J. Dairy Sci.*, 1955, **38**, 1208—1214).—*Streptococcus lactis* (*L*) and *S. lactis* var. *maltigenes* (*M*) require leucine (**I**), *iso*leucine and valine for growth. 5-Methyl-2-oxovaleric acid (α-keto*iso*caproic acid) (**II**) satisfies the **I** requirements of *L* and *M*, resting cells of which synthesise **I** from **II** in the

presence of glutamic acid. *M* converts both **I** and **II** to 3-methylbutanal (**III**), and although both *L* and *M* degrade **I** to **II**, *L* forms little or no **III** from either **I** or **II**. The physiological difference between *L* and *M* lies apparently in a difference in ability to decarboxylate **II** or in ability to degrade **III**. S. C. JOLLY.

Hydrogen-ion concentration of milk. I. pH of milk of animals of different breeds and individuals. M. Bhimasena Rao and Noshir N. Dastur (*Indian J. Dairy Sci.*, 1955, **8**, 158—172).—The pH of samples of cows' milk varied from 6·40 to 6·80, the average for all cow herd samples being 6·63 ± 0·08. In individual animals (four Cross-bred cows) the average pH of the milk varied from 6·57 to 6·63. The average acidity for all cows' milk samples was 0·13 ± 0·01% the acidity varying from 0·08 to 0·18% in the samples. Fat content varied from 4·0 to 7·0% and in buffalo milk samples from 5·0 to 9·5%. In cows' milk samples total solids varied from 12·50 to 16·00%; in buffalo samples from 14·00 to 19·00%. In cows' milk no significant correlation between pH and fat and pH and solids-not-fat was found. E. M. J.

Amylases of milk. E. J. Guy (*Dissert. Abstr.*, 1955, **15**, 1998).—It was found that very low concn. of an α-amylase (**I**) and a β-amylase (**II**) are present in whole cows' milk, skim milk and in milk serum protein. **I** was measured primarily by starch liquefaction in the presence of $CaCl_2$ activator and **II** by saccharification in the absence of ionic activators. Heat inactivation studies for 30 min. at pH 6·4 showed that **I** and **II** of lactoglobulin protein are not concerned in the loaf-volume-depressant action of unheated milk. **I** separated in quant. yield into the whey fraction of undialysed whole milk and about 50% of this into the classical "lactoglobulin" fraction. **I** activity was exhibited by all prep. of dialysed milk serum protein and in amounts varying by 250% in lactoglobulin, and **II** activity in variable amounts by some but not all of the purified preparations. By adding 15% ethylene glycol to a 28% ethanol solution of the enzyme, **I** of lactoglobulin was almost selectively adsorbed upon starch in high yield and could then be eluted, while **II** was left in the filtrate and could be further fractionated with EtOH and $(NH_4)_2SO_4$. Preparations were obtained in which the overall enrichment over that of lactoglobulin for **II** was 23-fold (31·0% yield) and for **I** 30-fold (20% yield) and 51-fold (12% yield). Purified **I** of cows' milk reacts optimally at pH 7·4 up to 30 min. time with tris (hydroxymethyl)-aminomethane buffer, 0·06—0·075M-$CaCl_2$ at 34°. Its dependence upon chloride ion distinguishes it from the action of other amylases. Purified **II** obtained from the lactoglobulin of milk serum resembles other β-amylases but is distinguished somewhat by its broad pH optimum at 5·5—6·5 at both 48° and 34°. O. M. WHITTON.

Syntheses of some carbonyl compounds associated with milk fat deterioration. W. Gasser (*Dissert. Abstr.*, 1955, **15**, 2156—2157).—Synthetic methods for prep. of, and physical properties and deriv. of, the following carbonyl compounds associated with milk fat deterioration are given: non-2-en-4-one, non-4-en-3-one, non-4-en-6-one, non-3-en-5-one, hept-1-en-4-one and -5-one. None of these substances had the flavour or odour of oxidised fat. O. M. WHITTON.

Detection of cane sugar in milk and its products. S. N. Mitra and S. C. Roy (*J. Indian chem. Soc. Industr. Edn*, 1955, **18**, 168—173).—Optimum acid concn. for the resorcinol–HCl (Seliwanoff) reagent used in the detection of sucrose in milk and milk products is given by dissolving the resorcinol (0·5 g.) in conc. HCl diluted with 1·5 vol. of water; optimum heating time is 1 min. At this concn. as little as 0·25% of added sucrose is detectable, but false positives are not given with boiled milk and reconstituted milk as are given with acid diluted 1 : 1. Weaker acid (1 : 2) fails to detect added sugar at concn. <0·5%. To overcome interference from formalin the amount of resorcinol should be increased to 1·0 g. S. C. JOLLY.

Colour of milk and milk products. H. Slump (*Conserva*, 1956, **4**, 238—239).—A review covering theories and knowledge concerning the discoloration of heated milk, condensed milk and milk powder. P. S. ARUP.

Development of instant milk. D. D. Peebles (*Food Technol.*, 1956, **10**, 64—65).—The process described produces a non-fat dry milk with excellent flavour and shelf life. It is very readily reconstituted, has good pouring characteristics and is non-caking. E. M. J.

Degradation of amino-acids by *Lactobacillus casei*; factors influencing the deamination of serine. T. Kristoffersen and F. E. Nelson (*Appl. Microbiol.*, 1955, **3**, 268—273).—Suspensions of washed cells of *L. casei* in PO_4''' buffer solution liberated NH_3 from serine, cysteine and asparagine but not from phosphoserine. Deamination was favoured by anærobic conditions but was depressed in presence of glucose. Probably two deaminase systems are concerned. Possible relations between deaminase activity and the longevity of *L. casei* in Cheddar cheese and also the influence of pasteurisation of milk on the O_2 balance and thence on deaminase activity are discussed. A. G. POLLARD.

Influence of the content and composition of protein in milk on the manufacture of cottage cheese. J. H. Henson and T. B. Miller (*J. Dairy Res.*, 1955, **22**, 211—218).—Curd produced in cottage-cheese manufacture in New Zealand from Jersey milk (*J*) was satisfactory, but that (*H*) from Holsteins was invariably unsatisfactory; addition of $CaCl_2$ to milk did not improve unsatisfactory curd. Dilution of *J* to the same level of precipitable casein as in *H*, or addition of 10% of *H* to *J*, also resulted in unsatisfactory curd. The Walker formol titration for the determination of casein gave significantly high values with *H*, probably due to different distribution of N in *H*. S. C. JOLLY.

Chemical investigation of the volatile flavour principle of Cheddar cheese. J. C. Dacre (*J. Dairy Res.*, 1955, **22**, 219—223).—After removal of volatile fatty acids from steam distillates containing the flavouring substance(s) from Cheddar cheese, only ethanol, butyraldehyde and Et acetate and butyrate were identified in the distillates. None of these substances apparently contributes to the typical flavour. Some properties of the flavouring substance are reported. Suggestions that lower fatty acids, diacetyl and acetylmethyl carbinol contribute to the flavour were not confirmed. Numerous other compounds were shown not to contribute to the flavour. S. C. JOLLY.

Quantitative estimation of the amino-acids in Cheddar cheese and their importance in flavour. L. A. Mabbitt (*J. Dairy Res.*, 1955, **22**, 224—231).—The amounts of individual amino-acids in the aq. phase of Cheddar cheese during the ripening process differed from the amounts in casein by the larger amounts of basic amino-acids, the smaller amount of proline and the presence of ornithine. The amino-acids contribute an important background flavour to the cheese. An unidentified substance(s), representing 7—9% of the ninhydrin-positive material in the serum of ripe cheese, was detected. S. C. JOLLY.

Fatty acid oxidation by *Penicillium roqueforti*. R. L. Girolami and S. G. Knight (*Appl. Microbiol.*, 1955, **3**, 264—267).—Resting cells of *P. roqueforti* in a suspension containing Mg, PO_4''' and a substrate of low concn. oxidised fatty acids having ≯10 C. Me ketones containing one less C than the original acid were among the products of oxidation. In general, the ketones inhibited the growth of the organism. The significance of these observations in the ripening process of cheese is indicated. A. G. POLLARD.

Methods of preparation and characteristics of soft cheese made in India. T. K. Pandit and J. V. Bhat (*Indian J. Dairy Sci.*, 1955, **8**, 173—176).—Four methods are described for the prep. of this variety of cottage cheese, and the product from each of two of the methods is examined. One of the products (*a*) contained more moisture than (*b*) which tended to improve the palatability score, but was conducive to early spoilage; (*b*) contained ~18% of protein, (*a*) ~10%; initial acidity and rate of development of acidity was lower in (*a*) than in (*b*); (*a*) retained its agreeable aroma and fresh taste at the end of 60 hr., and was rated more digestible than (*b*). E. M. J.

Relation of serine deamination and hydrogen sulphide production by *Lactobacillus casei* to Cheddar cheese flavour. T. Kristoffersen and F. E. Nelson (*J. Dairy Sci.*, 1955, **38**, 1319—1325).—Strains of *Lactobacillus casei* capable of producing H_2S in the growth medium were isolated only from American Cheddar cheeses with good flavour scores. The ability of these strains to deaminate serine varied, the most active strains coming from the better samples of cheese. In experimental cheeses, both SH groups and "free" H_2S increased as the cheeses matured; at six months cheeses with the highest relative "free" H_2S concn. had the highest Cheddar flavour intensity scores. S. C. JOLLY.

Effect of high temperature storage on the content of *Salmonella* and on the functional properties of dried egg white. G. J. Banwart and J. C. Ayres (*Food Technol.*, 1956, **10**, 68—73).—The effect of moisture content of the albumin, the temp. and time of storage on the *Salmonella* population and on the functional properties of pan dried and spray dried albumins were studied. Under these conditions *S. orianenburg* is more resistant to destruction during storage of dried albumin than are either *S. senftenberg* or *S. pullorum*. Dried albumin containing 1·5, 3, or 6% of moisture may be stored at 50°, or albumin containing 1·5 or 3% of moisture at 60° or 70° and eliminate large no. of *Salmonella* without significant impairment of functional properties, e.g., angel cake making. (33 references.) E. M. J.

Influence of environment on lysozyme activity in shell eggs. A. A. Kraft and A. W. Brant (*Food Technol.*, 1956, **10**, 45—47).—Environmental factors, such as time and temp. and pH of the albumin were studied in relation to the lysozyme activity in stored shell eggs and the effects of these factors on the bacterial infection of eggs were examined. Lysozyme activity increased early during storage at 25° then declined in the 21-day period. Pseudomonas bacteria were not

lysed or inhibited in growth by either lysozyme or egg albumin. (20 references.) E. M. J.

