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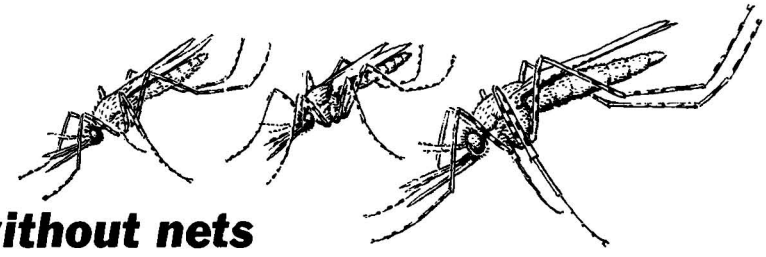

Night without nets

Night has a thousand small and secret sounds. Wind whisper and creak of board, sudden skitter of lizard feet, click and tap, slither and rustle, the ceaseless *crik-crik* of cicadas under the great glittering moon. And among those sounds, the thin, wavering whine of a killer: unseen in the darkness, riding on diaphanous wings, bringing each year disease and misery and death to millions in many parts of the world. It is estimated that in South East Asia alone, before malaria control was introduced, at least 50,000,000 cases occurred annually and that of these half a million died as a direct result of the disease. Today the menace is being driven from the scene by eradication campaigns like that in the Philippines. Slowly but surely. Progressively. By degrees—and by insecticides like dieldrin. Used as a residual spray to kill malaria-carrying mosquitoes (chiefly *Anopheles minimus flavirostris*) and also as a larvicide, this powerful insecticide developed by Shell is playing a major part in a nation-wide house spraying campaign to eradicate malaria completely in the Philippines. Already results are greatly encouraging; in the *barrios* typical of the rural areas, sickness has fallen sharply, in some cases by as much as 75%, and infants are growing up free of the malaria menace. One day soon, it is believed, the night will be made safe for man, without nets. *And not only in the Philippines, but throughout the world.*

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AN INVESTIGATION ON POLYPHENOLIC COMPOUNDS OF THE CACAO LEAF IN CONNEXION WITH A CHEMICAL METHOD FOR DETECTING VIRUS INFECTION

By MARGARET HOLDEN

Polyphenolic substances in acid extracts of cacao leaves have been separated by paper partition chromatography. The substance which gives a red colour when cacao leaf extracts are heated with alkali, a reaction which has been used as the basis of a ' colour-test ' for detecting infection with swollen shoot virus, has the properties of a *leuco*-anthocyanin. The amount of red-producing *leuco*-anthocyanin varies with the total tannin content of the leaf. In addition to virus infection, other factors such as age of leaf and variety of cacao which affect the total tannin content also affect the *leuco*-anthocyanin content. The bearing of this on the applicability of the ' colour-test ' is discussed.

Introduction

Lindner and his colleagues described[1-3] a chemical test for detecting virus infection in cherry and peach trees, depending on the use of a reagent containing sodium hydroxide, copper sulphate and sodium citrate with which healthy leaves gave a green colour whereas diseased leaves gave varying intensities of red. It was suggested that the colour reaction of infected tissues was due to an accumulation of ' polyhydroxy phenols possibly of the tannin group '. The same authors later[4] gave details of a staining technique for detection of virus infection in woody plants which was also said to be due to a higher concentration of polyphenols in diseased tissue. After removal of chlorophyll, the polyphenols were fixed by means of ethanol and formaldehyde. Subsequent heating with aqueous sodium hydroxide gave a blue colour with diseased leaves and a yellow one with healthy leaves. The blue colour was localized in certain areas of the leaf and when exposed to the air or on acidification it changed to a more stable red. Attafuah[5] applied the staining test to cacao leaves infected with swollen shoot virus and showed that the blue pigmentation occurred all over the infected leaf, while healthy leaves also gave a faint blue.

Tinsley & Usher[6] developed a colour test for detecting infection with swollen shoot virus in cacao which involved heating an aqueous extract of mature leaves with sodium hydroxide; healthy leaves gave a lime-green or green-brown colour and diseased leaves, both with and without symptoms, red or red-brown. It was important to obtain information about the nature of the substance responsible for the colour test, for it was hoped that this simple test could be used for large-scale detection of latent infection and further work had shown that anomalous results were sometimes given. The present paper gives the results of an investigation on polyphenolic (' tannin ') compounds in healthy and infected cacao leaves. Forsyth[7-9] described the fractionation of acid-extractable polyphenolic substances of the cacao bean. He found that nearly half of the ' tannin ' was (−)-*epi*catechin and the other major components were *leuco*-anthocyanins. Bate-Smith[10] and Bate-Smith & Lerner[11] gave an account of the detection and systematic distribution of *leuco*-anthocyanins in leaves. Except for tea, there is comparatively little known about the constituents of the ' tannin ' fraction of leaves, although there is a great deal of information on the distribution of anthoxanthin pigments (flavones, flavonols, flavanones, etc.) which has been reviewed by Geissman & Hinreiner.[12] Some attention was given to the anthoxanthins in the present investigation as some of them develop a red colour in alkaline solution. There was therefore a distinct possibility that the colour test could be due to the presence of one or more of these substances. It will, however, be shown in this paper that the red-producing substance has the reactions of a *leuco*-anthocyanin and that the anthoxanthin pigments play only a minor rôle in the colour changes which occur when leaf extracts are heated with alkali.

Experimental

Material and methods

Leaves of cacao (*Theobroma cacao* L.) were taken from mature trees in the Gold Coast and unless otherwise stated were of the West African Amelonado variety. Cacao seedlings were grown in boxes and baskets in an insectary. The New Juaben virus (IA) was used when beans

were infected by insect transmission (Posnette[13]) for growing infected seedlings. Leaves from diseased trees found in the field were probably also infected with this strain.

Preparation of extracts from leaves.—It is not possible to extract ' sap ' from macerated mature cacao leaves because the dry-matter content is so high—about 40% of the wet weight. In addition, they do not grind well because of their tough consistency and thus few of the cells are ruptured to liberate their contents. Young flush leaves, which are soft-textured and have a much lower dry-matter content (about 10% of the wet weight), can be ground more easily but give a mucilaginous extract which is difficult to separate from the fibre.

Extracts were made by grinding fresh leaves, from which the mid-ribs had been removed, in either a Kenmix or Nelco Blender with water or dilute acid (0·1 or 0·33N-HCl), with a ratio of not more than 40 g. of leaf/100 ml. of solution. The extract was separated by squeezing by hand through calico and clarified by centrifuging, followed by filtration through a layer of kieselguhr on a Buchner funnel.

Dry matter.—Leaves were dried overnight in an oven, with a fan, at 100–105°. Material to be used for extraction with acetone for ' tannin ' determinations was then ground finely in a C. & N. Junior Laboratory Mill (A. Gallenkamp & Co. Ltd.).

Absorption spectra.—Those in the visible region were obtained with a Unicam diffraction-grating spectrophotometer and those in the ultra-violet with a Unicam quartz spectrophotometer.

' *Tannin.*'—This was determined by a method based on that used by Duthie[14] which involves precipitation of the polyphenols with Stiasny reagent (100 ml. of conc. HCl, 150 ml. of 36% w/v HCHO and 100 ml. of water). The modifications were the reduction of the volumes of fluids and the collection of precipitates on sintered glass crucibles instead of on Gooch crucibles with asbestos. This made it possible to estimate much smaller quantities of ' tannin '. Determinations were made on aqueous acetone (40% v/v) extracts of dried leaves and clarified acid extracts of fresh leaves. The acetone extracts were made by soaking the dry ground leaf material at room temperature overnight and re-extracting the residue several times with small volumes of acetone solution. Acetone was added to acid extracts of fresh leaves to give a final concentration of 40% v/v and any precipitate formed was removed by centrifuging before addition of the Stiasny reagent.

In this method the weight of precipitate is usually taken as the amount of ' tannin ' present, with no allowance being made for the formaldehyde condensed. Forsyth[9] has commented on this, as he found that (−)-*epi*catechin and catechol gave a value corresponding to a 138% yield of the condensed product. The figures given in the present paper for ' tannin ' content have not been adjusted, because with a complex mixture it is difficult to know what correction to apply, and all figures given in previous published work are uncorrected.

Chromatography.—Descending chromatograms were run on Whatman No. 1 filter paper. The solvents used for one-way chromatograms were water and the organic layer of butanol–acetic acid–water (4 : 1 : 5). Two-way chromatograms were run using water as the first solvent and butanol–acetic acid as the second. The temperature was controlled at 30° (i.e., 1–2° above the normal day-time temperature) in a thermostat cabinet. After allowing the solvent to run a suitable distance, the papers were dried at room temperature and any visibly coloured spots, such as those of the anthocyanin pigments, were marked. ' Anthoxanthins ' were detected by holding the paper over a solution of ammonia and marking the yellow spots which were temporarily made visible. The term ' anthoxanthin ' is used here for substances giving the ammonia reaction and will include chlorogenic acid, caffeic acid and some coumarins, if present, in addition to anthoxanthin pigments. The appearance of spots which fluoresced in ultra-violet light before and after treatment with NH_3 vapour was noted. Papers were sprayed with the potassium ferricyanide–ferric chloride reagent of Barton *et al.*[15] which detects most polyphenols. On other papers, catechins and *leuco*-anthocyanins were marked by spraying with vanillin–HCl (4 vol. of saturated solution of vanillin in ethanol to 1 vol. of conc. HCl). To distinguish between these two groups, the vanillin-reacting spots from several strips were heated in stoppered tubes in a boiling water-bath for 5 min. with a mixture of *n*-butanol (9 vol.) and conc. HCl (1 vol.) and the production of the pink colour characteristic of *leuco*-anthocyanins was noted.

A method similar to that of Forsyth[9] was used for quantitative chromatograms. One-ml. lots of leaf extract, made with 0·33N-HCl, were streaked across 20 cm. of filter paper and

chromatographed with either water or butanol–acetic acid until the solvent front had travelled 30 cm. from the starting line. After the papers had been dried they were examined in ultra-violet light and cut into 1-cm. horizontal strips. Each strip was titrated with 0·01N-$KMnO_4$ after suspending in 10 ml. 1% w/v H_2SO_4. Marker strips at each side of the streak were run for treatment with the ferricyanide–ferric chloride reagent and vanillin–HCl to locate substances in the various bands.

Results

Tinsley & Usher[6] used water extracts of leaves for their colour test. These extracts are dark brown from mature leaves, with infected leaves tending to give darker extracts than those from comparable healthy ones. When dilute acid is used instead of water the extracts remain green, presumably due to the inhibition of polyphenoloxidase activity. After being clarified by filtration through kieselguhr, acid extracts from healthy, mature Amelonado leaves were colourless or straw-coloured. Both pink and green flush leaves, when extracted with acid, gave deep pink solutions with maximum absorption in the visible region of the spectrum at 510 mμ, due to the presence of anthocyanin pigments. Clarified extracts of diseased, mature leaves and healthy, mature leaves of some Trinitario and Upper Amazon selections were sometimes a faint pink.