Monomolecular surface film method for determining small quantities of yolk or fat in egg albumin. D. H. Bergquist and F. Wells (*Food Technol.*, 1956, **10,** 48—50).—The micro method of Heinemann and Rohr for determining fat in skim milk is modified to determine yolk or fat in egg white. The fat is extracted with ethanol, ether and light petroleum; an aliquot portion of the fat redissolved in light petroleum is spread as a monolayer on the surface of an acetic acid solution. The area of the spread is a measure of the quantity of yolk present. E. M. J.

Colloid chemistry of phosphatides. I. Properties of egg-phosphatide suspensions; transformation in coacervated systems by alcohols. IIA. IIB. Transformation of egg-phosphatide suspensions; chemistry of long-chain electrolytes. H. G. Bungenberg de Jong, A. de Bakker and D. Andriesse (*Proc. K. Ned. Akad. Wet.*, 1955, **B, 58,** 238—250, 251—256, 257—265).—I. Using "Lecithin ex ovo puriss." an investigation of some properties of egg-phosphatide suspensions (form and nature of the particles, stability, flocculation and myelinisation, elasticity, and influence of $CaCl_2$, NaCl and pH on elasticity) and the transformation in coacervated systems by alcohols is carried out. A series of six characteristic kinds of colloid systems can be distinguished for anionic and cationic long-chain electrolytes, which can be obtained, one from another, in the sequence: (*i*) non-elastic solution, (*ii*) elastic–viscous solution, (*iii*) *o*-coacervate, (*iv*) smectic phase, (*v*) solution, and (*vi*) *P*-coacervate. All systems after the smectic phase are obtained by adding *iso*amyl alcohol, without salt.

IIA. The same phosphatide prep. and methods of purification were used to study the transformation of egg-phosphatide suspensions into *o*-coacervates, elastic–viscous and non-elastic solutions and to investigate the unity in the colloid chemistry of anionic, cationic and amphoionic long-chain electrolytes. Inorg. salts, e.g., NaCl and $MgSO_4$, at high concn. did not produce transformation into *o*-coacervates. At room temp. Na salicylate concn. from 1 to 1·4 mol. per l. transform the suspension into a coacervated system. At higher concn. (1·5—1·7 mol. per l.) a clear elastic–viscous system is formed, while at still higher concn. (1·8—2 mol. per l.) a clear non-elastic solution is obtained. The influence of temp. on the coacervation limit is reversible and marked.

IIB. The influence of the first ten of the homologous series of normal alcohols on the elastic–viscous systems and coacervates obtained from a phosphatide suspension by Na salicylate was examined. The damping is increased by all the alcohols. Moreover, methanol exerts a salicylate-sparing influence, and *n*-decanol a salicylate-demanding influence. A close correspondence exists between the colloid chemistry of cationic or anionic association colloids and ampho-ionic association colloids, e.g., phosphatides. This explains the diversity of means needed to arrive at analogous colloid systems. R. J. MAGEE.

Post mortem changes in meat and their possible relation to tenderness together with some comparisons of meat from heifers, bulls, steers and diethylstilbœstrol-treated bulls and steers. E. Wierbiki, L. E. Kunkle, V. R. Cahill and F. E. Deatherage (*Food Technol.*, 1956, **10,** 80—86).—Tenderness and biochemical characteristics of the meat from 32 animals were determined at 3 and 13 days post mortem. No great differences were noted between groups, on tenderness at 13 days post mortem although the hormone treatment tended to produce slightly tougher meat at 3 and 13 days post mortem. There were changes in pH which might contribute to increased protein hydration during ageing. Important qualities of meat tenderness, shrink on cooling, drip on freezing and rehydration after dehydration may all be primarily related to the degree of hydration of the meat proteins. (18 references.) E. M. J.

Effect of post mortem chilling on the keeping quality of frozen pork. D. L. Harrison, J. L. Hall, D. L. Mackintosh and G. E. Vail (*Food Technol.*, 1956, **10,** 104—108).—Both palatability and chemical tests indicated that pork from carcasses chilled (30° or 40°F.) for seven days before freezing deteriorated to a greater extent during frozen storage than pork from carcasses chilled for three or one days. There was little difference in the quality of the meat that was chilled for three or one days. E. M. J.

Factors affecting the preservation of cured pork. M. C. Heck, E. S. Ruby and M. J. Burris (*Arkans. agric. Exp. Sta.*, 1955, *Bull.* 559, 15 pp.).—Delaying the chilling of pork carcasses lowered the quality of the cured meat; the latter was satisfactory when carcasses were chilled within one hour of slaughter and then held for four days prior to curing. Carcasses held chilled for 168 hr. prior to curing lost much of their external qualities, but organoleptic qualities were not reduced after curing. A. H. CORNFIELD.

Preparation of dehydrated pork of lowered glucose content. R. L. Henrickson (*Dissert. Abstr.*, 1955, **15,** 1947—1948).—Attempts to reduce the content of glucose in dehydrated pork, which would react with amino-compounds to produce undesirable flavour and colour, are described. Pork fermented with yeast developed rancidity on subsequent storage. Glucose present in dehydrated pork was reduced by 50% in 4 hr. by enzymic oxidation to gluconic acid, using glucose-oxidase (4 parts per 1000 parts) catalysed with H_2O_2. In both methods, cooked pork gave a more satisfactory product than did uncooked pork. In the second method, injection of insulin into the blood of the live hog before slaughter is recommended. O. M. WHITTON.

Freeze curing of bacon. B. M. Watts (*Food Technol.*, 1956, **10,** 101—103).—Sliced raw pork dipped into curing brines containing NaCl, $NaNO_3$, Na ascorbate and liquid smoke and then frozen results in an excellent bacon-like product. The undenatured cured meat pigment nitric oxide myoglobin develops within a few days in the freezer and is stable over many months. The ascorbate and smoke together prevent the development of rancidity. E. M. J.

Effect of cooling and freezing procedures on consumer acceptability factors of turkey meat. J. V. Spencer, W. E. Matson, W. J. Stadelman and M. C. Ahrens (*Food Technol.*, 1956, **10,** 16—18).—The effects of five cooling treatments on appearance, wt. changes and tenderness of turkeys frozen at three different temp. were studied. Turkeys cooled in ice water had a better appearance, gave a net gain in wt. during cooling and freezing, but lost the most wt. during thawing and cooking. The appearance of frozen turkeys was influenced by freezing rate, and the lower the freezing temp. the better was the appearance of the frozen bird. E. M. J.

Effect of freezing conditions on appearance of frozen turkeys. A. A. Klose and M. F. Pool (*Food Technol.*, 1956, **10,** 34—38).—Effects that were studied on packaged, ready to cook, 140°F.-scalded turkeys, included air blast temp. air blast velocity, degree of finish (amount of fat in skin layer) etc. The results emphasise the beneficial effect on frozen appearance of good finish and freezing on open shelves in a blast tunnel, and also indicate the extent of improvement to be derived from lower air blast temp. and higher air velocity. E. M. J.

Effects of ice water chilling on flavour of chicken. E. L. Pippen and A. A. Klose (*Poultry Sci.*, 1955, **34,** 1139—1146).—The flavour of broth prepared from carcasses which had been chilled in ice water for 3—20 hours was significantly poorer than where air-chilled carcasses were used. Flavour was fully recovered by adding, during the prep. of the broth, the material extracted during ice-water chilling, and was restored to a considerable extent when the neutralised ash of the material was added. In general, there was no difference in flavour of roasted or fried chicken between ice-water-chilled and air-chilled carcasses. A. H. CORNFIELD.

Uses of Gelsoy in prepared fruit products. E. F. Glabe, P. F. Goldman, Perry W. Anderson, L. A. Finn and Allan K. Smith (*Food Technol.*, 1956, **10,** 51—56).—A brief outline on the prep. and proportions of the substance (Gelsoy) isolated from soya-beans is presented. A yellowish powder of low *d*, sol. in water to ~50% concentration at 77°F., it contains 50—60% of protein, 1% of reducing sugar, 15—20% of hydrolysable sugars, 9% of ash, and 8% of moisture, and is useful as a water-binding material in frankfurters, meat loaf and canned meat. Na hexametaphosphate increases the water-binding and fat-binding capacity. (15 references.) E. M. J.

Rapid procedures for approximation of bacterial counts in shrimp and oysters. A. F. Novak, E. A. Fieger and M. E. Bailey (*Food Technol.*, 1956, **10,** 66—67).—Two methods are discussed: (i) the growth of the micro-organisms in a carbohydrate-containing medium; the formation of acid which is proportional to the no. of bacteria present in the added sample, the acid being measured by a colour change in an indicator. (ii) A modification of the methylene blue reductase test is used. Sterilised, non-fat dry milk solids serve as a medium. The time required for reduction of methylene blue in a synthetic medium by bacterial reductases is measured, the length of times being an indication of the no. of bacteria present. E. M. J.

The biological value of the proteins of shrimps and dried cod. G. Varela (*Ann. Bromatologia*, 1955, **7,** 127—140).—The coeff. of apparent digestibilities of codfish protein and shrimp protein were found by the method of Mitchell (cf. *J. biol. Chem.*, 1924, **58,** 873 etc.) to be 77 and 67% respectively, the real digestibility coeff. being 89 and 80%, respectively. The biological value of the proteins were 69 and 73% respectively. L. G. L. UNSTEAD-JOSS.

Colour test for measuring freshness of fish by determining volatile bases. Y. Tsuchiya and M. Kayama (*Tohoku J. agric. Res.*, 1954, **5,** 37—46).—An aq. extract of the fish is placed in the lower half of a petri dish, and filter paper, to which is added a solution containing citric acid, veronal, boric acid and a "universal" indicator

(dimethylaminoazobenzene, methyl red, bromothymol blue, phenolphthalein and thymolphthalein) is placed in the upper half. The mixed amines in the extract, liberated by addition of aq. K_2CO_3, are absorbed by the indicator mixture on the filter paper. Under prescribed conditions absorption is complete in 55 min. at 40°. The colour of the filter paper is matched against standards and thence the total N of the mixed amino-acids is calculated.
A. G. POLLARD.

Tortelli-Jaffe reaction for the study of fish oils. G. Bigoui (*Olii min.*, 1955, **32**, 193—194).—A brief account of the Tortelli-Jaffe reaction, the effect of which on fish oils and a rectified fraction from fish oils is compared with the Tosonotti reaction (using dichloromethane, bromine and formic acid). The results of the two colour reactions are tabulated and compared. C. A. FINCH.

Fatty acid composition of saury oil by the spectrophotometric method. Y. Tsuchiya and M. Kayama (*Tohoku J. agric. Res.*, 1955, **5**, 269—276).—Analysis of this fish (*Cololabis saira*, Brevoort) oil are recorded. A. G. POLLARD.

Fixed oil of *Calophyllum inophyllum* (Linn.). I, II. K. G. Das and P. P. Pillay (*Bull. cent. Res. Inst., Univ. Travancore*, 1955, **A, 4**, 1–8, 9—10).—I. The fixed oil of *C. inophyllum* was isolated and purified and its physical constants established (sp. gr. 0·9174 at 28°, m.p. 8°, *n* 1·4659 at 28°, saponification value 212, iodine value 86, Reichert Meissl value 0·18). The fatty acid content consists of 60% oleic, 20% palmitic and 13% stearic acids. (15 references.)

II. The resin obtained from the oil contained both free fatty acids and acids of phenolic type (giving a deep blue colour with $FeCl_3$ in neutral alcoholic solution). The two types were separated by treating the NH_4 salts with saturated $MgSO_4$ and dissolving the second type of acids out with alcohol. The proportions found of the free fatty acids were: oleic 31·9%, palmitic 29·3% and stearic 33·6%.
J. S. C.

Glyceride structure of the fixed oil from the seeds of *Gnetum scandens*. K. Vasudevan Nair and N. S. Varier (*Bull. cent. Res. Inst., Univ. Travancore*, 1955, **A, 4**, 13—17).—The fixed oil from the seeds of *G. scandens* was extracted, its physical constants established, and its detailed glyceride structure calculated as 2·81% tristearin, 56·3% distearo-olein, 38·8% oleostearopalmitin, 0·5% dioleopalmitin and 1·6% dioleostearin. J. S. C.

Glyceride structure of the fixed oil from the seeds of *Calophyllum Wightianum*. II. K. Vasudevan Nair and N. S. Varier (*Bull. cent. Res. Inst., Univ. Travancore*, 1955, **A, 4**, 19—22).—The oil contains 22% of saturated and 78% of unsaturated acids and consists of 3·41% mono-, 59·18% di- and 37·41% tri-unsaturated glycerides and is therefore a vegetable fat conforming to the rule of even distribution.
J. S. C.

Chromatographic separation of the component glycerides in the oil of *Calophyllum Wightianum*. K. Vasudevan Nair and N. S. Varier (*Bull. cent. Res. Inst., Univ. Travancore*, 1955, **A, 4**, 23—26).—The neutral oil was chromatographically separated into six fractions with I val. ranging between 139·5 and 67·3 and a possible glyceride composition is suggested. Glycerides with unsaturation, ranging from 2 to 5 double bonds, are shown to be present. J. S. C.

Blanching of oils and vegetable fats. S. H. Bertram (*Rev. Ferment. Industr. aliment.*, 1955, **10**, 203—205).—Colouring matters occurring in oils and fats, e.g., carotene, α- and β-chlorophyll, gossypol etc., the difficulties connected with removal of colouring matter and the use of absorbent earth (Floridin etc.) earths activated by HCl or H_2SO_4 (Tonsil, Clarit etc.) are discussed. E. M. J.

Oil-extraction experiments carried out in 1954–5. Instituto de la Grasa (*Grasas y Aceites*, 1955, **6**, 169—179).—Trials on olives carried out on two machines, one of the filter-press and the other of the super-centrifuge type, are reported. L. A. O'NEILL.

Citric acid in the oil and fat industry. G. Steinkarys (*Grasas y Aceites*, 1955, **6**, 184—186).—The acid is used as synergist and anti-oxidant and to modify pH and reduce bacterial fermentation, e.g., in margarine. L. A. O'NEILL.

Urea adducts of fatty acids. VI. Component fatty acids of coconut oil. T. N. Mehta and M. G. Kokatnur (*J. Indian chem. Soc., Industr. Edn*, 1955, **18**, 158—163).—Fractionation of the Me esters of the fatty acids of coconut oil may be effected by a decreasing solvent crystallisation method (separation of urea adduct fractions of Me esters by progressive concentration of a MeOH solution of the mixture of urea and esters) or a urea-adduct elution method after preliminary removal of acids up to C_{16} by fractional distillation. The approximate fatty acid composition of coconut oil determined by these methods is reported. The urea fractionation method could probably replace with advantage Hilditch's lengthy Pb salt–alcohol method for coconut and similar fats. S. C. JOLLY.

Quality of raw cocoa as it affects the manufacturer. R. V. Wadsworth (*Trop. Agriculture, Trin.*, 1955, **32**, 1—9).—Desirable and undesirable properties of commercial cocoa beans are discussed.
A. G. POLLARD.

Standardised diet for metabolic studies: its development and application. Frieda L. Meyer, Myrtle L. Brown, Harriet J. Wright and M. L. Hathaway (*U.S. Dep. Agric. Wash., D.C.*, 1955, *Tech. Bull.* No. 1126, 81 pp.).—A standardised diet developed by the Human Nutrition Research Branch of the Agricultural Research Service, to study human nutritional requirements, utilisation of various nutrients, or interrelationship of nutrients is composed of a core group of foods, which remains constant and supplies amounts of most nutrients at restricted or deficiency levels, and complements I and II, which provide sources of nutrients to bring the intakes to reference levels and for alteration in level of single nutrients. The diet was tested on six women students aged 19—23 years during a 40-day period. There was wide variation in the metabolic response to the levels of intake. Changing the fat content from 76 to 24 g. (34—11% of the calories) for three subjects for 20 days had no apparent effect on N, Ca, Mg and P retention, on thiamine and riboflavin excretion, on fæcal lipin excretion, or on the proportion of fæcal lipin as fatty acids, neutral fat, or unsaponifiable material. Extensive data are presented. (192 references.) E. M. J.

Infant foods. V. Subrahmanyan (*Bull. cent. Food tech. Res. Inst. Mysore*, 1955, **5**, 4—7).—The prep. of infant foods in India and research experiments at the Cent. Food Tech. Res. Inst. Mysore are reviewed including various prep. from milk and malted products. A standardised process was evolved and an easily reconstitutable baby food of excellent keeping qualities was produced. The use of the process in districts where milk is available, e.g., at Anand, and the establishment of a plant are discussed. Where there is shortage of milk supply suggestions are made for the use of vegetable milk from soya-bean, groundnut, cashew kernel, etc. E. M. J.

Fearon's amidine–pentacyanoamminoferrate reaction in paper chromatography. P. H. List (*Hoppe-Seyl. Z.*, 1956, **303**, 27—29).—A modification of Fearon's colour reaction for the identification of compounds, e.g., guanidine, urea, thiourea is described. The reagent used as a spray in a paper chromatographic method is a 1% aq. solution of Na pentacyanoamminoferrate II, $Na_3[Fe(CN)_5NH_3]$, (15 ml.), added to 20% NaOH (5 ml.) + 1 drop of conc. H_2O_2 solution. A table giving the colour reactions of 15 compounds and the sensitivity of the tests is presented. E. M. J.

Structure of gelatin. J. Pouradier (*Chim. et Industr.*, 1955, **74**, 1175—1184).—Recent work on the structure of gelatin, based on studies of the iso-electric point, mol. mass, repartition of mol. masses and the forms of mol. held in solution, is reviewed. (32 references.) J. S. C.

Iodimetric determination of tyrosine, tryptophan and methionine in soluble unhydrolysed proteins. J. Baraud and L. Genevois (*Bull. Soc. chim. Fr.*, 1955, 1499—1501).—The iodimetric method for tyrosine, tryptophan and methionine (*idem, Chim. anal.*, 1955, 37) is applied to unhydrolysed proteins whose purification is described. Excess of 0·01N-I solution, citric buffer (pH 6) and portions of the protein solution are placed in two stoppered Erlenmeyer flasks. The first is set aside for 2 hr. and the excess of I titrated with thiosulphate, giving a titre of I consumed equivalent to tyrosine (4), tryptophan (6) and methionine (2 equiv. per mol.), with a histidine correction. After removal of the excess I the solution is made strongly acid; this liberates I from the methionine complex, which is then titrated. The histidine error (proportional to time) is obtained by similar titration of the contents of the second flask after 3 hr. and subtracting twice the difference in I consumed from the first amount. The titration is repeated with the buffer at pH 4; after 2 hr. the contents are strongly acidified and titrated with thiosulphate, the I consumed being equivalent to the tryptophan. That the results accord with determinations on hydrolysed proteins is taken as evidence that ω-groups of amino-acids in proteins are quant. functional. E. J. H. BIRCH.

Microbiological method for determination of cystine in foods. M. J. Horn and A. E. Blum (*Cereal Chem.*, 1956, **33**, 18—28).—Reproducible standard curves for the microbiological determination of cystine can be obtained by using a new basal medium containing acid-hydrolysed "lanthionised" casein with tryptophan and arginine as a source of amino-acids. Data are presented of the cystine content of 60 proteins and foods. A period of 2 hr. is recommended as optimum for hydrolysis of proteins prior to cystine determination. (30 references.) S. C. JOLLY.

Ion-exchange resins in the isolation of basic amino-acids from hydrolysed proteins. P. M. Strocchi and P. Drago (*Ann. Chim., Roma*, 1955, **45**, 818—823).—Various techniques are discussed and the advantages of a differential exchange procedure (H cycle)

indicated. A carboxylic resin is convenient for the isolation of the arginine/lysine fraction. L. A. O'NEILL.

Isolation of arginine and lysine from hydrolysed proteins by means of ion-exchange resins. I. Preparation of the solutions. P. M. Strocchi and P. Drago (*Ann. Chim., Roma*, 1955, **45**, 824—831).—To improve the yield of basic amino-acids a preliminary concentration is suggested. The sulphuric hydrolysate is neutralised with $Ca(OH)_2$ to pH 3·2, the $CaSO_4$ filtered off, the filtrate concentrated under vac., filtered after 15 days, neutralised with $Ba(OH)_2$ to pH 6, the $BaSO_4$ filtered off, the filtrate concentrated, filtered, the residual SO_4'' pptd. with $Ba(OH)_2$, and the $BaSO_4$ filtered off. L. A. O'NEILL.

Effects of ionising radiations on some protein components of food. F. J. McArdle (*Dissert. Abstr.*, 1955, **15**, 2158).—Effects of cathode-ray irradiation on casein and egg albumin, both in their natural environment and in aq. solution, were studied. Molecular changes of the proteins in the solution were determined by studying SH-group activity, enzyme reaction rates, relative viscosity, and electrophoretic behaviour. The effects observed were reduced in the presence of ascorbic acid. The coagulation time of rennet was reduced by irradiation and substantial destruction of thick albumin occurred. O. M. WHITTON.