Effect of alkali

The addition of alkali to clarified acid extracts of mature leaves caused the immediate appearance of a deep yellow to orange colour, which was indicative of the presence of anthoxanthins. Flush-leaf extracts became dark blue, rapidly changing to green due to the change in colour of the anthocyanins superimposed on the anthoxanthin reaction. When acid extracts were heated to boiling in 0·5N-NaOH, or left for several hours at room temperature with 5N-NaOH, a red colour resulted, the intensity of which depended on a number of factors. These included infection with swollen shoot virus, the age of the leaves and the variety of cacao used.

Infected, mature leaves always gave dark red and comparable healthy ones usually, but not invariably, gave a much less intense red colour. The difference therefore between infected and healthy leaves when acid extracts were used was the variation in intensity of the same colour instead of the difference of hue found when water extracts were heated with alkali. When Tinsley & Usher[6] described the colour-test they said that reliable results could only be obtained with mature leaves, as they had found that flush leaves of both infected and healthy trees gave a red colour when heated with alkali (Tinsley & Usher[16]). This was confirmed using both water and acid extracts; the acid extracts gave a clearer, darker red than the water extracts which tended to be red-brown. Extracts which had been clarified before heating with alkali gave a lower intensity of colour than crude extracts, indicating that much of the precursor of the pigment is associated with the insoluble fraction.

Fig. 1 shows the absorption curves in the visible region of the spectrum for acid extracts of fresh flush and mature leaves from healthy and infected trees after heating with 0·5N-NaOH. Extracts from flush leaves and infected mature leaves absorbed much more strongly than those from healthy leaves. The general shapes of the curves were similar for all extracts, but whereas in mature-leaf extracts there was only a shoulder in the 500-mμ region, flush-leaf extracts showed a small peak.

Shaking the alkaline solution with organic solvents did not extract the red pigment, but after acidification, which changed the red to yellow, it was readily extracted by amyl and butyl alcohols and partly by ethyl acetate.

Acid extracts of fresh ripe cacao beans behaved like those of flush leaves when treated with alkali, first becoming dark blue and then dark red on heating.

Usher[17] has made a detailed colour-test survey of trees in ten selections of Trinitario and Upper Amazon cacao. The assessment was made by a visual 'scoring' method, the samples being assigned a number 0, 1 . . . 5 depending partly on the colour and partly on the intensity. Green and green-brown were scored low and red-brown and dark red were scored high. Although water extracts of individual leaves on the same tree often showed wide variation in the colour given on heating with alkali, bulked samples of leaves from most of trees of a selection gave a

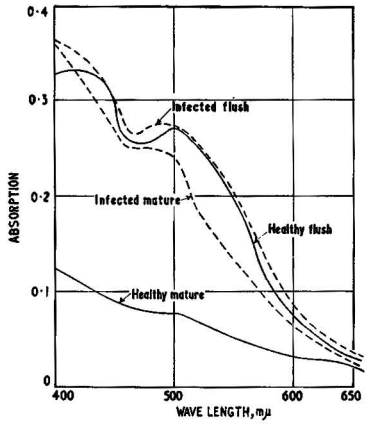

FIG. 1.—*Absorption curves in the visible region of the spectrum of cacao leaf extracts after heating with alkali*

20-g. lots of leaves ground with 150 ml. of 0·1N-HCl 1-ml. aliquots of crude extracts boiled with 1 ml. of N-NaOH, the solutions diluted to 40 ml. with distilled water and filtered

' score ' which was characteristic for that particular selection. For example, most trees of T.60 and T.63 (Parinari × Nanay) gave a low ' score ' and those of T.72 and T.73 (Nanay × Iquitos) and T.76 (Parinari × Nanay) gave a high ' score '. When the trees were re-tested several months later, similar, though not identical, ' scores ' were obtained for the different selections.

Holden & Usher[18] reported that the leaves of infected seedlings gave a positive colour-test value several days before symptoms became apparent. It should, however, be mentioned that when extracts of hardened leaves of young infected seedlings are heated with alkali, although they become appreciably darker than those from comparable healthy leaves, the colour which develops is brown with little trace of red.

Effect of acid

When acid extracts of mature leaves were heated at 100°, a red-brown precipitate, so called ' phlobaphene ' (Forsyth[19]) and a red solution, due to the presence of cyanidin, were formed by the breakdown of *leuco*-anthocyanins. The cyanidin was identified by its absorption spectrum in the visible region of the spectrum and by the R_F values when chromatographed with various solvents. Extracts from infected mature leaves gave more colour and a heavier precipitate than those from corresponding healthy leaves with a low colour-test ' score '.

Qualitative tests for tannin components

Neutralized leaf extracts reduced $AgNO_3$ and gave a green colour with $FeCl_3$. Those from infected leaves gave a deeper colour with $FeCl_3$ and a much more rapid reduction of $AgNO_3$ than those from healthy leaves with a low colour-test ' score ', although healthy leaves with a high ' score ' behaved like infected leaves. This was also true when the vanillin test, which detects both catechins and *leuco*-anthocyanins, was applied to methanol extracts of fresh leaves (Bate-Smith & Lerner[11]). Chlorophyll was removed from the methanol extracts by shaking with light petroleum, leaving a yellow or orange solution. The addition of vanillin in ethanol followed by a few drops of conc. HCl caused a deep red colour in extracts from infected leaves whereas there was little change in extracts from healthy leaves.

' Tannin ' content of cacao leaf

' Acetone-soluble tannin ' determinations on a large number of samples of dried material of healthy mature leaves showed wide variations ranging from 0·8 to 4·1% of the dry matter. The samples were mostly of Amelonado cacao leaves but the values for those of Upper Amazon and Trinitario selections fell within the same range. A series of samples of diseased mature leaves (Amelonado only, as infected material of other types of cacao is rarely available) gave a range of

tannin content from 4·4 to 10·7% of the dry matter. One sample of infected leaves from the Upper Amazon selection, T.73, had a tannin content of 8·5% dry matter compared with 2·9% dry matter for healthy leaves (average of 3 samples). Flush leaves of all trees had a very high ' tannin ' content with values up to 20% of the dry weight.

The hardened leaves of young seedlings tended to have a lower ' tannin ' content than that of mature leaves from older plants ; no values as high as 4% were found for this type of leaf. A comparison was made of the ' acetone-soluble tannin ' content of healthy and infected seedlings of different ages. During the first few weeks after germination there was little difference, but at eight weeks, infected seedlings had a significantly higher ' tannin ' content expressed as percentage dry matter than the healthy controls. The dry weight of the infected seedlings was about 20% less than that of the controls so that the total amount of tannin was approximately the same in the two batches.

Aqueous acetone did not extract all the ' tannin ' from finely ground dried leaves, as additional polyphenolic material could be removed by extraction of the residue with dil. NaOH. A similar fraction is said to occur in the cacao bean, but in recent work it has received little attention. The alkali-soluble polyphenols are thought to be either a series of compounds based on the same structure but having different molecular weights, or a mixture of different substances of molecular weights between 1000 and 2000 (Swain[20]). Alkaline extracts of cacao leaves were dark red and contained substances which co-precipitated with the ' tannin ', causing the results of tannin analyses to be erratic and completely unreliable. It is clear that this fraction may account for a not insignificant proportion of the total ' tannin ' of the leaf.

' Tannin ' determinations on acid extracts of fresh leaves showed wide variation depending on the variety of cacao, the age of the leaf and whether or not it was infected. The intensity of colour given on heating with alkali was correlated with, though not strictly proportional to, the concentration of ' tannin ' present.

Effect of illumination on colour-test ' score ' and ' tannin ' content of leaves

Preliminary results had indicated that the high colour-test ' score ' given by some apparently healthy leaves might be due to those leaves receiving more illumination than those with a low ' score '. Material was available for colour tests and ' tannin ' analyses from an experiment in which seedling cacao was grown with different fertilizer treatments in pots which were either placed in full light, or under shade in a plant barn. The plants were harvested when they were 16 weeks old. Duplicate ' tannin ' determinations were made on aqueous acetone extracts of the dried, ground leaf material. The aqueous-acetone-soluble ' tannin ' content of the twelve batches of ' shade ' leaves varied between 1·55 and 3·46% of the dry matter, with a mean of 2·18%. The ' light ' leaves had a range of values from 2·56 to 3·58% with a mean of 3·15%. Fertilizer treatment influenced the ' tannin ' content, but it is not possible to draw any conclusions from the limited amount of data. In each pair having the same fertilizer treatment the ' light ' seedlings had a higher ' tannin ' content than the shade-grown. For example, the leaves from the ' shade ' and ' light ' seedlings with no added fertilizer had values of 1·62 and 3·11% respectively ; similarly those with added N, P and K had 2·07% for the ' shade ' leaves and 3·47% for ' the light ' leaves.

As it was necessary to dry all the leaf material, the colour test could not be applied in the normal way to extracts of fresh leaves. When the test was done on extracts made by heating the dry leaf powder with water it was clear that for all pairs the ' light ' leaves had a higher ' score ' than the ' shade ' leaves.

Absorption curves in the ultra-violet region

A comparison was made between the ultra-violet absorption curves of clarified acid (0·1N-HCl) extracts of flush and mature leaves from healthy and infected trees to see whether there were any marked differences. The same ratio of acid to wet weight was used for all batches of leaves and the ' tannin ' content of the clarified extracts was determined. The extracts were diluted 1 in 50 for measuring the absorption over the range 240–390 mμ. All curves showed the well-defined maximum at about 280 mμ and minimum between 255 and 260 mμ (Fig. 2), which are characteristic features of the curves given by *leuco*-anthocyanins and catechins (Bate-Smith

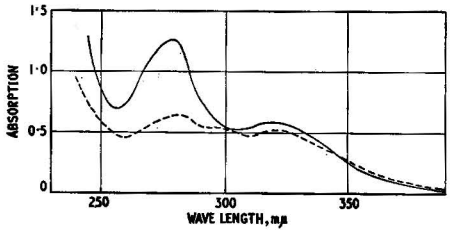

FIG. 2.—*Ultra-violet absorption curves of acid extracts of cacao leaves*
25-g. lots of leaves ground with 150 ml. of 0·1N-HCl. Extracts clarified and ' tannin ' determined
flush leaf, 2·55 g./l. mature leaf, 0·82 g./l
Diluted 1 in 50 for absorption measurements
——— flush leaf extract
– – – – mature leaf extract

& Swain[21]). The curves for extracts of infected leaves were similar in shape to those from healthy leaves of the same age. The extract from infected mature leaves, which had a higher ' tannin ' content than that from comparable healthy ones, absorbed more strongly throughout the wavelength range.

Separation of polyphenols by partition chromatography

Acid extracts of both flush and mature leaves from healthy and diseased trees, and extracts of hardened seedling leaves were chromatographed with the various solvent systems. Flush leaf extracts gave better separation of the spots than those from mature leaves, due partly to their higher ' tannin ' content and also to their being clarified more satisfactorily. There were no qualitative differences between the polyphenols of the different types of leaves.

Anthocyanins.—When acid extracts of flush leaves were chromatographed with butanol–acetic acid two anthocyanins separated. They were not separable from the two main pigments of bean extracts. A_1 (R_F 0·46) was present in much greater amount than A_2 (R_F 0·37) and neither was detectable on chromatograms of mature leaf extracts. There was also a trace of a pigment with R_F 0·17.

Catechins and leuco-*anthocyanins.*—Butanol–acetic acid chromatograms of extracts of all types of leaves, when treated with the ferric chloride–ferricyanide reagent, showed seven well-defined spots and a trail of material from the origin ending in the first spot. The trail and five of the separate spots gave reactions with vanillin and the two others were ' anthoxanthins '. The fastest moving vanillin-reacting spot was (—)-*epi*catechin with R_F about 0·68 and the others with R_F values 0·58, 0·47, 0·39 and 0·26 and the trail gave a pink colour on heating with butanol and HCl, indicating *leuco*-anthocyanins. The first three of these probably correspond with *leuco*-anthocyanins L_1, L_2 and L_3 of the cacao bean as described by Forsyth,[9] although the R_F values were all rather higher than he found. Other catechins, such as occur in the cacao bean, must, if present, be in very low concentrations. The R_F values of two of them are such that they would probably overlap with the *leuco*-anthocyanins, but two-way chromatography does not increase the number of vanillin-reacting spots.

' *Anthoxanthins* ' were conspicuous on chromatograms of extracts of all types of cacao leaves. On two-way chromatograms of Amelonado leaf extracts, at least eight spots appeared yellow with ammonia in visible light. Four of these were apparently due to the presence of isomers of chlorogenic acid. The separation and identification of the ' anthoxanthins ' and related substances will be discussed in another paper.

Quantitative chromatograms and separation of the red-producing substance (*R*)

Quantitative differences in the various polyphenolic components of different types of leaves were compared by running streak chromatograms of acid extracts with butanol–acetic acid and with water and titrating with $KMnO_4$. Fig. 3 compares the titrations of water chromatograms of extracts from healthy and infected mature leaves and flush leaves. The ' tannin ' content (as determined by precipitation with Stiasny reagent) was 6·6 g./l. for flush, 4·9 g./l. for infected, mature leaf and 2·3 g./l. for healthy, mature leaf extracts and the titration figures for 1-ml. aliquots of each after chromatographing were 25·9 ml., 22·3 ml. and 19·4 ml. of 0·0115N-$KMnO_4$ respectively. With the mature leaf extracts the *leuco*-anthocyanin peaks were not obvious. There was a good deal of oxidizable material left at the starting line and there were high titrations

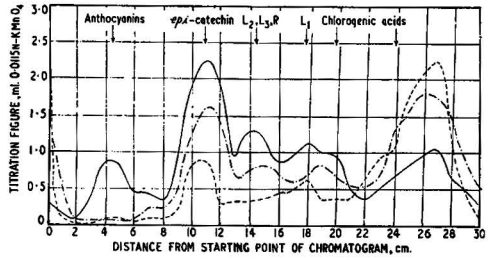

FIG. 3.—*Quantitative paper chromatograms of cacao leaf extracts, with water as solvent*

1-ml. lots of leaf extracts (40 g. of leaves/100 ml. of 0·33N-HCl) streaked across 22 cm. paper

——— flush, 'tannin' 6·6 g./l.
– – – – healthy mature, 2·3 g./l.
——·—— infected mature, 4·9 g./l.

Solvent run for 30 cm. and each 1-cm. horizontal strip titrated with $KMnO_4$

in the strips, which did not contain polyphenols, near the solvent front. It was intended to express the results for the different groups of polyphenols as a percentage of the total titration for the sheet (Williams[22]), but it was clearly impossible to do this since the total bore little relation to the polyphenol content of the extract. For example, the *epi*catechin in the flush leaf extract accounted for 35% of the total titration and 14% of the 'tannin'.

Fig. 4 compares the titrations of butanol–acetic acid chromatograms of the same extracts as were used for water chromatograms. There was good agreement between the figures for the total titration for each extract run with the two solvents.

To locate the position of the red-producing substance (R), chromatograms were run as for quantitative comparisons, the 1-cm. strips cut out and 1 ml. of 0·5N-NaOH added to each. Flush leaf extracts with their high 'tannin' content were far more satisfactory than even infected leaf extracts for locating colour-producing substances. Colours before and after heating the strips with the alkali were noted. The strips containing the 'anthoxanthins' all gave yellow colours with some browning of the chlorogenic acid but on heating these, there were no obvious colour changes; the strips containing the *epi*catechin gave a faint brown. On water chromatograms, the red-producing substance was diffused over a large area of the paper (R_F 0·25–0·60) in the strips containing the *epi*catechin and the *leuco*-anthocyanins, but on butanol–acetic acid chromatograms it was rather more localized. When a 0·1N-HCl extract was used, only the strips between R_F 0·2 and 0·3 gave a definite red colour on heating with

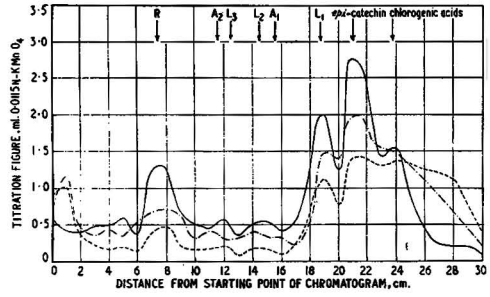

FIG. 4.—*Quantitative paper chromatograms of cacao leaf extracts with butanol–acetic acid as solvent*

1-ml. lots of leaf extracts (40 g. of leaves/100 ml. of 0·33N-HCl) streaked across 22 cm. paper

——— flush, 'tannin' 6·6 g./l.
– – – – healthy mature, 2·3 g./l.
——·—— infected mature, 4·9 g./l.

Solvent run for 30 cm. and each 1-cm. horizontal strip titrated with $KMnO_4$

alkali although with 0·33N-HCl extracts, the whole area from the origin to $R_F \sim 0{\cdot}3$ gave some colour. With both concentrations of acid the highest intensity of colour occurred at about R_F 0·25. This corresponded to the strips with a relatively high permanganate titration which contained a high concentration of *leuco*-anthocyanin-reacting material.

The same extracts which were used for the experiments described above were used for comparing the amount of *leuco*-anthocyanin in this band. Horizontal strips from 1-ml. streak chromatograms run with butanol-acetic acid were heated with *n*-butanol and HCl and the intensity of the red colour (cyanidin) in the solutions measured in a colorimeter. As with the permanganate titration figures, the extracts from flush leaves gave the highest values, those from healthy mature leaves the lowest, with those from infected mature leaves giving intermediate colorimeter readings.

Attempts have been made to separate this *leuco*-anthocyanin fraction in larger amounts by the use of a column of cellulose pulp, but so far these have been unsuccessful.

Discussion

The present investigation has shown that like most other chemical tests for the detection of virus infection, the Tinsley–Usher colour-test, which had earlier given promising results, is not suitable for large-scale application. If a suitable sampling technique is used, there seems little chance of an infected tree failing to give a positive reaction in the test (i.e. a high ' score ' due to a high intensity of red colour) but not all trees which do so are infected with virus.

The substance which is mainly responsible for the red colour of cacao leaf extracts which have been heated with alkali has the reactions of a *leuco*-anthocyanin. It is present in both healthy and infected leaves and varies with the ' tannin ' content. Therefore any factor which affects the ' tannin ' content will also affect the amount of *leuco*-anthocyanin and the ' score ' in the colour-test. The ' tannin ' content of young flush leaves is very high compared with that of mature leaves and extracts from them always give a high intensity of red colour when heated with alkali, whether they are healthy or infected. The ' tannin ' content of mature leaves is variable depending on whether or not the tree is infected with virus, on the amount of illumination it has received, on the variety of cacao and probably on other factors such as the nutritional status of the tree and attacks by other pathogens. There are thus too many variables to be taken into account to apply the colour-test for routine testing.

A satisfactory chemical test for virus infection should depend on the presence, or absence, of a particular substance in the infected leaves, or on the substance being in such different concentrations in healthy and infected leaves, and affected only by infection with virus, that unequivocal results are obtained.

Although the investigation has proved disappointing from the point of view of establishing a chemical test for detecting virus infection, it has provided information on polyphenolic and related substances of the cacao leaf. This will be of use in connexion with the study of the mechanical transmission of swollen shoot virus which is being made.

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References

[1] Lindner, R. C., *Science*, 1948, **107**, 17
[2] Lindner, R. C., Weeks, T. E., & Kirkpatrick, H. C., *Phytopathology*, 1951, **41**, 809
[3] Lindner, R. C., Weeks, T. E., & Kirkpatrick, H. C., *Phytopathology*, 1949, **39**, 1059
[4] Lindner, R. C., Kirkpatrick, H. C., & Weeks, T. E., *Science*, 1950, **112**, 119
[5] Attafuah, A., personal communication
[6] Tinsley, T. W., & Usher, G., *Nature, Lond.*, 1954, **174**, 87

[7] Forsyth, W. G. C., *Biochem. J.*, 1952, **51**, 511
[8] Forsyth, W. G. C., *Rep. London Cocoa Conference*, 1953, p. 32
[9] Forsyth, W. G. C., *Biochem. J.*, 1955, **60**, 108
[10] Bate-Smith, E. C., *Biochem. J.*, 1954, **58**, 122
[11] Bate-Smith, E. C., & Lerner, N. H., *Biochem. J.*, 1954, **58**, 126
[12] Geissman, T. A., & Hinreiner, E. H., *Bot. Rev.*, 1952, **18**, 77
[13] Posnette, A. F., *Nature, Lond.*, 1947, **159**, 500
[14] Duthie, D. W., *Analyst*, 1938, **63**, 27
[15] Barton, G. M., Evans, R. S., & Gardner, J. A. F., *Nature, Lond.*, 1952, **170**, 249
[16] Tinsley, T. W., & Usher, G., personal communication
[17] Usher, G., personal communication
[18] Holden, M., & Usher, G., *Rep. W. Afr. Cocoa Res. Inst.*, 1954–55, p. 38
[19] Forsyth, W. G. C., *Nature, Lond.*, 1953, **172**, 726
[20] Swain, T., Brit. Food Manufacturing Ind. Res. Ass., Sci. & Tech. Surv., 1954, No. 23
[21] Bate-Smith, E. C., & Swain, T., *Chem. & Ind.*, 1953, p. 377
[22] Williams, A. H., *Chem. & Ind.*, 1953, p. 340

THE TOXICITY OF ORGANIC SULPHIDES TO THE EGGS AND LARVAE OF THE GLASSHOUSE RED SPIDER MITE. II.* Miscellaneous Sulphides

By R. F. BROOKES, J. E. CRANHAM, D. GREENWOOD and H. A. STEVENSON

The activities against the eggs and young mites of the glasshouse red spider (*Tetranychus telarius* L.) shown by a number of compounds, all containing two benzene nuclei linked by various sulphur-containing bridges, are tabulated and discussed.