Nutritional and biochemical effects of irradiation. R. R. Becker, H.-C. Kung, N. F. Barr, C. S. Pearson and C. G. King (*Food Technol.*, 1956, **10**, 61—64).—Results of a long-term feeding experiment with albino rats through three generations in which the butterfat portion of the diet was irradiated from a ^{60}Co source (dose = $1{\cdot}68 \times 10^6$ rep) indicated no instance of carcinogenesis. Nutrient loss was greatest in ascorbic acid and in the fat sol. constituents, vitamin A, carotenes and vitamin E. (12 references.) E. M. J.

Programme of the Vitamin Commission of the International Union of Pure and Applied Chemistry. B. L. Oser (*Food Technol.*, 1956, **10**, 23—25). E. M. J.

Vitamin A and sesame oil in vanaspati (edible hydrogenated oil). L. B. Mathur, K. S. Tilara and R. Sahai (*J. Indian chem. Soc., Industr. Edn.*, 1955, **18**, 123—125).—In the absence of vitamin A, the sesamolin content in vanaspati is stable for more than eight months, whereas in presence of vitamin A it shows a definite trend towards instability after one month and increasingly so in later months. It is suggested that vitamin-A acetate gradually hydrolyses, liberating acetic acid, which may react with sesamolin and thus obliterate the Villavecchia test. G. HELMS.

Multiple regression study of the Carr–Price reaction for vitamin A in the presence of carotene. J. E. Rousseau, jun., H. D. Eaton, G. Beall and H. L. Lucas, jun. (*J. Dairy Sci.*, 1955, **38**, 902—903).—The validity of the correction used by Dann and Evelyn (*Biochem. J.*, 1938, **32**, 1008) to correct for interfering compounds in the Carr–Price test for determining vitamin A is confirmed. A method is described whereby multiple regression analysis may be used to estimate the magnitude of the interference due to carotenoid pigments in applying the test to biological materials. S. C. JOLLY.

Nutrition education: opportunity and responsibility. H. L. Sipple (*Food Technol.*, 1955, **9**, 563—565). E. M. J.

Flavomatics in food. H. L. Janovsky (*Food Technol.*, 1955, **9**, 500—502).—A term suggested for synthetic aromatic org. chemicals used in food flavouring; about 47 such compounds are listed and their use is discussed. E. M. J.

Physics in foodstuffs technology. R. Heiss (*Chem. Tech., Berlin*, 1955, **7**, 615—620).—A critical survey is given of the physical and chemico-physical methods for evaluating the processability of the raw materials and controlling the properties of the materials in the course of manufacture, drying and packaging. Methods of determining properties, and their bearing on the manufacturing processes, particularly described, concern η, particle size, water adsorption, crystallisation velocity, adhesiveness, solubility, and dependence of inversion constants on temp. A discussion is given of their use in the manufacture of chocolate, caramels and artificial honey and in potato drying. A greater use of scientific, instead of empirical, methods is advised. H. L. WHITEHEAD.

Determinations of enthalpies involved in food freezing. H. C. Mannheim, M. P. Steinberg and A. I. Nelson (*Food Technol.*, 1955, **9**, 556—559).—The calorimeter is described and the enthalpy values in food freezing determined were not significantly different from those calculated using data from the literature. From an energy stand-point freezing and thawing of foods yielded essentially the same results. (11 references.) E. M. J.

Internal corrosion of tin-plate cans by acid foodstuffs. H. Cheftel, J. Monvoisin and Malwina Swirski (*J. Sci. Food Agric.*, 1955, **6**, 652—655).—The anodic behaviour of Sn *vs.* Fe in the corrosion of tin plate by acid foodstuffs is in agreement with theory by calculation from Nernst's equation. The amount of H_2 evolved is less than the amount corresponding to the metals dissolved, this discrepancy being partly accounted for by an electrochemical mechanism. In fruits caramelisation from sucrose has no effect, but that from glucose accelerates corrosion. (12 references.) E. M. J.

Analytical scheme for the detection of poisons in suspected foods. M. A. Guatelli (*Monit. Farm.*, 1955, **61**, 365—369, 385—389).—A complete scheme for the isolation and identification of poisons, based on well-known techniques, is presented. It includes: CN′, P, formaldehyde, chloral hydrate, P, Hg, Bi, As, Sb, F′, Ba, H_3BO_3, Zn, Te, Sn, Pb, Cu, Cd, ether, barbiturates, glucosides, oxalates, and other drugs and alkaloids. T. R. MANLEY.

Supplementary Report on Colouring Matters. Food Standards Commee, Ministry of Agriculture, Fisheries and Food (H.M.S.O., Lond., 1955, 15 pp.).—The report deals with the use of colouring matters in foods and includes a description of 98 coal-tar colours as to their suitability for use for this purpose, and a list of recommended colours. H. S. R.

Highlights on newly-developed flavouring aromatics. A. Katz (*Food Technol.*, 1955, **9**, 636—638).—Two lists are presented (*a*) synthetics now in use, aromatics employed and typical formula and (*b*) check list of newly developed aromatics. The selection and use of these products are discussed. (16 references.) E. M. J.

Volatile oil of *Dacrydium biforme*. R. E. Corbett and C-K. Wong (*J. Sci. Food Agric.*, 1955, **6**, 739—743).—A complete examination of the spring essential oil of *D. biforme* (a native pine of New Zealand) indicated at least 15 constituents, eight of which were identified with known compounds, viz., myrcene, β-terpinene, (+)-longifolene, (+)-aromadendrene, (−)-metrosiderene, (+)-δ-cadinene, (+)-phyllocladene, and α-camphorene. Other substances found included a new sesquiterpene, oxygenated terpenes, and a solid sesquiterpene alcohol, obtained in fraction 11, which crystallised in the still-head. Data on the fractionation are given. (20 references.) E. M. J.

Simple test for occurrence and prevention of microbial lipolytic spoilage in foods. D. A. A. Mossell and F. D. Tollenaar (*Leeuwenhoek ned. Tijdschr.*, 1955, **21**, 247—251).—In this test for the efficacy of anti-lipolytic preservatives, the food is represented by a layer of molten hydrogenated coconut oil (m.p. 27°) in contact with a glucose yeast-extract nutrient solution, both of which have been sterilised. The nutrient solution is adjusted to the desired pH, treated with the preservative, and inoculated with an active strain of *Candida lipolytica*. The system is incubated at 30° for two weeks, after which it is pasteurised at 100° for 1 min.; the acid value then found for the oil phase is an inverse measure of the efficacy of the preservative, the results being expressed in terms of concn. of the preservatives required to halve the degree of hydrolysis, in comparison with that occurring in the unpreserved blank. Bu and octyl, but not dodecyl, gallates are efficient preservatives; Na dehydroacetate, Na sorbate and Na benzoate are efficient in varying degrees at pH 5, but much less so at pH 7. P. S. ARUP.

Chemical composition of the cultivated *Salvia officinalis*, L. J. Tucakov (*Perfum. essent. Oil Rec.*, 1955, **46**, 293—297).—Comparison between stems, leaves, flowers and petioles of sage (*Salvia officinalis* L.) grown around Belgrade shows that the petioles contain the lowest proportion of moisture and the highest proportion of SiO_2 ash. The essential oil contains: borneol (free) 2, borneol (combined) 4·55, thujone 27, and cineole 18%. The sp. gr. of the essential oil obtained by distilling fresh leaves and flowers collected in May and June is low (average 0·8985) compared with that of the oil from commercial sage collected after flowering and distilled several months later (average 0·922); the ester value after acetylation is also lower, viz. 23·70 against 45. G. HELMS.

Flavouring and aromatic substances in foods and luxury comestibles. L. Kuiper (*Conserva*, 1956, **4**, 206—212).—A review covering general considerations, testing for safety in use, applications in food industries, and classification. P. S. ARUP.

Quantitative estimation of allicin in fresh garlic. H. Jager (*Arch. Pharm., Berl.*, 1955, **288**, 145—148).—The total S content of fresh garlic is determined by first oxidising the S with HNO_3 (*d* 1·4); after neutralising with anhyd. NaOH the residue is fused with KNO_3, the cooled melt acidified with HCl, and the H_2SO_4 determined titrimetrically with $BaCl_2$ and benzidine solution. Allicin is determined colorimetrically by enzymic decomposition for 1 hr. at 30–35°, when the resultant mixture is treated with trichloroacetic acid, followed by the formation of the 2 : 4-dinitrophenylhydrazone of the pyruvic acid formed. After extraction with Et acetate the hydrazones are absorbed in 2N-aq. NH_3 solution, and determined colorimetrically. G. R. WHAILEY.

Monosodium glutamate: a versatile seasoning and flavouring agent for processed foods. M. Narayana Rao and M. Swaminathan (*Bull. cent. Food Technol. Res. Inst. Mysore*, 1954, **4**, 137—139).—A review of the discovery, manufacture and use of monosodium glutamate. N. M. WALLER.

Influence of monosodium glutamate on taste perception. F. J. Pilgrim, H. G. Schutz and D. R. Peryam (*Food Res.*, 1955, **20**, 310—313).—No consistent pattern of the effects of monosodium glutamate (**I**) emerged from tests undertaken in regard to palatability or to enhancement of the natural flavours of foods by increasing the sensitivity of the taste receptors. (10 references.) E. M. J.

Positional bias in sensory assessments. J. M. Harries (*Food Technol.*, 1956, **10**, 86—90). E. M. J.

Correction factors for heat penetration thermocouples. O. F. Ecklund (*Food Technol.*, 1956, **10**, 43—44).—Minor changes in construction of heat penetration thermocouples have justified a re-determination of the correction factors which compensate for heat conducted into the product by thermocouple wires and fittings. A suggestion is made in which the correction factor is applied to the lag factor "j." E. M. J.

Determination of benzoic and salicylic acids in food products. D. T. Englis, B. B. Burnett, R. A. Schreiber and J. W. Miles (*J. agric. Food Chem.*, 1955, **3**, 964—969).—The acids are generally extracted from an aq. solution acidified with HCl, with an org. solvent. In ether solution benzoic and salicylic acids on spectrophotometric examination have absorption peaks at 227 and 236 mμ. respectively; salicylic acid has a secondary max. near 306 mμ. Using this method benzoic acid has been determined in samples of ketchup and orange-base concentrate. The benzoate may be extracted directly from margarine samples with dil. NaOH, the extract being clarified with alumina cream. (24 references.) E. M. J.