Introduction

The method used for laboratory testing of a series of *SS'*-disubstituted alkane-$\alpha\omega$-dithiols against the red spider mite has already been described.[1] Two of the most active compounds of this series (bisphenylthiomethane and 1 : 2-bisphenylthioethane) were tested in the field and found to be phytotoxic. The activity against the red spider mite, however, was sufficient to warrant further synthesis of similar compounds in the hope of discovering a non-phytotoxic substance which retained the activity against the mites. All of the compounds tested consisted of two benzene nuclei linked by some variation of the sulphur-containing bridge.

As with the work already described, the present work formed part of a larger programme involving further tests on promisingly active compounds.

Experimental

Synthesis of compounds

A. *Benzyl thiolobenzoates.*—This series of compounds was prepared by the action of the appropriate benzoyl chloride on an alkali-metal salt of the substituted phenylmethanethiol.

B. *Disulphides.*—The phenyl disulphides were prepared by oxidation of the corresponding thiols or by reduction of the sulphonyl chlorides, and the benzyl disulphides were obtained from the appropriate benzyl halides and sodium disulphide.

C. *Aryl phenylthioloacetates.*—These substances were prepared from the appropriately substituted arylacetyl chlorides and arenethiols in the presence of alkali.

D. *Aryl phenacyl sulphides.*—Similarly obtained by the action of a phenacyl halide on an alkali-metal salt of an arenethiol.

E. *Aryl thiolobenzoates.*—From the benzoyl chloride and arenethiol.

F. *Sulphides.*—The unsymmetrical sulphides were usually prepared from the appropriate thiols and halides but *2-hydroxy-2-phenylethyl phenyl sulphide* (Ref. No. 3353) was obtained by the Ponndorf reduction of phenyl phenacyl sulphide.

G. *Bis-sulphides.*—By the action of the appropriate dihalide on the alkali-metal salt of a thiol.

* Part I: *J. Sci. Fd Agric.*, 1957, **8**, 31

H. N-*Benzyl*-N-*methylbenzenesulphenamides*.—Prepared by the reaction of an arenesulphenyl chloride (usually prepared *in situ* by the chlorinolysis of the corresponding disulphide in carbon tetrachloride) with the *N*-methylbenzylamine in the presence of a *tertiary* base (e.g. triethylamine).

Biological methods

The methods of rearing mites and of testing have been described in a previous communication.[1] Compounds were first tested by the dipping technique at 0·1% and 0·025% concentration of the test chemical or, with certain compounds, only at 0·1%. A ' formulation control ' of suspension medium only, and a ' standard ' acaricide were included in each test. Bisphenylthiomethane was used as the standard.

Results

Table I gives the initial ' total mortality '[1] (i.e. kill of eggs and young mites) obtained at 0·1% concentration of each compound, and at 0·025% where carried out, corrected by the method of Finney[2] for mortality in the ' formulation controls '. The results of further tests on certain active compounds are summarized in Table II.

Discussion of results

The most active groups in laboratory tests were the dibenzyl disulphides and the benzyl thiolobenzoates. No compounds of comparable activity occurred in other groups with the exception of 1 : 2-dichloro-1 : 2-bisphenylthioethylene (Ref. No. 2547). The dibenzyl disulphides were more active than the corresponding diphenyl disulphides or the dibenzyl monosulphides.

Table I

A. *Benzyl thiolobenzoates*

$XC_6H_4{\cdot}CO{\cdot}S{\cdot}CH_2{\cdot}C_6H_4Y$

Ref. No.	X	Y	% 'Total' mortality 0·1%	0·025%	M.p., °c	Formula	Analysis Found % C	% H	Required % C	% H	Reference
2476	H	H	99	76	37–38	$C_{14}H_{12}OS$	—		—		3
2485	H	*p*-Cl	100	98	42–43	$C_{14}H_{11}OClS$	64·1	4·1	64·1	4·2	*
2477	*p*-Cl	H	100	92	53–54·5	$C_{14}H_{11}OClS$	63·9	4·4	64·1	4·2	*
2478	*p*-Cl	*p*-Cl	92	62	119–120	$C_{14}H_{10}OCl_2S$	56·6	3·4	56·6	3·4	*
							% N		% N		
2699	H	*p*-NO_2	49	0	92–92·5	$C_{14}H_{11}O_3NS$	5·05		5·1		*
2675	*p*-NO_2	H	100	99	83–84	$C_{14}H_{11}O_3NS$	5·3		5·1		*
2753	*p*-Cl	*p*-NO_2	21	0	115–115·5	$C_{14}H_{10}O_3NClS$	4·7		4·6		*
2701	*p*-NO_2	*p*-Cl	7	0	74–75	$C_{14}H_{10}O_3NClS$	4·75		4·6		*

* Prepared by R. F. B.

B. *Disulphides*

R·S·S·R

Ref No.	R	% 'Total' mortality 0·1%	0·025%	M.p., °c or b.p., °c/mm.	Formula	Analysis Found % C	% H	Required % C	% H	Reference
2139	$PhCH_2$	99	98	70	$C_{14}H_{14}S_2$	—		—		4
2462	*p*-$FC_6H_4{\cdot}CH_2$	99	76	62–63	$C_{14}H_{12}F_2S_2$	59·75	4·3	59·6	4·3	††
2335	*p*-$ClC_6H_4{\cdot}CH_2$	100	66	59	$C_{14}H_{12}Cl_2S_2$	—		—		5
2418	$PhCH_2{\cdot}CH_2$	97	88	188–192/1·5	$C_{16}H_{18}S_2$	—		—		6
2013	Ph	43	—	61	$C_{12}H_{10}S_2$	—		—		7
2463	*p*-FC_6H_4	27	—	131/1·0	$C_{12}H_8F_2S_2$	57·0	3·2	56·7	3·15	††
2236	*p*-ClC_6H_4	52	—	72	$C_{12}H_8Cl_2S_2$	—		—		8
2237	*o*-ClC_6H_4	5	—	87–88	$C_{12}H_8Cl_2S_2$	—		—		9
2427	2 : 4 : 5-$Cl_3C_6H_2$	0	0	148	$C_{12}H_4Cl_6S_2$	34·7	1·2	33·9	0·9	**
1893	*o*-$AcO{\cdot}C_6H_4$	0	—	57	$C_{16}H_{14}O_4S_2$	57·35	3·8	57·5	4·2	**
4340	3-NO_2-4-NH_2-C_6H_3	5	3	168–169	$C_{12}H_{10}O_4N_4S_2$	—		—		10
2605	$C_{10}H_7$-2	15	—	139	$C_{20}H_{14}S_2$	—		—		11

†† Prepared by N. G. Clark. ** Prepared by D. G.

Table I (*contd.*)

C. *Aryl phenylthioloacetates*

$XC_6H_4{\cdot}CH_2{\cdot}CO{\cdot}S{\cdot}C_6H_4Y$

Ref. No.	X	Y	% 'Total' mortality 0·1%	% 'Total' mortality 0·025%	M.p., °c	Formula	Analysis Found %C	Found %H	Required %C	Required %H	Reference
2523	H	H	26	0	34–35	$C_{14}H_{12}OS$	73·6	5·2	73·7	5·3	*
2534	H	*p*-Cl	81	29	62–63	$C_{14}H_{11}OClS$	64·1	4·0	64·0	4·2	*
2639	*p*-Cl	H	54	12	59·5–60·5	$C_{14}H_{11}OClS$	63·7	4·1	64·0	4·2	*
2679	*p*-Cl	*p*-Cl	97	53	63–64	$C_{14}H_{10}OCl_2S$	56·5	3·7	56·6	3·4	*
							% N		% N		
2700	H	*p*-NO_2	0	0	69–70	$C_{14}H_{11}O_3NS$	5·3		5·1		*
2535	*p*-NO_2	H	0	0	61–61	$C_{14}H_{11}O_3NS$	5·3		5·1		*
2536	*p*-NO_2	*p*-Cl	P	0	104–105	$C_{14}H_{10}O_3NClS$	4·85		4·55		*
2676	*p*-Cl	*p*-NO_2	26	0	89–90	$C_{14}H_{10}O_3NClS$	4·7		4·55		*

* Prepared by R. F. B. P No assessment due to phytotoxicity

D. *Aryl phenacyl sulphides*

$XC_6H_4{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}C_6H_4Y$

Ref. No.	X	Y	% 'Total' mortality 0·1%	% 'Total' mortality 0·025%	M.p., °c	Formula	Analysis Found %C	Found %H	Required %C	Required %H	Reference
2524	H	H	29	0	53–54	$C_{14}H_{12}OS$	—		—		12
2525	H	*p*-Cl	28	0	80–81	$C_{14}H_{11}OClS$	—		—		13
2640	*p*-Cl	H	24	0	57–57·5	$C_{14}H_{11}OClS$	63·9	3·8	64·0	4·2	*
2641	*p*-Cl	*p*-Cl	0	0	115–116	$C_{14}H_{10}OCl_2S$	56·2	3·2	56·6	3·4	*
2643	*p*-Cl	*p*-NO_2	21	29	138–139	$C_{14}H_{10}O_3NClS$	54·5	2·9	54·6	3·3	*
							% N		% N		
2638	H	*p*-NO_2	0	0	118	$C_{14}H_{11}O_3NS$	—		—		14
2805	*p*-NO_2	H	57	15	100–101	$C_{14}H_{11}O_3NS$	5·2		5·1		*
2644	*p*-NO_2	*p*-Cl	11	8	104–105	$C_{14}H_{10}O_3NClS$	4·75		4·55		*

* Prepared by R. F. B.

E. *Aryl thiolobenzoates*

$XC_6H_4{\cdot}CO{\cdot}S{\cdot}C_6H_4Y$

Ref. No.	X	Y	% 'Total' mortality 0·1%	% 'Total' mortality 0·025%	M.p., °c	Formula	Analysis Found %C	Found %H	Required %C	Required %H	Reference
2442	H	H	23	—	55–56	$C_{13}H_{10}OS$	—		—		15
2441	H	*p*-Cl	97	36	74–75	$C_{13}H_9OClS$	—		—		16
2445	*p*-Cl	H	64	8	81–82	$C_{13}H_9OClS$	63·0	3·7	62·8	3·6	*
2440	*p*-Cl	*p*-Cl	P	0	134–135	$C_{13}H_8OCl_2S$	55·2	2·9	55·0	2·8	*
							% N		% N		
2980	*p*-NO_2	*p*-Cl	98	47	74–75	$C_{13}H_8O_3NClS$	4·8		4·8		*

* Prepared by R. F. B. P No assessment due to phytotoxicity

F. *Sulphides*

X·S·Y

Ref. No.	X	Y	% 'Total' mortality 0·1%	% 'Total' mortality 0·025%	M.p., °c or b.p., °c/mm.	Formula	Analysis Found %C	Found %H	Required %C	Required %H	Reference
2495	*p*-ClC_6H_4	*p*-ClC_6H_4	100	38	91–92	$C_{12}H_8Cl_2S$	—		—		17
2433	$PhCH_2$	$PhCH_2$	74	11	49–50	$C_{14}H_{14}S$	—		—		18
2432	*p*-$ClC_6H_4{\cdot}CH_2$	*p*-$ClC_6H_4{\cdot}CH_2$	98	32	40–42	$C_{14}H_{12}Cl_2S$	—		—		5
2464	$PhCH_2{\cdot}CH_2$	$PhCH_2{\cdot}CH_2$	75	13	164–166/1·5	$C_{16}H_{18}S$	—		—		19
2416	Ph	$PhCH_2{\cdot}CH_2$	16	0	160–162/3·5	$C_{14}H_{14}S$	—		—		20
2469	*p*-ClC_6H_4	$PhCH_2{\cdot}CH_2$	96	36	150–155/1·0	$C_{14}H_{13}ClS$	67·1	5·3	67·5	5·2	†
3151	Ph	PhCH:CH	P	26	150–151/1·5	$C_{14}H_{12}S$	78·5	5·2	79·2	5·7	**
3152	*p*-ClC_6H_4	PhCH:CH	66	15	164–165/1·0	$C_{14}H_{11}ClS$	67·8	4·0	68·2	4·5	**
3191	*p*-ClC_6H_4	*p*-ClC_6H_4CH:CH	P	13	99–100	$C_{14}H_{10}Cl_2S$	59·4	3·3	59·8	3·55	**
2406	Ph	$PhOCH_2{\cdot}CH_2$	92	19	65–67	$C_{14}H_{14}OS$	73·4	6·3	73·0	6·1	†
3353	Ph	$PhCH(OH){\cdot}CH_2$	30	10	168/2·0	$C_{14}H_{14}OS$	72·85	6·3	73·0	6·1	**

† Prepared by B. S. Jackson ** Prepared by D. G. P No assessment due to phytotoxicity

Table I (*contd.*)

G. *Bis-sulphides*

X·S·R·S·X

Ref. No.	X	R	% 'Total' mortality 0·1%	0·025%	M.p., °C	Formula	Analysis Found % C	% H	Required % C	% H	Reference
2547	Ph	CCl:CCl	99	88	69–70	$C_{14}H_{10}Cl_2S_2$	—		—		21
2956	*p*-ClC_6H_4	CCl:CCl	82	3	89–90	$C_{14}H_8Cl_4S_2$	44·2	2·1	44·0	2·1	**
3750	*p*-ClC_6H_4	CH_2·CH(OH)·CH_2	17	3	45	$C_{15}H_{14}OCl_2S_2$	52·4	4·0	52·2	4·1	***
3751	*p*-ClC_6H_4	CH_2·CHCl·CH_2	15	6	85–86	$C_{15}H_{13}Cl_3S_2$	49·4	3·5	49·5	3·6	***
2221	$PhCH_2$	CH:CH	88	28	60	$C_{16}H_{16}S_2$	—		—		22
2362	*p*-ClC_6H_4·CH_2	CH:CH	16	0	88	$C_{16}H_{14}Cl_2S_2$	56·2	4·0	56·3	4·1	†
2388	Ph	CH_2·CH_2·S·CH_2·CH_2	94	13	52	$C_{16}H_{18}S_2$	—		—		23
2051	Ph	CO	30	—	41–42	$C_{13}H_{10}OS_2$	—		—		24
2052	Ph	CS	6	—	96	$C_{13}H_{10}S_3$	—		—		25
2957	*p*-ClC_6H_4	CMe_2	100	3	54	$C_{15}H_{14}Cl_2S_2$	—		—		26

** Prepared by D. G. *** Prepared by J. Fraser † Prepared by B. S. Jackson

H. *N-Benzyl-N-methylbenzenesulphenamides*

XC_6H_4·CH_2·N(CH_3)·S·C_6H_4Y

Ref. No.	X	Y	% 'Total' mortality 0·1%	0·025%	M.p., °C or b.p., °C/mm.	Formula	Analysis Found % N	Required % N	Reference
2601	H	H	19	—	145–146/1·0	$C_{14}H_{15}NS$	5·8	6·1	*
2642	*p*-Cl	*p*-Cl	9	—	47·5–48	$C_{14}H_{13}NCl_2S$	4·8	4·7	*
2602	*p*-Cl	*p*-NO_2	32	—	59·5–60·5	$C_{14}H_{13}O_2N_2SCl$	9·2	9·1	*
2740	*p*-NO_2	H	19	—	49·5–50·5	$C_{14}H_{14}O_2N_2S$	10·0	10·2	*
2678	*p*-NO_2	*p*-Cl	41	20	59·0–60·0	$C_{14}H_{13}O_2N_2ClS$	9·1	9·1	*
2600	*p*-NO_2	*p*-NO_2	17	—	96·5–97·5	$C_{14}H_{13}O_4N_3S$	13·2	13·2	*

* Prepared by R. F. B.

Table II

The activity of various organic sulphides against eggs and young mites of red spider (further tests)

Test	Ref. No.	Substance	% 'Total' mortality at 0·05%	0·025%	0·0125%	0·00625%
I	2139	Dibenzyl disulphide	100	92	—	—
	2335	Bis-*p*-chlorobenzyl disulphide	100	52	—	—
II	2139	Dibenzyl disulphide	—	94	87	79
	2335	Bis-*p*-chlorobenzyl disulphide	—	71	36	7
III	2441	*p*-Chlorophenyl thiolobenzoate	54	9	—	—
	2388	Bis-2-phenylthiolethyl sulphide	48	4	—	—
	2432	Bis-*p*-chlorobenzyl sulphide	31	12	—	—
	2433	Dibenzyl sulphide	26	6	—	—
IV	2462	Bis-*p*-fluorobenzyl disulphide	99	72	—	—
	2418	Bis-2-phenylethyl disulphide	95	85	59	—
	2476	Benzyl thiolobenzoate	97	71	48	17
	2477	Benzyl *p*-chlorothiolobenzoate	99	79	72	60
	2485	*p*-Chlorobenzyl thiolobenzoate	100	94	78	—
V	2469	*p*-Chlorophenyl 2-phenylethyl sulphide	65	40	—	—
	2478	*p*-Chlorobenzyl *p*-chlorothiolobenzoate	91	57	—	—
	2495	Bis-*p*-chlorophenyl sulphide	70	21	—	—
VI	2675	Benzyl *p*-nitrothiolobenzoate	100	100	76	48
	2547	1 : 2-Dichloro-1 : 2-bisphenylthioethylene	84	82	53	37
	2957	2 : 2-Bis-*p*-chlorophenylthiopropane	62	32	18	6
VII	2547	1 : 2-Dichloro-1 : 2-bisphenylthioethylene	92	76	48	28

The benzyl thiolobenzoates (—CO·S·CH_2—) were generally more active than the isomeric aryl phenylthioloacetates (—S·CO·CH_2—) and the corresponding phenyl thiolobenzoates (—CO·S—). The aryl phenacyl sulphides (—S·CH_2·CO—) were least active.

In comparing the activity of compounds substituted by chlorine in the *para* position of the

nucleus against the corresponding unsubstituted compounds there was no general rule. Sometimes the unsubstituted compounds were the most active, e.g. dibenzyl disulphide (Ref. No. 2139), 1 : 2-dichloro-1 : 2-bisphenylthioethylene (Ref. No. 2547) and 1 : 2-bisbenzylthioethylene (Ref. No. 2221) were more active than the corresponding nuclear substituted compounds (Ref. Nos. 2335, 2956 and 2362). In other cases, however, the unsubstituted compounds were either inactive or much less active than the *para*-chlorine-substituted compounds. Thus, phenyl phenylthioloacetate (Ref. No. 2523) and phenyl 2-phenylethyl sulphide (Ref. No. 2416) were less active than the corresponding substituted compounds (Ref. Nos. 2534, 2639, 2679 and 2469). In other active groups—e.g. the benzyl thiolobenzoates and the dibenzyl sulphides—the substituted and the unsubstituted compounds had the same order of activity.

Similar variation is found on comparing the effect on activity of bis-*para*-chlorination against mono-*para*-chlorination. In the phenyl phenylthioloacetates, the bis-*para*-chlorinated derivative (Ref. No. 2679) was the most active compound but in the phenyl thiolobenzoates the bis-*para*-chlorinated derivative (Ref. No. 2440) was probably less active than either of the mono-*para*-chlorinated compounds (Ref. Nos. 2441 and 2445). In the benzyl thiolobenzoates the bis- (Ref. No. 2478) and mono-*para*-chlorinated derivatives had a very similar order of activity.

Eaton & Davies[27] found that, in a series of compounds containing two benzene nuclei connected by certain bridging groups, activity to the summer eggs and adults of fruit tree red spider (*M. ulmi* Koch) could be influenced by substitution in the benzene nuclei. Maximum activity appeared to be associated with chlorine substitution in the *para* position in one nucleus and also with compounds of this type having unsubstituted nuclei. Kenaga[28] found with a series of substituted phenyl benzoates, and Kenaga & Hummer[29] with a series of substituted phenyl benzenesulphonates, that maximum ovicidal activity (two-spotted spider mite) occurred where both benzene nuclei were substituted with chlorine in the *para* position.

The present findings show that no general conclusions of this type can be applied to different groups of organic compounds containing two benzene nuclei connected by a bridging group, although they confirm that *para*-chlorination often has a marked effect and may yield more active compounds.

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References

[1] Brookes, R. F., Cranham, J. E., Cummings, W. A. W., Greenwood, D., Jackson, B. S., & Stevenson, H. A., *J. Sci. Fd Agric.*, 1957, **8**, 31
[2] Finney, D. J., 'Probit Analysis', 1947 (London: Cambridge Univ. Press)
[3] Otto, R., & Lüders, R., *Ber. dtsch. chem. Ges.*, 1880, **13**, 1283
[4] Märcker, C., *Liebigs Ann.*, 1865, **136**, 75
[5] Jackson, C. L., & White, J. F., *Amer. chem. J.*, 1880, **2**, 158
[6] McMillan, F. H., & King, J. A., *J. Amer. chem. Soc.*, 1948, **70**, 4143
[7] Hübner, H., & Alsberg, J., *Liebigs Ann.*, 1870, **156**, 308
[8] Otto, R., *Liebigs Ann.*, 1867, **143**, 100
[9] Friedlander, P., & Mauthner, F., *Z. Farb.-u. Textilchem.*, 1904, **3**, 333
[10] Challenger, F., & Peters, A. T., *J. chem. Soc.*, 1928, **130**, 1364
[11] Fries, K., & Schürmann, G., *Ber. dtsch. chem. Ges.*, 1914, **47**, 1195
[12] Delisle, A., *Ber. dtsch. chem. Ges.*, 1889, **22**, 306
[13] Carmack, I. V. M., *J. Amer. chem. Soc.*, 1946, **68**, 1867
[14] Waldron, W. R., & Reid, E. E., *J. Amer. chem. Soc.*, 1923, **45**, 2399
[15] Schiller, R., & Otto, R., *Ber. dtsch. chem. Ges.*, 1876, **9**, 1634
[16] Daccomo, G., *Ann. chim. farm.*, 1891, **14**, 1
[17] Krafft, F., *Ber. dtsch. chem. Ges.*, 1874, **7**, 1164
[18] Price, T. S., & Twiss, D. F., *J. chem. Soc.*, 1910, **97**, 1175
[19] Denison, G. H., & Condit, P. C., *Industr. Engng Chem.*, 1945, **37**, 1102
[20] v. Braun, J., & Weissbach, K., *Ber. dtsch. chem. Ges.*, 1929, **62B**, 2416
[21] Cusa, N. W., & McCombie, H., *J. chem. Soc.*, 1937, p. 767
[22] Fromm, E., Benzinger, H., & Schafer, H., *Liebigs Ann.*, 1912, **394**, 325
[23] Alexander, J. R., & McCombie, H., *J. chem. Soc.*, 1931, **133**, 1913
[24] Rivier, M. H., *Bull. Soc. chim. Fr.*, 1907, [iv], **1**, 733
[25] Autenrieth, W., & Hefner, H., *Ber. dtsch. chem. Ges.*, 1925, **58**, 2151
[26] du Pont de Nemours & Co., E. I., U.S.P. 2,580,550
[27] Eaton, J. K., & Davies, R. G., *Ann. appl. Biol.*, 1950, **37**, 471
[28] Kenaga, E. E., *J. econ. Ent.*, 1949, **42**, 999
[29] Kenaga, E. E., & Hummer, R. W., *J. econ. Ent.* 1949, **42**, 996