Factors influencing food sterilisation and preservation. [Methods of culturing putrefactive anaërobe 3679]. A. J. Lund (*A. R. Hormel Inst.*, 1954–55, 82—90).—Poor spore yields (⩾10%) obtained with putrefactive anaërobe 3679-h (PA3679-h) grown on brain-heart infusion medium were not improved by treating the medium with activated charcoal, adding sol. starch or saponifying the dehydrated medium and extracting with $CHCl_3$, but they can be improved to a limited extent by selection. Spent medium contains a spore factor that is sol. in acidic ethanol, partially sol. in acidic acetone, insol. in ether, ethyl acetate and acetone, and is destroyed in neutral ethanol. Prevention of spore germination is a factor to be overcome in order to obtain high spore yields. The spontaneous lysis of vegetative cells occurring in some media is a characteristic of the organism itself and is not due to lytic material in the media. Several species of bacteria produce a substance, which is adsorbed by charcoal and ion-exchange resins, that will increase sporulation of PA3679-h. S. C. JOLLY.

Evaluation of radiation sources as a means for processing foods. B. S. Evans, jun. (*Food Technol.*, 1955, **9**, 615—620).—Sources of radiation—their merits and limitations are discussed; electrons and γ-rays are compared. Of γ-ray sources, the most active is at the Material Testing Reactor, located at the National Reacting Testing Station in Idaho. In April 1955, a new γ-source became available at the Dugway Proving Ground, Utah. A third fuel element facility is established at Argonne National Laboratory and there are a no. of other Co sources in use part-time by participants in the Radiation Sterilisation Project. These and four different types of electron accelerating machines are described. Future developments are outlined. E. M. J.

Cold sterilisation of foods [by ionising radiation]. B. E. Procter and S. A. Goldblith (*Chem. Engng Progr.*, 1955, **51**, 480—482).—The effect of radiation on micro-organisms of all types is highly selective, and no set level of radiation for complete sterilisation has been determined. Enzyme action is checked, but is generally much less affected than is bacterial life. There is no evidence of harmful effects persisting in irradiated food. Because of the wide dispersion of food plants and their seasonal operation, radiation sterilisation becomes expensive compared with chemical and physical means. The destruction of insects and the inhibition of sprouting in potatoes, by radiation, are briefly discussed. F. RUMFORD.

"Cold" sterilisation of foods. C. A. Greenleaf (*Conserva*, 1955, **4**, 138—139; from *Calif. Fruit News*).—A review of exploratory investigations carried out in the U.S.A. into the possibilities of the use of radioactive by-products for the sterilisation of food. P. S. ARUP.

Preservation of foods. VIII. Preservation by refrigeration. ii. Physiological aspects of preservation of [plant] products at low temperatures in the living condition. J. E. Boeke (*Conserva*, 1955, **4**, 153—162; cf. J.S.F.A. Abstr., 1955, ii, 44, 123, 193, 300; 1956, i, 47).—A review covering general principles, respiration phenomena during cold storage at different temp., influence of gases and vapours on ripening, and effects of freezing on vegetable tissues. P. S. ARUP.

Preservation of foods. VIII. Preservation by refrigeration. IV. P. Noordzij (*Conserva*, 1956, **4**, 241—249; cf. *ibid.*, 1955, **4**, 181).—A review covering types of cold stores, atmospheric conditions and loss in wt. in cold stores, hygienic aspects, condensation problems, and the technique of insulation. P. S. ARUP.

Grain storage studies. XIX. Influence of mould infestation and temperature on deterioration of wheat during storage at approximately 12% moisture. M. Golubchuk, H. Sorger-Domenigg, L. S. Cuendet, C. M. Christensen and W. F. Geddes. **XXII. Influence of oxygen and carbon dioxide concentrations on mould growth and grain deterioration.** Anne Peterson, V. Schlegel, B. Hummel, L. S. Cuendet, W. F. Geddes and C. M. Christensen (*Cereal Chem.*, 1956, **33**, 45—52, 53—66).—XIX. Fat acidity and losses in viability increased in mould-infected samples of hard red spring wheat during temporary storage at 18% moisture for seven days at room temp. During subsequent storage at 12% moisture and 24° and 38°, mould counts generally declined (initially ~31,000 per g.), but the fat acidity continued to increase. Germ damage increased markedly at 38°. High temp. and mould infection together cause greater damage than either factor alone.

XXII. Mould growth, germ damage, fat acidity and respiration rate of sound hard red spring wheat (88% viability) during 16-days' storage at 38% moisture and 30° were progressively decreased by decreasing O_2 concn. of the atm. from 21·0 to 0·2%. Some mould growth occurred at the lowest concn., but viability was maintained; in samples aspirated with air viability was only 7% after 16 days. At O_2 concn. of 21·0%, increasing levels of CO_2 had little effect until concn. exceeded 13·8—18·6%, when respiration rate, mould growth and development of fat acidity were sharply inhibited. At high CO_2 concn. (50 and 79%), viability remained high, and there was little or no germ damage. S. C. JOLLY.

Wheat storage research. J. L. Schmidt (*U.S. Dep. Agric.*, 1955, *Tech. Bull.* 1113, 98 pp.).—Research studies are reported into bin construction for wheat storage, measurement of wheat temp., grain ventilation, etc. Management studies are discussed, also pertinent data relating to insect infestation of stored grain. N. M. WALLER.

Use of moisture-proof wrappers to improve the condition of grapes during long-term storage. H. Malan (*Fmg, S. Afr.*, 1955, **30**, 231—232, 236).—Storage tests are reported on Barlinka and Waltham Cross grapes packed in Pliofilm, Cellophane, grease-proof paper and ordinary sulphite paper. Wastage, due to fungal infection, was high in bunches wrapped in Pliofilm and Cellophane, but when these materials were used as box liners the results were promising provided only sound grapes of good quality were packed. Grease-proof and sulphite paper had no effect and normal desiccation of the stalks took place. E. G. BRICKELL.

Use of film box liners to extend storage life of pears and apples. F. Gerhardt (*U.S. Dep. Agric.*, 1955, *Circ.* 965, 28 pp.).—The appearance, storage life, and dessert quality of fall and winter pears and Golden Delicious apples are improved by the use of sealed film box liners made from such materials as Pliofilms 75FF, 80 and 100 FMI, 80 and 100 HP, Cellophane 300 LSAT, and polyethylene 100 and 150. E. G. BRICKELL.

Purity of tin for coatings. Anon. (*Tin Uses*, 1955, No. 33, 7).—Purity criteria for Sn linings of food cans, etc., are reviewed, with particular reference to the presence of Pb. If Sn of purity ⩽99·75% is used for the can lining and for coating dairy utensils and food processing equipment, there should be no danger, even in the worst imaginable conditions, of the Pb content of food reaching the British statutory limit of 1·4 p.p.m. J. S. C.

Refrigerated stores for fruit. Anon. (*Bull. Minist. Agric. & Dep. Sci. industr. Res.*, 1955, No. 159, 26 pp.).—The design, construction and operation of refrigerated stores and refrigerated gas stores for fruit are described and illustrated. J. S. C.

Starch cooking apparatus. Springs Cotton Mills (B.P. 735,161, 16.9.53. U.S., 24.10.52).—The apparatus of B.P. 718,465 for starch cooking has the disadvantage that gelled starch tends to accumulate on the vat walls. This is prevented by making the return conduit to the cylindrical vat of an L-shape, with slot-like openings placed down one side of the vertical portion and half-way across the base. The other half of the base has its openings on the opposite side. The returning cooked starch thus gives a swirling motion to the vat contents and prevents any adhesion to the sides. K. RIDGWAY.

Milling of whole grain kernels for producing a non-rancidifying product. Process Millers, Inc. (Inventors: C. S. F. D. de Sollano and J. M. Berriozabal) (B.P. 735,530, 3.10.52).—Before milling, cereal grains are steeped in a hot aq. bath to destroy the lipase enzymes and give a sterilised product and are then simultaneously comminuted and dehydrated in a stream of hot gases. The bath may be alkaline (pH 11·5—14) or acid (pH 1—4), steeping temp. 68—82°, air temp. for drying 180—1200°, and final water content of grain $\geq 10\%$. J. S. C.

Manufacture of dough and baked products. Baker Process Co., formerly Wallace & Tiernan Process Co. (B.P. 735,218, 3.8.51. U.S., 3.8.50).—The dough ingredients are mixed with a yeast-activated broth which constitutes almost the entire liquid content of the dough. The broth is prepared from water, sugar and yeast and is allowed to ferment until at least 1% ethanol is present, together with sufficient other fermentation products to impart the desired flavour to the final dough; sufficient yeast must be present in the broth to perform at least part of the raising of the dough and an improver, e.g., KIO_3, may be added to produce the desired grain structure. The dough can be made more quickly in this way and the control of the quality of the final product is easier.
J. A. BARNARD.

Testing of dough. Wallace & Tiernan Process Co. (B.P. 735,204, 13.3.53. U.S., 27.6.52).—The free-gas content of dough, which has an important effect on the texture of the final loaf, is measured by compressing the dough in a closed vessel with a piston, thus driving the gas into solution in the dough; the travel of the piston is a measure of the reduction in volume and hence of the free-gas content of the original dough. J. A. BARNARD.

Adsorption of organic substances from liquids [sugar solutions]. N. V. Octrooien-Maats. "Activit" (B.P. 735,081, 29.6.53. Neth., 27.6.52).—Org. substances, e.g., colouring, odorous or flavoured matter, are removed from liquids by adsorption with insol. surface-active artificial resins containing polar groups of a moderate to strong basic character, i.e., capable of binding anions of carboxylic or glutamic acid, at temp. >70°. The prep. of several such resins is described, e.g., from aniline, tetraethylene pentamine and epichlorohydrin. (Cf. B.P. 650,706 and 733,376.) I. JONES.

Caramel colour composition. Union Starch & Refining Co. (Inventors: J. E. Cleland and J. B. Longenecker) (B.P. 729,219, 18.6.52. Addn. to B.P. 698,105, 5.6.51).—The colouring compound of the parent specification is mixed (30—60) with water and a stabiliser (2—20%), e.g., propylene glycol, to provide an improved caramel colour composition. F. R. BASFORD.

Preparation of citrus fruit liquors or beverages. Northern Dairy Engineers, Ltd. and J. W. Shearman (B.P. 729,199 and 729,200, 30.11.53).—A. The fruit, e.g., orange, is finely shredded while immersed in sugar syrup (at ~38°), to absorb immediately volatile aromatic oils and juices, to give (after separation of unwanted solids) a beverage of improved flavour.
B. Apparatus for carrying out the process is figured and described.
F. R. BASFORD.

Juice extractor [for attachment to food machines]. Kenwood Manufacturing Co., Ltd. (Inventor: L. E. Lancy) (B.P. 730,105, 18.11.52). K. RIDGWAY.

Machine for turning grain in malt production. E. Fawcett, Ltd. and Harry White (Inventors: Harry White and Jack R. Hall) (B.P. 734,411, 21.2. and 13.8.52). K. RIDGWAY.