THE TOXICITY OF ORGANIC SULPHIDES TO THE EGGS AND LARVAE OF THE GLASSHOUSE RED SPIDER MITE. III.*— Benzyl Phenyl Sulphides Substituted only by Halogens

By N. G. CLARK, J. E. CRANHAM, D. GREENWOOD, J. R. MARSHALL and H. A. STEVENSON

The activities against the eggs and young mites of the glasshouse red spider (*Tetranychus telarius* L.) have been determined for a series of benzyl phenyl sulphides containing only halogen nuclear substituents. The results, together with the results from some of the corresponding sulphoxides and sulphones, are tabulated and discussed.

Introduction

In earlier papers of this series[1, 2] a description has been given of the activities against the red spider mite, in laboratory tests, of a series of *SS'*-disubstituted alkane-$\alpha\omega$-dithiols and, also, of a series of compounds consisting of two benzene nuclei linked by various sulphur-containing bridges. During the preparation of the latter series of compounds, benzyl phenyl sulphide was synthesized and, although the activity of this unsubstituted parent compound was low, it soon became apparent that substitution by halogens in either or both of the benzene nuclei had a profound effect on the activity. As, in addition, these compounds had little or no phytotoxicity, a series of benzyl phenyl sulphides containing only halogen nuclear substituents was prepared and tested.

Many of the sulphides were oxidized to the corresponding sulphoxides and sulphones which were also tested for activity, since there was evidence to indicate that oxidation of *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside) could occur after application on leaf surfaces.[3]

Experimental

Synthesis of compounds

The sulphides were prepared by refluxing one equivalent each of the appropriate arenethiol and benzyl halide in alcohol, containing one equivalent of dissolved sodium, for one hour.

The sulphoxides and sulphones were obtained by oxidizing the sulphides with one equivalent of hydrogen peroxide in acetic acid for 24 hours at 20–30°, and with excess of hydrogen peroxide in acetic acid at 100° for 2 hours, respectively.

The bromobenzyl sulphides were prepared from *p*-bromobenzyl bromide,[4] as this intermediate can be more readily obtained in a pure state than *p*-bromobenzyl chloride. Chlorination of *p*-bromotoluene gave a mixture consisting probably of *p*-bromobenzyl and *p*-chlorobenzyl halides. Attempted side-chain chlorination of *p*-iodotoluene similarly resulted in considerable displacement of the nuclear iodine, but *p*-iodobenzyl bromide was readily obtained with little or no replacement of iodine.

Biological methods

The methods of rearing mites and of testing have been described in a previous paper.[1] Compounds were first tested (Test A) by the dipping technique at 0·1% and 0·025% concentration of test chemical. A ' formulation control ' of suspension medium only, and a ' standard ' acaricide were included in each test. Bisphenylthiomethane was used as a standard until the outstanding activity of *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside) was discovered, when this became the standard. Compounds promisingly active in this first test were retested (Test B) at 0·02% and 0·01% of toxicant applied by spraying as previously described.[1] This method of application was more precise and it gave a more severe test of activity since the spray did not wet the leaves completely.

Results

The compounds prepared with their chemical analysis, m.p. or b.p. and biological activity are shown in Tables I and II.

* Part II : preceding paper

Table I

Halogen-substituted benzyl phenyl sulphides

$XC_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_6H_4Y$

Ref. No.	X	Y	% Mortality Test A 0·1%	Test A 0·025%	Test B 0·02%	Test B 0·01%	M.p., ° c, or b.p., ° c/mm.	Formula	Analysis Found % C	Found % H	Required % C	Required % H	Reference
2126	H	H	16	0	—	—	44	$C_{13}H_{12}S$	—		—		5
2452	H	*p*-F	7	0	—	—	32·5–33·0	$C_{13}H_{11}FS$	71·8	5·5	71·55	5·05	*
2127	H	*p*-Cl	45	0	—	—	52–53	$C_{13}H_{11}ClS$	—		—		6
3880	H	2 : 5-Cl_2	0	0	—	—	65	$C_{13}H_{10}Cl_2S$	57·95	3·7	58·0	3·7	**
2426	H	2 : 4 : 5-Cl_3	22	0	—	—	118–119	$C_{13}H_9Cl_3S$	51·7	2·9	51·4	3·0	**
3506	H	*p*-Br	84	27	30	12	64–65	$C_{13}H_{11}BrS$	—		—		6
3564	H	*p*-I	100	89	10	13	77	$C_{13}H_{11}IS$	48·3	3·4	47·9	3·4	†
2450	*p*-F	H	100	59	23	5	62·0–62·5	$C_{13}H_{11}FS$	71·15	4·75	71·55	5·05	*
2451	*p*-F	*p*-F	31	0	—	—	44·5–45·5	$C_{13}H_{10}F_2S$	66·0	4·3	66·1	4·2	*
2453	*p*-F	*p*-Cl	100	60	23	18	49–50	$C_{13}H_{10}ClFS$	61·95	3·75	61·8	4·0	*
3306	*p*-F	*p*-Br	100	55	43	34	56·5–57·5	$C_{13}H_{10}BrFS$	52·9	3·4	52·5	3·4	†
3572	*p*-F	*p*-I	88	86	12	10	75	$C_{13}H_{10}IFS$	45·7	2·8	45·3	2·9	*
3034	*o*-Cl	*p*-F	33	39	—	—	141–143/1·5	$C_{13}H_{10}ClFS$	61·8	3·9	61·8	4·0	**
2718	*o*-Cl	*p*-Cl	42	14	—	—	32;170/2·0	$C_{13}H_{10}Cl_2S$	57·5	3·5	58·0	3·7	*
3035	*m*-Cl	*p*-F	98	65	57	18	158–160/2·0	$C_{13}H_{10}ClFS$	61·7	3·7	61·8	4·0	**
2719	*m*-Cl	*p*-Cl	100	34	44	21	172–175/2·0	$C_{13}H_{10}Cl_2S$	57·6	3·6	58·0	3·7	**
2313	*p*-Cl	H	100	100	32	16	78	$C_{13}H_{11}ClS$	66·9	4·65	66·5	4·7	*
2454	*p*-Cl	*p*-F	100	100	76	27	34·5–35·5	$C_{13}H_{10}ClFS$	62·0	4·0	61·8	4·0	**
2195	*p*-Cl	*p*-Cl	100	100	98	63	72	$C_{13}H_{10}Cl_2S$	57·75	3·7	58·0	3·7	**
3879	*p*-Cl	2 : 5-Cl_2	98	13	0	3	113–114	$C_{13}H_9Cl_3S$	51·4	3·0	51·4	3·0	**
2425	*p*-Cl	2 : 4 : 5-Cl_3	94	23	8	11	76–77	$C_{13}H_8Cl_4S$	46·1	2·4	46·15	2·4	*
3309	*p*-Cl	*p*-Br	100	100	97	28	87–88	$C_{13}H_{10}ClBrS$	49·6	3·2	49·8	3·2	†
3497	*p*-Cl	*p*-I	97	65	53	33	102	$C_{13}H_{10}ClIS$	43·6	2·8	43·3	2·8	**
3825	2 : 4-Cl_2	H	90	27	17	5	163–165/1·5	$C_{13}H_{10}Cl_2S$	58·45	3·7	58·0	3·7	**
4166	2 : 4-Cl_2	*p*-F	100	100	48	55	167–2·5	$C_{13}H_9Cl_2FS$	54·4	3·3	54·4	3·1	**
3824	2 : 4-Cl_2	*p*-Cl	100	28	17	14	58–59	$C_{13}H_9Cl_3S$	51·1	3·0	51·4	3·0	**
3828	2 : 6-Cl_2	H	0	1	—	—	39–40	$C_{13}H_{10}Cl_2S$	57·6	3·7	58·0	3·7	**
4164	2 : 6-Cl_2	*p*-F	8	0	—	—	51	$C_{13}H_9Cl_2FS$	54·4	3·2	54·4	3·1	**
3827	2 : 6-Cl_2	*p*-Cl	11	2	—	—	69–70	$C_{13}H_9Cl_3S$	51·4	2·9	51·4	3·0	**
3341	*p*-Br	H	100	100	59	46	78	$C_{13}H_{11}BrS$	55·6	4·0	55·9	3·9	**
3343	*p*-Br	*p*-F	100	100	87	88	44–45	$C_{13}H_{10}BrFS$	52·4	3·3	52·5	3·4	**
3352	*p*-Br	*p*-Cl	100	100	92	88	83–84	$C_{13}H_{10}ClBrS$	49·6	3·05	49·8	3·2	**
3236	*p*-Br	*p*-Br	100	100	89	81	101	$C_{13}H_{10}Br_2S$	43·9	2·7	43·6	2·8	†
3635	*p*-Br	*p*-I	64	100	83	66	116	$C_{13}H_{10}BrIS$	38·5	2·5	38·5	2·5	†
3571	*p*-I	H	99	95	100	96	88	$C_{13}H_{11}IS$	48·0	3·3	47·9	3·4	†
3569	*p*-I	*p*-F	100	100	100	90	56	$C_{13}H_{10}IFS$	45·3	3·0	45·3	2·9	†
3518	*p*-I	*p*-Cl	100	71	100	100	101	$C_{13}H_{10}ClIS$	43·5	2·8	43·3	2·8	†
3575	*p*-I	*p*-Br	100	68	92	100	118	$C_{13}H_{10}BrIS$	38·8	2·4	38·5	2·5	†
3550	*p*-I	*p*-I	32	6	0	0	131	$C_{13}H_{10}I_2S$	34·6	2·2	34·5	2·2	†

* Prepared by N. G. C. ** Prepared by D. G. † Prepared by J. R. M.