Manufacturing butter. C. Zeuthen (B.P. 735,608, 29.9.53).—Butter is made by churning cream in a closed, rotating drum provided with beaters; then kneaded by rollers introduced through the base of the drum; and finally, the rollers being withdrawn, further kneaded by rotation with the drum under vacuum.
J. S. C.

Manufacture of artificial sausage casings from animal fibrous material. Anstalt Unda (B.P. 736,673, 19.9.50. Switz., 23.9.49).—Sausage casings of improved strength are formed by extruding (through an annular nozzle) a paste prepared from fresh fibrous animal material which has not been treated with chemicals. Similar material treated with an agent to cause swelling of the tissue may also be added before the extrusion. F. R. BASFORD.

Device for use in the manufacture of margarine and other semi-solid edible fats. C. M. Sorensen (B.P. 729,609, 16.3.53).—A device for further working of margarine, etc., subsequent to normal working in a kneading machine, is figured and claimed.
F. R. BASFORD.

Manufacturing fats. H. F. R. Knollenberg, trading as Schröder & Co. (B.P. 735,734, 10.3.53. Ger., 27.3.52).—A mixture of vegetable and/or animal fats and air, in the required proportions (about 30% by vol.), is obtained by intimate mixing in an emulsion machine, preferably similar in form to a cross-beater mill; followed by simultaneous beating and cooling in a cylinder, and then by further heat treatment in an emulsion machine from which the final product flows in a continuous stream. J. S. C.

Extracting valuable components from fats and oils. O. Notevarp, A. S. Roald and P. A. Sletnes (B.P. 732,988, 24.9.52. Nor., 25.11.51).—Vitamins and sterols from animal or vegetable fats or oils are extracted after saponification with aq. NaOH to form a solid soap of <20% water content (or if >20%, the soap is dried to the required degree). The soap is broken up into particles and extracted with a water-miscible solvent in such quantities that the water content of the solution is <5% (wt.) The solvent may be either an aliphatic ketone or monohydric alcohol. J. S. C.

Degassing cream or similar liquid foods. S. Ørum-Hansen (B.P. 734,037, 15.12.52. Den., 17.12.51 and 9.4.52).—Cream is degassed by heating under pressure to a temp. slightly below its normal b.p. and allowing it to flow through a slot into a tank at normal pressure. This treatment is more convenient and effective than the usual treatment of heating at atm. pressure and discharging into a tank under vac. K. RIDGWAY.

Straining of viscous substances [e.g., chocolate]. Baker Perkins Ltd. (B.P. 731,488, 29.5.53. Germ., 29.5.52).—Apparatus is illustrated and described. L. S.

[Preparation of] infant foodstuffs. American Home Products Corp., Assees. of P. Gyoergy, R. Kuhn and F. Zilliken (B.P. 736,708, 2.2.53. U.S., 22.4.52).—Infant food composition, derived from cows' milk and containing proteins, fats and carbohydrates, is compounded with 0·1—5 (0·1—1) wt.-% of hydrolysed chitin to provide a growth stimulant for *Lactobacillus bifidus* (an organism present in infants' intestines) which is lacking in the cows' milk.
F. R. BASFORD.

Preparation of condiments. Victor M. Lewis (B.P. 734,382, 20.4.53. Austral., 21.5.52).—A stable mustard-flavoured condiment is prepared from an *iso*thiocyanic acid ester (mustard oil) mixed with fat and emulsified in an aq. medium, using, if necessary, a fat emulsifying agent. J. S. C.

[Common] salt compositions. Columbia-Southern Chemical Corp. (Inventor: F. Waldo) (B.P. 735,014, 28.11.53).—NaCl, for use as condiment, is stabilised against agglomeration by compounding with 0·5—5% of finely-divided (<0·1 μ) pptd. Ca silicate, viz., $CaO,(SiO_2)_x$ or hydrated SiO_2, viz., $H_2O(SiO_2)_y$ (x is 2—4, y is 3—50). F. R. BASFORD.

Preservation of foodstuffs and the like. Minister of Supply (Inventor: John King) (B.P. 734,197, 23.6.52).—Foodstuffs etc. are preserved in sealed containers from which substantially all residual O_2 has been removed by the introduction of H_2 with inert gas in conjunction with a catalyst (e.g., Pd on asbestos) capable of causing H_2 to combine with O_2. J. S. C.

Apparatus for cleansing [food] containers. J. Lyons & Co., Ltd. (Inventors: Percy White and R. W. Money) (B.P. 734,496, 8.11.51).—Containers consisting of a flexible polyvinyl chloride bag inside a rigid metal drum are cleansed by a machine which fits to the neck of the bag, inflates it with compressed air and injects a cleansing fluid. (Cf. also B.P. 708,813.) K. RIDGWAY.

Machines for moulding and wrapping plastic material, e.g., butter. Brecknell, Munro & Rogers, Ltd., and Clifford W. Lawson (B.P. 734,407, 31.10.51 and 24.6.52).—The machine is of the single moulding-chamber type, with the chamber formed in a sector-shaped structure which can swing from side to side. Although the chamber movements are oscillatory, because the distances in the machine are kept small, it has a production rate higher than normal single-chamber machines. K. RIDGWAY.

Protective wrapping for [frozen] articles. Algida Industria Alimenti Gelati S.r.l. (B.P. 732,026 and 732,032. [A] 10.9.53. It., 13.9.52; [B] 29.10.52. It., 29.10.52).—A. Frozen comestibles, e.g., ice-cream, on sticks are covered with a wrapping having an easily-tearable strip round the centre. The upper part of the wrapping may be removed, leaving the lower part as a protective cup.
B. The method is extended to ice-cream blocks.
K. RIDGWAY.

Filling flowable substance [liquid confections] into containers. T. Wall & Sons, Ltd. (Inventors: G. A. Stonestreet and [A] G. H. Searle) (B.P. 734,290, and 734,292, 5.9.52).—Apparatus is described for continuously filling a flowable substance, e.g., a liquid or free-flowing powder, into leak-proof bags and freezing it whilst contained in them. J. S. C.

3.—SANITATION

Fumigation of agricultural products. XI. Sorption of mercury vapour by wheat. B. S. Gorringe (*J. Sci. Food Agric.*, 1955, **6**, 791—799).—The design of an amplifying circuit and construction of apparatus to provide a more sensitive modification of a u.v. absorption method for detecting Hg vapour in air is described, capable of detecting 10^{-10} g. of Hg vapour in ~50 ml of air. Sorption of Hg vapour by wheat is affected by changes in moisture content to a much greater extent than changes in temp. in practical wheat storage. In tests on the effect of moisture content, 100 g. of wheat that had sorbed 4·25 μg. of Hg gave up 0·01 μg. after eight days, 4·24 μg. being firmly retained. Most of the Hg sorbed is chemically combined, but with drier grain some Hg can be recovered by airing. Tests indicated that after two years Hg is still reacting with the wheat tissues. Control of *Calandra* eggs, not resistant to Hg vapour, is achieved if no part of the grain mass is further than 2 ft. from the source of vapour. The residues of combined Hg in the grain may occur as insoluble unmetabolisable S compounds. E. M. J.

Fumigation of agricultural products. XII. Sorption of methyl bromide on groundnuts. H. M. B. Somade (*J. Sci. Food Agric.*, 1955, **6**, 799—804).—Groundnuts treated with MeBr should not have a moisture content >5% or the germination may be seriously affected. Careful control of dosage and circulation of fumigant are desirable to keep the concentration to ~30 mg./l. at any part of the bulk of the nuts. At any given moisture content a sufficiently high dose will kill the seed, but unfumigated nuts will die before germinating if of >10% moisture content. At concentrations lower than that critical for a particular moisture content a slight stimulating action has been observed; fungal attack is suppressed. With doses sufficiently high to kill the seed there is damage to the radicle. No evidence was found of reaction of MeBr with groundnut oil, or with the steroids of the germ. E. M. J.

A comparison of Cyclethrin, allethrin, pyrethrins, and mixtures of piperonyl butoxide or sulphoxide with them in house-fly sprays. W. A. Gersdorff and P. G. Piquett (*J. econ. Ent.*, 1955, **48**, 407—409).—Cyclethrin was 0·60 times as toxic as allethrin and 1·5 times as toxic as pyrethrins. Piperonyl butoxide and sulphoxide synergised Cyclethrin equally and more strongly than they did allethrin; sulphoxide synergised pyrethrins more strongly than it did Cyclethrin. Cyclethrin alone was slightly less effective than allethrin in the knockdown of flies but Cyclethrin mixtures with either synergist were slightly more effective in knockdown than were the comparable allethrin mixtures. A. A. MARSDEN.

Effect of pyrethrins in combination with chlorinated hydrocarbons on resistant and non-resistant house flies. D. E. Born and R. H. Davidson (*J. econ. Ent.*, 1955, **48**, 413—414).—Six chlorinated hydrocarbon compounds when combined with pyrethrin sprays increased the mortality of DDT-resistant flies. This increase was approx. equal to the sum of the mortalities of the compounds tested alone. For non-resistant flies, the results were additive for all compounds except heptachlor and Isodrin, which showed antagonism in combination with pyrethrins. This apparent antagonism is probably due to physiological differences between the two strains of flies. A. A. MARSDEN.

Residual effectiveness of mixtures of organic phosphorus insecticides with chlorinated terphenyls. I. Hornstein, W. N. Sullivan and C. H. Tsao (*J. econ. Ent.*, 1955, **48**, 482—483).—Addition of chlorinated terphenyls (Aroclor 5460) to six volatile org. P insecticides increased the residual effectiveness of all these materials. A mixture of dimethyl 2:2-dichlorovinyl phosphate and chlorinated terphenyls (1:4) gave 100% kill of house flies, cockroaches and flour beetles after 60 days whilst almost as good results were obtained with the ethyl homologue. The effectiveness of Diazinon and Bayer L13-59 was significantly improved, but Malathion was little affected by the addition of chlorinated terphenyls. A. A. MARSDEN.

Insecticidal phosphorus compounds. J. A. Fluno (*Soap, N.Y.*, 1955, **31**, No. 11, 151—154, 203).—The effectiveness, in varying service conditions, of org. P insecticides is reviewed, including dialkyl 2:2:2-trichloro-1-hydroxyethyl phosphonates, dialkyl 2:2-dichlorovinyl phosphates, dialkyl 2-chlorovinyl phosphates and acetates of dialkyl 2:2:2-trichloro-1-hydroxyethyl phosphonates. Efficacy against early fourth-instar larvæ of *Anopheles quadrimaculatus*, body lice and house flies was evaluated in detail and the results are tabulated. J. S. C.

Mechanism of action of certain synergists for DDT against resistant house flies. H. H. Moorefield and C. W. Kearns (*J. econ. Ent.*, 1955, **48**, 403—406).—Analogues of DDT which are recognised as synergists for DDT against resistant house flies were found to inhibit the enzyme DDT-dehydrochlorinase which catalyses the dehydrochlorination of DDT to a non-toxic derivative. Other compounds related to DDT but lacking a synergic effect did not inhibit this enzyme. DDT-dehydrochlorinase is an important factor in the cause of resistance of house flies and was found to be present in larger quantities in the synergist-resistant strains: susceptible flies have not apparently a measurable quantity of this enzyme. A. A. MARSDEN.

Insecticidal action of esters and ethers of 2:2:2-trichloro-1-*p*-chlorophenylethanol. M. J. Kolbezen, F. A. Gunther, R. C. Blinn and G. E. Carman (*J. Amer. chem. Soc.*, 1955, **77**, 5410—5411).—Fifteen esters and ethers of the alcohol named in the title are prepared by standard methods and tested by bio-assay against *Culex quinquefasciatus* Say, *Heliothrips haemorrhoidalis* (Bouché) and *Metatetranychus citri* (McGregor), no marked differences in toxicity being observed, all compounds being reasonably effective. Against the confused flour beetle, *Tribolium confusum* Dur, however, the most toxic compounds were the *n*-butyrate, caprate and the methyl ester. M.p. and empirical formulæ are given for all the compounds made. M. DAVIS.

Determination of methylenedioxyphenyl-containing synergists used in analysis of fly sprays. M. Beroza (*J. agric. Food Chem.*, 1956, **4**, 53—56).—The method is based on the liberation of formaldehyde from methylenedioxyl groups by strong H_2SO_4 and its determination with chromatotropic acid in the same acid medium. The satisfactory estimation of piperonyl butoxide, sulphoxide, piperonyl cyclonene and "*n*-propyl isome" in fly sprays is described, the method being sensitive to 1 μg. of piperonyl butoxide. Preliminary tests indicate that the method may also be applicable to synergists in aërosal formulations. N. M. WALLER.

3:4-Methylenedioxyphenoxy compounds as synergists for natural and synthetic pyrethrins. M. Beroza (*J. agric. Food Chem.*, 1956, **4**, 49—53).—The preparation and properties are described of 66 compounds containing the 3:4-methylenedioxyphenoxy-group. Preliminary tests with the housefly showed that almost all ethers, acetals and sulphonates are effective synergists for natural and synthetic pyrethrins. The esters of carboxylic acids show practically no synergism and urethanes show only slight activity. The acetals are the most promising candidates for synergists of commercial value. N. M. WALLER.

Laboratory comparison of some insecticides as larvicides against non-resistant house flies. R. H. McCauley, jun., M. M. Grainger, D. A. Lindquist and R. W. Fay (*J. econ. Ent.*, 1955, **48**, 269—273).—In laboratory tests against pupæ and fully-grown larvæ chlordane was the most effective insecticide examined. Against 1—3-day-old larvæ γ-$C_6H_6Cl_6$ (95%) gave 100% mortalities at 25 mg. per sq. ft. whilst Aldrin, toxaphene and Dieldrin were more effective than chlordane at dosages <250 mg. per sq. ft. A. A. MARSDEN.

[Control of] the house fly. (*U.S. Dep. Agric.*, 1955, *Leafl.* 390, 12 pp.).—The life-cycle of, and health hazards due to the house fly are described. Methods of fly control in the home and on the farm are given; they include elimination of breeding places, screening of windows and doors, and the use of surface and volume sprays, poisoned baits, electric grids and traps. K. E. J.

[Control of] wood ticks. (*U.S. Dep. Agric.*, 1955, *Leafl.* 387, 8 pp.).—The control of wood ticks in infested places indoors and in the open is described. N. M. WALLER.

[Control of] fleas. (*U.S. Dep. Agric.*, 1955, *Leafl.* 392, 8 pp.).—Details are given of insecticide control of various types of flea in domestic premises, animal quarters and yards, and pets' habitations. K. E. J.

Thermal decomposition of some phosphorothioate insecticides. J. B. McPherson, jun. and Gerald A. Johnson (*J. agric. Food Chem.*, 1956, **4**, 42—49).—A study is made of the nature of the decomposition of parathion (*OO*-diethyl *O p*-nitrophenyl phosphorothioate), its methyl homologue, Insecticide 4124, Chlorothion and Malathion, and of their stable life at temp. 65—115°. Prolonged heating of the methyl homologue results in two-step decomposition after preliminary isomerisation. The first step, which can be hastened catalytically, generates dimethyl sulphide and SO_2 and leaves a mixture containing poly(arylmetaphosphates). This mixture on further heating decomposes, sometimes explosively leaving a carbonaceous residue. Estimated decomposition times are given (for the methyl homologue approx. 40 min. at 150°). N. M. WALLER.

Evaluation of medium containing Tergitol-7 and triphenyltetrazolium chloride for differentiation of coliform bacteria from drinking water and foods. J. H. Bekker and D. A. A. Mossel (*Leeuwenhoek ned. Tijdschr.*, 1955, **21**, 252—256).—Tests on coliform isolates from numerous water samples show that the above (agar) medium (T.T. agar) is of the same order of selectivity at 37° as Endo agar, but is somewhat more selective at 45°. The correlation between

behaviour on the two media is good. Tests on a large no. of various foods show a low incidence of *E. coli*. For this purpose, brilliant green–bile–lactose–peptone–water is a satisfactory medium for selective enrichment of coliform bacteria. P. S. ARUP.

Fungi from trickling filters. A. E. Feldman (*Sewage industr. Wastes*, 1955, **27**, 1243—1244).—Six species of fungi (three *Fusarium*, two *Geotrichum* spp., and *Alternaria tenuis*) were isolated from high-rate trickling filters receiving a diluted chemical waste of high org. content. J. S. C.

Particle-size distribution of ground garbage. E. R. Baumann, D. A. Dorman and M. T. Skodje (*Sewage industr. Wastes*, 1955, **27**, 1245—1252).—Proposals for establishing a uniform particle-size distribution code for garbage ground in household garbage grinders and a reproducible test method (cf. Wolff, J.A.C. Abstr., 1955, i, 697) were investigated. A detailed method is now recommended and a series of results obtained by its use are reported in tabular and graphical form and discussed in regard to their reproducibility and the practicability of some existing municipal codes in the U.S. J. S. C.

Relation of phosphorus content to algæ blooms. R. J. Benoit (*Sewage industr. Wastes*, 1955, **27**, 1267—1269).—The P content of natural water is a limiting factor for algal growth and blooming. It is shown that all forms of P in water, whether org. or inorg., sol. of insol., must be considered in this connexion and that there is a possibility of a high rate of P-turnover during a time of low momentary concn. of phosphate. J. S. C.

Effect of sewage-borne phosphorus on algæ. J. J. Curry and S. L. Wilson (*Sewage industr. Wastes*, 1955, **27**, 1262—1266).—The problem of removing or reducing the sol. phosphate level introduced into Lake Zoar, Connecticut, U.S.A., by sewage treatment plant effluents, and thus to eliminate algal bloom (which is fertilised by the nitrite and phosphate) from the lake, is reviewed and discussed. J. S. C.

Distribution of coliform bacteria and other pollutants in tidal estuaries. B. H. Ketchum (*Sewage industr. Wastes*, 1955, **27**, 1288—1296).—Methods of predicting the distribution of both " conservative " and time-variable pollutants in an estuary from the results of a salinity survey are developed mathematically. The relative merits of different locations for an outfall within an estuary can thus be evaluated. J. S. C.

B.O.D. test and total load. A. M. Buswell (*Sewage industr. Wastes*, 1955, **27**, 1297—1298).—The various analytical procedures for estimating the total pollution load of a waste are discussed and it is concluded that, to obtain the best estimate, the following determinations are needed: (1) ordinary B.O.D., (2) total C (Van Slyke combustion method), (3) one or more determinations of chemical oxygen demand, (4) ammonia N, and (5) count of nitrosomonas organisms. J. S. C.

Statistical analysis of coliform data. R. Pomeroy (*Sewage industr. Wastes*, 1955, **27**, 1299—1301).—A discussion of the earlier paper by Thomas (see J.S.F.A. Abstr., 1955, ii, 48) in which the main points considered are the practicability of using arithmetic mean values and the no. of tubes and dilutions used in tests. J. S. C.

Laboratory evaluation of high-rate sludge digestion. C. N. Sawyer and H. K. Roy (*Sewage industr. Wastes*, 1955, **27**, 1356—1363).—Five experimental sewage sludge digestion units were operated for 77 days at respective detention times of 6, 8, 10, 15 and 20 days. The results for the 6-day (**I**) and 20-day (**II**) detention times are given, respectively, as follows: volatile matter destruction 52·2%, 58·2%; grease destruction, 53·0%, 71·4%; protein degradation, **I** 86% of **II**; N and P contents of digested sludge both lower in **I** but uniform in the remainder; grease content of digested sludge, 9·50% in **I** and 6·65% in **II**. J. S. C.

Full-scale modified digestion of meat packing wastes. A. J. Steffen (*Sewage industr. Wastes*, 1955, **27**, 1364—1368).—A process of anaërobic digestion, coupled with vacuum degasification, for the treatment of meat processing wastes, is described. The digestion period is 12 hr. with daily loadings of 0·22 lb. of B.O.D./cu. ft. of digester capacity and digestion temp. is 95°F. The extent of B.O.D. and suspended solids removal are, respectively, 95% and 97%. Vacuum degasification is operated by a baffled cascade arrangement in an elevated degasifier, giving ~20 in. of vacuum. The pilot plant studies and the design of the first plant to be operated on this basis are described fully. The final treatment is aërobic and will take place in a single-pass high-rate trickling filter followed by clarification and chlorination. J. S. C.

Control and treatment of dairy waste. H. A. Trebler and H. G. Harding (*Sewage industr. Wastes*, 1955, **27**, 1369—1382).—Current (U.S.) practice in the treatment and disposal of dairy wastes is reviewed. Discharge to municipal sewers is preferable although irrigation processes are receiving considerable attention. High-rate recirculating trickling filters and many types of aëration tanks and devices are widely used. The important factors are (*a*) maintenance of temp. >70°F. (80—90°F.) and (*b*) good agitation with aëration devices which do not cause foaming. (34 references.) J. S. C.