Table II

Halogen-substituted sulphoxides and sulphones

$XC_6H_4{\cdot}CH_2{\cdot}SO_n{\cdot}C_6H_4Y$

Ref. No.	X	Y	n	% Mortality Test A 0·1%	Test A 0·025%	Test B 0·02%	Test B 0·01%	M.p., ° c, or b.p., ° c/mm.	Formula	Analysis Found % C	Found % H	Required % C	Required % H	Reference
3777	H	*p*-F	1	7	4	—	—	138–140	$C_{13}H_{11}OFS$	66·8	4·7	66·7	4·7	*
3699	H	*p*-F	2	16	16	—	—	153·5–154·5	$C_{13}H_{11}O_2FS$	62·5	4·4	62·4	4·4	*
2568	H	*p*-Cl	1	38	16	—	—	134	$C_{13}H_{11}OClS$	62·1	4·2	62·3	4·4	**
2566	H	*p*-Cl	2	31	25	—	—	144–145	$C_{13}H_{11}O_2ClS$	58·8	3·85	58·5	4·1	**
3835	H	*p*-Br	1	0	3	—	—	141–142	$C_{13}H_{11}OBrS$	53·3	3·8	52·9	3·7	*
3507	H	*p*-Br	2	9	6	—	—	158–159	$C_{13}H_{11}O_2BrS$	—	—	—	—	†
3576	H	*p*-I	1	10	8	—	—	128	$C_{13}H_{11}OIS$	45·5	3·1	45·6	3·2	†
3591	H	*p*-I	2	8	4	—	—	182	$C_{13}H_{11}O_2IS$	43·6	3·1	43·6	3·1	†
3775	*p*-F	*p*-F	1	8	6	—	—	160–161	$C_{13}H_{10}OF_2S$	62·0	3·85	61·9	4·0	*
3776	*p*-F	*p*-F	2	9	4	—	—	186–187	$C_{13}H_{10}O_2F_2S$	58·0	3·6	58·2	3·7	*
3936	*p*-F	*p*-Cl	2	42	12	—	—	150–157	$C_{13}H_{10}O_2ClFS$	54·9	3·8	54·8	3·5	*
3367	*p*-F	*p*-Br	2	0	0	—	—	171·5–172·0	$C_{13}H_{10}O_2BrFS$	47·1	3·0	47·4	3·0	*
3584	*p*-F	*p*-I	1	23	28	14	10	171	$C_{13}H_{10}OIFS$	42·95	2·8	43·3	2·8	†
3593	*p*-F	*p*-I	2	16	13	—	—	201	$C_{13}H_{10}O_2IFS$	41·9	2·65	41·5	2·7	†
3043	*o*-Cl	*p*-F	2	50	39	—	—	107–108	$C_{13}H_{10}O_2ClFS$	54·7	3·45	54·8	3·5	**
2817	*o*-Cl	*p*-Cl	1	37	6	—	—	73–74	$C_{13}H_{10}OCl_2S$	55·2	3·7	54·7	3·5	**
2815	*o*-Cl	*p*-Cl	2	71	87	10	13	120–121	$C_{13}H_{10}O_2Cl_2S$	51·7	3·2	51·8	3·3	**
3252	*m*-Cl	*p*-F	1	98	59	36	10	82·5–83·5	$C_{13}H_{10}OClFS$	58·0	3·9	58·1	3·7	*
3044	*m*-Cl	*p*-F	2	29	29	—	—	135–136	$C_{13}H_{10}O_2ClFS$	54·9	3·5	54·8	3·5	*
2818	*m*-Cl	*p*-Cl	1	98	18	—	—	94–96	$C_{13}H_{10}OCl_2S$	55·0	3·4	54·7	3·5	**
2816	*m*-Cl	*p*-Cl	2	19	8	—	—	125 & 130	$C_{13}H_{10}O_2Cl_2S$	51·9	3·2	51·8	3·3	**
2565	*p*-Cl	H	1	23	0	—	—	173	$C_{13}H_{11}OClS$	62·2	4·2	62·3	4·4	**
2567	*p*-Cl	H	2	10	0	—	—	190	$C_{13}H_{11}O_2ClS$	58·7	4·3	58·5	4·1	**
3003	*p*-Cl	*p*-F	1	100	100	85	64	125–126	$C_{13}H_{10}OClFS$	58·0	3·65	58·1	3·7	*
3004	*p*-Cl	*p*-Cl	2	100	100	44	24	144–145	$C_{13}H_{10}O_2ClFS$	54·8	3·6	54·8	3·5	*
2493	*p*-Cl	*p*-Cl	1	100	100	95	96	124	$C_{13}H_{10}OCl_2S$	54·5	3·5	54·7	3·5	**
2421	*p*-Cl	*p*-Cl	2	100	100	68	28	150	$C_{13}H_{10}O_2Cl_2S$	51·7	2·8	51·8	2·3	**
3778	*p*-Cl	*p*-Br	1	80	10	30	22	132–133	$C_{13}H_{10}OClBrS$	47·2	2·8	47·3	3·0	*
3324	*p*-Cl	*p*-Br	2	1	1	—	—	169–170	$C_{13}H_{10}O_2ClBrS$	45·0	2·8	45·15	2·9	†
3545	*p*-Cl	*p*-I	1	60	25	10	8	159	$C_{13}H_{10}OClIS$	41·2	2·6	41·4	2·7	†
3563	*p*-Cl	*p*-I	2	13	12	—	—	194	$C_{13}H_{10}O_2ClIS$	40·05	2·5	39·7	2·6	†

* Prepared by N. G. C. ** Prepared by D. G. † Prepared by J. R. M.

Table II (*contd.*)

Ref. No.	X	Y	*n*	% Mortality Test A 0·1%	Test A 0·025%	Test B 0·02%	Test B 0·01%	M.p. ° c, or b.p., ° c/mm.	Formula	Analysis Found % C	Found % H	Required % C	Required % H	Reference
3655	*p*-Br	H	1	6	4	—	—	179	$C_{13}H_{11}OBrS$	53·25	3·6	52·9	3·7	**
3554	*p*-Br	H	2	18	0	—	—	192–193	$C_{13}H_{11}O_2BrS$	50·0	3·3	50·2	3·5	**
3711	*p*-Br	*p*-F	1	92	42	18	9	141	$C_{13}H_{10}OBrFS$	49·6	3·2	49·8	3·2	**
3530	*p*-Br	*p*-F	2	74	27	14	11	160–161	$C_{13}H_{10}O_2BrFS$	47·0	2·9	47·4	3·0	**
3656	*p*-Br	*p*-Cl	1	52	12	—	—	135–136	$C_{13}H_{10}OClBrS$	47·2	3·0	47·3	3·0	**
3532	*p*-Br	*p*-Cl	2	1	0	—	—	158–159	$C_{13}H_{10}O_2ClBrS$	45·9	2·6	45·1	2·9	**
3710	*p*-Br	*p*-Br	1	7	23	—	—	145–146	$C_{13}H_{10}OBr_2S$	41·55	2·7	41·7	2·7	**
3531	*p*-Br	*p*-Br	2	1	1	—	—	179–180	$C_{13}H_{10}O_2Br_2S$	40·0	2·5	40·0	2·6	**
3044	*p*-Br	*p*-I	1	0	0	—	—	180	$C_{13}H_{10}OBrIS$	37·0	2·4	37·1	2·4	†
3076	*p*-Br	*p*-I	2	10	22	—	—	213	$C_{13}H_{10}O_2BrIS$	35·8	2·2	35·7	2·3	†
3588	*p*-I	H	1	0	7	—	—	191	$C_{13}H_{11}OIS$	45·7	3·2	45·6	3·2	†
3595	*p*-I	H	2	18	7	—	—	209	$C_{13}H_{11}O_2IS$	44·0	3·0	43·6	3·1	†
3592	*p*-I	*p*-F	1	82	51	5	7	171	$C_{13}H_{10}OIFS$	43·7	2·8	43·3	2·8	†
3072	*p*-I	*p*-F	2	0	0	—	—	196	$C_{13}H_{10}O_2IFS$	41·9	2·7	41·5	2·7	†
3565	*p*-I	*p*-Cl	1	100	69	19	19	153	$C_{13}H_{10}OClIS$	41·5	2·6	41·4	2·7	†
3585	*p*-I	*p*-Cl	2	15	7	—	—	187	$C_{13}H_{10}O_2ClIS$	40·1	2·5	39·7	2·6	†
3590	*p*-I	*p*-Br	1	8	4	—	—	171	$C_{13}H_{10}OBrIS$	37·3	2·3	37·1	2·4	†
3596	*p*-I	*p*-Br	2	8	0	—	—	202	$C_{13}H_{10}O_2BrIS$	35·8	2·3	35·7	2·3	†
3544	*p*-I	*p*-I	1	6	1	—	—	197	$C_{13}H_{10}OI_2S$	33·4	2·2	33·3	2·1	†
3589	*p*-I	*p*-I	2	8	23	—	—	239	$C_{13}H_{10}O_2I_2S$	32·4	2·1	32·2	2·1	†

** Prepared by D. G. † Prepared by J. R. M.

Discussion of results

The numbers in Tables I and II give the percentage ' total ' mortalities (i.e. kill of eggs and newly-hatched immature mites) corrected for mortality in the formulation controls. The method of testing at two fixed concentrations in each test, A and B, was designed to establish large differences in effect. Repeat tests were made to confirm many of the points discussed below, but only one set of typical results is given in the tables for the sake of clarity. No attempt is made on the basis of the present data to compare the most active compounds, which were numerous. The work reported here formed part of a larger project and many active compounds were later tested in pot trials and in the field. This work will be reported in a later paper.

Examination of the experimental results clearly shows the profound effect of nuclear halogenation on the biological activity of benzyl phenyl sulphide, which was virtually inactive.

In the mono-substituted compounds there was a marked difference in activity depending on which of the two nuclei was substituted by halogen. Thus, substitution in the *para* position of the phenyl moiety gave compounds much less active than the corresponding compounds substituted in the *para* position of the benzyl moiety. With the substituted phenyl compounds there appeared to be a general rise in activity from fluorine through chlorine and bromine to iodine.

All other compounds substituted by halogen in the *para* position of both nuclei, or in the benzyl moiety only, were of high activity with the notable exceptions of *p*-fluorobenzyl *p*-fluorophenyl sulphide and *p*-iodobenzyl *p*-iodophenyl sulphide. These exceptions were all the more remarkable in view of the fact that the corresponding chloro- and bromo-compounds were highly active and all other combinations of fluorine or of iodine with other halogens produced compounds of high activity.

Substitution in the *meta* position of the benzyl moiety, when the phenyl moiety was *para*-substituted with fluorine or chlorine, gave compounds less active than the corresponding *para*-substituted benzyl derivatives; the *ortho*-substituted benzyl derivatives were least active (compare in Table I, 2718; 2719; 2195 and 3034; 3035; 2454). This makes an interesting comparison with the $\alpha\omega$-bisarylthioalkanes[1] where the *meta*-chlorine-substituted compounds were approximately as active as the *para*-chlorine-substituted ones, the *ortho*-chlorine-substituted derivatives being of variable activity.

Substitution by more than one halogen atom in either nucleus resulted in compounds of lower activity than the corresponding compounds substituted only in the *para* positions. The 2 : 6-dichlorobenzyl compounds were notably inactive.