Rapid bio-oxidation method of waste disposal. N. Porges (*Amer. Soc. Brew. Chem., Proc. annu. Mtg*, 1955, 56—64).—A simplified, almost fully automatic waste disposal system to handle dairy waste was investigated (cf. R. R. Kountz, J.S.F.A. Abstr., 1956, i, 176). A diagram is constructed to summarise the data, showing a reduction of 1000 p.p.m. C.O.D. (chemical oxygen demand) of milk by 500 p.p.m. sludge and hourly O_2 requirements. As much as 80 p.p.m. O_2/hr. are required. The rapid O_2 demand subsides in 6 hr. (if sludge is increased to 1000 p.p.m., in 3 hr.), during which time sol. wastes are consumed and ~50% of waste is converted to cell material. After this, a second period, characterised by an O_2 demand of ~10% of that initially found, consists of an endogenous phase wherein the sludge oxidises at the rate of 1%/hr. (21 references.) J. S. C.

Slime pollution in polluted waters. I. Laboratory and field study methods. H. Heukelekian and E. S. Crosby (*Sewage industr. Wastes*, 1955, **27**, 1391—1398).—Methods of studying slime formation in polluted waters are described, based on the immersion of microscope slides in varying conditions, with an account of field study equipment for assembling and holding the slides and test plates and for submerging the assembly in conduits carrying sewage and effluents, and of a special unit area sampler. J. S. C.

Constant temperature tank for fish bioassay aquaria. C. M. Weiss (*Sewage industr. Wastes*, 1955, **27**, 1399—1401).—A constant temp. bioassay tank of 200 gal. capacity, designed to hold 14 circular glass aquaria, each calibrated to take 15 l. of water, is described. J. S. C.

Chemicals involved in air pollution and their effects on vegetation. P. W. Zimmerman (*Boyce Thompson Inst., Professional Pap.*, 1955, **2**, 124—145).—Gases and vapours which may pollute the atmosphere and have deleterious effects on plants, include: SO_2, HF, Cl_2, H_2S, NH_3, Hg vapour, ethylene, CO, and vapours of 2:4-D and other hormone-like herbicides. The effects of these compounds on plants grown under different conditions are determined. (33 references.) R. H. HURST.

[Preparation of] *S*-ethylxanthoyl *O*-ethyl *O*-*p*-nitrophenyl dithiophosphate. Dow Chemical Co. (Inventor: H. Tolkmith) (B.P. 729,998, 24.11.53).—Interaction of *S*-ethylxanthoyl *O*-*p*-nitrophenyl dithiophosphoric chloride, $EtO{\cdot}CS{\cdot}S{\cdot}PS(O{\cdot}C_6H_4{\cdot}NO_2)Cl$, with 1 mol. proportion of an alkali metal alkoxide (NaOEt) in a solvent (benzene) for 6 hr. at 35—80° gives the corresponding *O-Et ester* d_4^{20} 1·3654, n_D^{20} 1·5587, useful as a parasiticide especially agains, flies, mites, beetles, cockroaches and aphids. F. R. BASFORD.

4.—APPARATUS AND UNCLASSIFIED

Semi-automatic apparatus for maintaining solvents with changing polarity in chromatographic columns. M. R. Sahasrabudhe and S. L. Tuckey (*J. Dairy Sci.*, 1955, **38**, 1392).—A simple apparatus is described that will provide solvent of changing polarity for flow under pressure through a chromatographic column and at the same time maintain a constant head of solvent above the column. S. C. JOLLY.

Use of isatin and its derivatives in paper chromatography of amino-acids and peptides. J. Noworytko and M. Sarnecka-Keller (*Acta Biochim. polon.*, 1955, **2**, 91—105).—Of a no. of developing agents examined for this purpose isatin was the most effective in separating acids of closely similar R_F value. The simultaneous use of isatin with 5-bromo- or 5-nitro-isatin and of different solvents makes possible the complete analysis of a mixture of amino-acids by one-dimensional chromatography. A. G. POLLARD.

Determination of the retention of creosote in preserved wood. A. E. Bernardi (*Industr. y Quim.*, 1955, **17**, 137—139, 143).—A method is described for determining the true retention of creosote in wood with a correction for the amount of moisture originally present and for the loss of preservative with time occurring by volatilisation of the lower-boiling constituents of the creosote. For this the initial sample is dried in an oven at 105° for 20 hr. before impregnating, and the water afterwards extracted by boiling with toluene in a Dean and Stark apparatus. The creosote not extracted by the toluene along with the water is removed by a Soxhlet extraction with benzene. Data obtained with samples of untreated-wood and industrial preserved wood are recorded. The method can also be used to detect the adulteration of creosote by addition of solvents. (34 references.) D. LEIGHTON.

SOCIETY OF CHEMICAL INDUSTRY

INSTRUCTIONS TO AUTHORS

inadequately prepared typescripts will cause unnecessary delay. Authors should therefore conform closely to the instructions given below.

I. Publishers and Publications

)lishes

of Applied Chemistry (formerly known as the *ety of Chemical Industry*), which appears monthly :rs (except those concerning food and agriculture) al investigations which have not been published els.

(*b*) *nal of the Science of Food and Agriculture*, which appears mo ly and contains papers describing original investigations on food and agriculture which have not been published elsewhere, and an invited review article.

(*c*) *Chemistry and Industry*, the Society's weekly news journal, containing review articles on some aspects of chemical industry, articles dealing with current plant practice, descriptions of new apparatus, historical articles and, occasionally, original work not suitable for inclusion in (*a*) or (*b*), news items, etc.

All papers and correspondence relating to them are to be sent to the Editor of the appropriate Journal, 56 Victoria Street, London, S.W.1.

II. General

(*a*) Papers offered for publication will be brought before the Publications Committee and subsequently submitted to a referee.

(*b*) Papers may not be offered for publication elsewhere while under consideration by the Publications Committee.

(*c*) Papers accepted by the Society for public tion may not be published elsewhere without permission of the Publications Committee, except as provided in VII below.

III. Style and Layout of Papers

(*a*) Papers must be written in clear and concise English.

(*b*) Although unnecessary standardization is not desired, and due allowance for the type of subject matter must be made, papers submitted to the journals I (*a*) and (*b*) should conform as far as possible to the following pattern :

Title.—This should be concise and explanatory of the purpose of the paper. Where a related series of papers is submitted each individual paper should have the same general heading, followed by a series number and title of the part.

Synopsis.—A short synopsis of the work, drawing attention to salient points, and intelligible without reference to the paper elf, should be given separately at the beginning of the paper.

Introduction.—The aim of the investigation should be given and also a brief statement of previous relevant work with references.

Experimental.—The methods and materials used should be clearly stated in sufficient detail to permit the work to be repeated if desired. Only new techniques need to be described in detail, but known methods should have adequate references.

Results.—These should be presented concisely, using tables or illustrations for clarity. Adequate indication of the level of experimental error and the statistical significance of results should be given. Only in exceptional cases will tables *and* graphs derived from them be accepted for publication.

Discussion.—In general, the discussion and interpretation of results should follow their presentation, in a separate section.

Conclusions.

Acknowledgments.

References.

Typescript

All manuscripts should be typed in double spacing on one f the paper only and adequate margins should be left. ipy should be retained by the author, and the top copy hou be sent to the appropriate Editor.

(*b*) The address where the work described in the paper was carried out should be given at the end of the paper immediately after any Acknowledgments.

(*c*) Tabulated matter should be clearly set out and the number of columns in each table kept as low as possible.

(*d*) Drawings intended for reproduction should be clear and drawn to a scale which, when reduced to the appropri te si will produce a legible figure. They should ink on plain white paper or board, tracing c faintly blue-lined paper ; *any lettering, wh in the body of the drawing, should not be in and lightly in blue pencil* (*blue does not app for reproduction*). The author's name an should be written on the back of each captions should be typed on a separate

V. Nomenclature and References to

(*a*) Symbols, formulae and equations n great care. The symbols recommended Symbols Committee of the Royal Society the Chemical Society), should be empl that formulae which require special sett structures) should be used, their numb minimum.

(*b*) References to the literature should by a small superior figure referring to the paper (*see* papers published during names of the journals should be abb the ' World List of Scientific Period ed. (London : Butterworths Sci name of the journal is not in this The abbreviated title of the jou indicate italic type and followed b olume r in arabic numerals underlined w to ind type, then by the number of th in arab When books are mentioned in ices, the be : author(s), initials, title, y number, followed (in brackets) by pla publication publisher.

VI. Proofs and Reprints

(*a*) The address to which the author's proofs are to be s must be clearly indicated. Authors living abroad may gi address in Great Britain of a person who will undertake t their proofs, and his or her name and address should set out.

(*b*) Proofs will be despatched to the author directly the has been set by the printer, and authors are requested t them corrected without delay to the Editor of the cerned. Failure to do this will result in delay i

(*c*) Correction of proofs by authors must printer's and similar errors. Any modificatio text is to be avoided.

(*d*) Twenty-five reprints of author's papers are s plied without charge and further copies may be orde form which is sent with the author's proofs.

VII. Copyright

(*a*) Copyright of all papers submitted to the Society rer the property of the author unless paid for by the Society, t Society has the sole right of publication for a period of six from the date of publication.

(*b*) Papers appearing in the publications of the Chemical Industry may be published elsewhere six the date of publication by the Society, provide of the original source of publication is gi

Printed in Great Britain by Butler & Tanner Ltd., Frome and London

JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE

CONTENTS

Nitrogen in commercial glasshouse practice .. ..
By O.

led insecticide residues in food products. V.—The nature and significance of ethylene dibr
umigated wheat 305
By R. G. Bri ges

exchangeable calcium in soils containing calcium carbonate 314
By S. K. Tobia and N. E. Milad

inces: ω-aryl- and ω-aryloxy-alkylcarboxylic acids 320
By K. Gaimster

nsecticidal emulsions in contact with sheep fleece 330
By A. F. Machin

ue of fish proteins 337
By D. S. Miller

icultural products. XIV.—Treatment of peas and beans with methyl bromide 343
By O. F. Lubatti and R. E. Blackith

ucture of milk crumb 349
By James Saunders

storage of peanuts 354
By P. B. Mathur, M. Prasad and K. Kirpal Singh

of treatment with chlorine dioxide on the properties of wheat flour. I.—The chemical com-
n of treated flours 361
By P. Meredith, H. G. Sammons and A. C. Frazer

f treatment with chlorine dioxide on the properties of wheat flour. II.—Nutritional value
d flours 371
By A. C. Frazer, J. R. Hickman, H. G. Sammons and M. Sharratt

udies treatment with chlorine dioxide on the properties of wheat flour. III.—Lipid changes
and of treated flours 375
By A. C. Frazer, J. R. Hickman, H. G. Sammons and M. Sharratt

acts i-241—i-296

SOCIETY OF CHEMICAL INDUSTRY

FOUNDED IN 1881 INCORPORATED BY ROYAL CHARTER, 1907

Offices of the Society : 56 Victoria Street, London, S.W.1
Telephone : Victoria 5215

Annual Subscription to the *Journal of the Science of Food and Agriculture*, £6 post free, single copies 15*s*. post free