In contrast to the high activity of most of the bis-*para*-halogen-substituted benzyl phenyl sulphides, the activity of the corresponding sulphoxides and sulphones was low or negligible except with those derived from *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside) and *p*-chlorobenzyl *p*-fluorophenyl sulphide. The practical significance of this has been mentioned previously[3] and will be enlarged upon in a later communication. In other derivatives, low activity occurred more generally in the sulphoxides but was usually absent in the sulphones. Such activity as there was appeared to depend on the lipoid solubility of the compounds, if solubility in benzene may be taken as a guide, and occurred usually in compounds *para*-substituted by fluorine or chlorine in the phenyl moiety and not in those substituted by bromine or iodine in this nucleus.

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References

[1] Brookes, R. F., Cranham, J. E., Cummings, W. A. W., Greenwood, D., Jackson, B. S., & Stevenson, H. A., *J. Sci. Fd Agric.*, 1957, **8**, 31
[2] Brookes, R. F., Cranham, J. E., Greenwood, D., & Stevenson, H. A., *J. Sci. Fd Agric.*, 1957, **8**, 601
[3] Cranham, J. E., Higgons, D. J., & Stevenson, H. A., *Chem. & Ind.*, 1953, p. 1206
[4] Weizmann, M., & Patai, S., *J. Amer. chem. Soc.* 1946, **68**, 150
[5] Pummerer, R., *Ber. dtsch. chem. Ges.*, 1910, **43**, 1406
[6] Tabourry, M. F., *Bull. Soc. chim. Fr.*, 1904, [iii], **31**, 1186
[7] Koenigs, E., & Wylezich, A., *J. prakt. Chem.*, 1931, **132**, 24

AN INVESTIGATION OF SUGAR-CANE CUTICULAR WAX

By D. H. S. HORN and M. MATIC

The saponified cuticular wax from sugar cane (N.Co 310 variety) was found to consist of an acid fraction (containing some triene-unsaturated acids), small amounts of hydrocarbons in the C_{27} C_{31} range, and of lower and higher molecular weight substances made up of aliphatic alcohols (of which *n*-octacosanol was identified as the main component), $\alpha\beta$-unsaturated and saturated ketones. Some of these unidentified compounds are shown to be artefacts produced on heating and saponification of the original wax.

Introduction

A great number of plant and insect waxes have already been studied particularly by Chibnall and his school,[1] and their compositions determined. A considerable amount of data is also available on the chemistry of refined sugar-cane wax (see Balch[2]) and sugar-cane oil (Whyte & Hengeveld[3]), both by-products of sugar manufacture, but very little is known of the composition of sugar-cane cuticular wax. Rindl[4] reported some analytical constants for sugar-cane cuticular wax and Kreger[5] concluded, on the strength of *X*-ray evidence, that its main component is *n*-octacosanol. Wijnberg[6] had earlier reported the main component to be *n*-triacontanol.

In this paper the separation of sugar-cane cuticular wax into several groups of compounds, and the identification of one of these, is described.

Methods

Molecular distillation

In order to separate from sugar-cane cuticular wax the higher-molecular-weight material found in some fractions, a one-stage falling-film molecular still was built (Fig. 1). This consisted essentially of a reservoir (A) fitted with a labyrinth screw valve (B) which controlled the flow rate of the charge, and a still proper (C), which contained a tube (D) filled with solvent and heated to

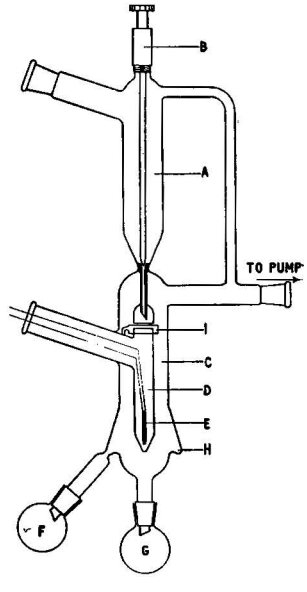

FIG. 1.—*Molecular still*

boiling by means of a small coil of resistance wire (E), and an inclined gutter (H) into which the distillate was collected and drained into receiving flask (F). The vertical surfaces of the tube (D) were roughened to aid film distribution, and a glass ring (I) was fixed around its top for the same purpose. The residue dripped directly from the bottom of the tube (D) into flask (G). The outer walls of the still (C) and the reservoir (A) were heated to about 70° by means of heating tape (Electrothermal Engineering Ltd., London) in order to keep the distillate and the charge in a molten state.

Chromatography

For all chromatographic experiments a jacketed column of appropriate size, packed with acid-washed alumina and kept at 50° by circulating water from a constant-temperature bath, was used. The course of the chromatograms was followed by collecting the eluate in 50-ml. aliquots, evaporating off the solvent, and weighing the residues. Infra-red spectra of chosen fractions were also recorded.

The alumina used was prepared as follows: alumina (Peter Spence, Widnes, grade H) was washed with 2N-HCl, then with warm and cold water until neutral, and finally with warm ethanol. It was reactivated by heating at 150° for 5 h.

The eluting solvents were purified by distillation, and when necessary, by refluxing over potassium hydroxide.

Molecular weight determinations

Molecular weights* were determined in benzene solution, using the ebulliometer designed by Ray,[7] as modified by Evelyn[8] and incorporating the suggestions made recently by Smith.[9]

Other physical measurements

Melting points were determined in capillary tubes immersed in an electrically heated and stirred paraffin bath and are corrected. Infra-red and ultra-violet absorption spectra were recorded with a Hilger spectrometer Model H 800, and a Unicam spectrophotometer, Model SP 500. Carbon disulphide and *iso*-octane solutions respectively were used. Crystal long-spacing was determined with a Philips *X*-ray diffraction apparatus.

Experimental and results

The scheme of separations carried out is shown in Fig. 2.

The isolation of sugar-cane cuticular wax and its saponification

Cuticular wax was scraped from mature sugar cane (N.Co 310 variety) with a knife and the scrapings extracted with *iso*hexane in a Soxhlet apparatus for 16 h. The light yellow wax obtained after removal of the solvent was found, on analysis, to contain ash 0·071%, and to have a sap. val. 30; acid value 1·9; I val. 26·6; and molecular weight 509. The ultra-violet spectrum of the wax showed, in addition to a typical conjugated triene absorption ($\lambda_{max.}$ 270 mμ, $E^{1\%}_{1\,cm.}$ 20·9), a maximum at 227·5 mμ ($E^{1\%}_{1\,cm.}$ 17·5) and a shoulder at 315 mμ, characteristic of an $\alpha\beta$-unsaturated ketone.

The wax (103·5 g.) was saponified with potassium hydroxide (25 g.) in ethanol (400 ml.) and *iso*heptane (250 ml.) for 9 h. Water (250 ml.) was then added and the hot solution extracted three times with hot *iso*heptane. The solvent was washed three times with hot 40% ethanol and the washings extracted twice with *iso*heptane. The combined *iso*heptane solutions gave 86·5 g. (83·5%) of yellow unsaponifiable material. The combined aqueous washings, after acidification with H_2SO_4 and extraction with hot *iso*heptane, gave 16 g. (15·5%) of brown acidic material (Found: equiv. wt., 464). The ultra-violet spectrum of this material showed only conjugated triene absorption ($\lambda_{max.}$ 270 mμ, $E^{1\%}_{1\,cm.}$ 39). The acids were not investigated further.

* Kindly determined by Dr. S. R. Evelyn, Leather Industries Research Institute, Grahamstown

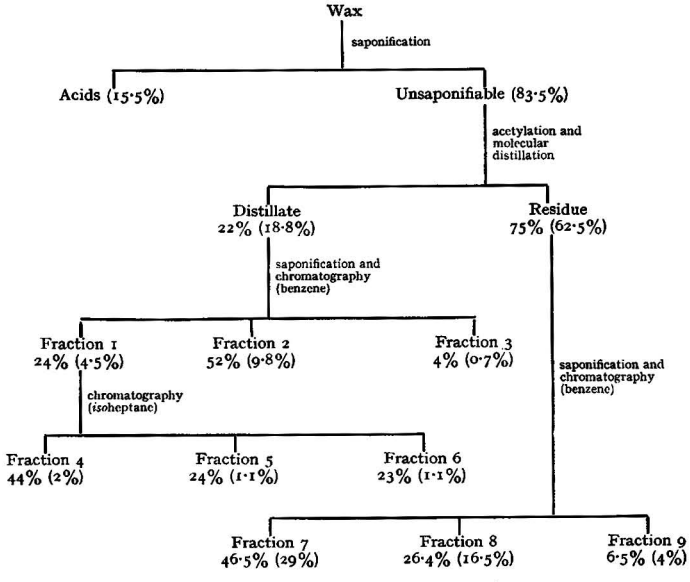

FIG. 2.—*Scheme of separations carried out on sugar-cane cuticular wax*
(Figures in brackets indicate the percentage of total wax)

Acetylation and molecular distillation of the unsaponifiable material

The unsaponifiable material (86 g.) was refluxed with acetic anhydride (300 ml.) and xylene (200 ml.) for 5 h. in order to acetylate the alcohols present. The xylene and the excess of acetic anhydride were distilled off *in vacuo*. The residue obtained (83·5 g.) was a light yellow waxy material (Found: molecular weight, 804).

Preliminary experiments indicated the presence of higher-molecular-weight substances (mol. wt. about 1000) in this acetylated material. In order to separate them from the lower-molecular-weight substances, the acetylated material (70 g.) was distilled in the molecular still described under Methods, at 215° (b.p. of *o*-anisidine) to give (i) distillate and (ii) residue. After the residue had been recycled twice at the same temperature, no more distillate was obtained. The distillates were combined to give 15·3 g. (22%) of white, waxy material. The light brown residue weighed 52·8 g. (75%).

Cuticular wax prepared in a similar way from another variety of sugar cane (Co 290) gave on molecular distillation a residue of 53%.

Chromatography of the distillate

The distillate from molecular distillation of the acetylated material was saponified and worked up as described before. Some of this saponified material (0·3236 g.) was chromatographed on acid-washed alumina (20 g.), using benzene as eluting solvent, to give three fractions (Fig. 2), viz. fraction 1 (0–100 ml. benzene), 0·0771 g.; fraction 2 (250–400 ml. benzene), 0·1674 g.; and fraction 3 [550–700 ml. benzene : ethanol (90 : 10, v/v)], 0·0235 g. Fraction 3 was not investigated further.

Fraction 1 had, in addition to the expected aliphatic hydrocarbon bands near 3·2, 7·3 and 14 μ in its infra-red spectrum, a normal ketone band near 5·8 μ and $\alpha\beta$-unsaturated ketone bands near 5·9 and 6·1 μ, and an unexplained band near 13·2 μ, but no alcohol bands near 2·8 and 9·5 μ

were present. The ultra-violet absorption spectrum showed a shoulder at 310 mμ and a maximum at 227·5 mμ ($E^{1\%}_{1\,cm.}$ 77) due to αβ-unsaturated ketone, as well as a maximum at 280 mμ due to normal ketones. Fraction 1 (0·1987 g.) was therefore rechromatographed on acid-washed alumina (20 g.), using *iso*heptane as eluting solvent and three further fractions were collected, viz. fraction 4 (0–100 ml. *iso*heptane), 0·0877 g.; fraction 5 (250–400 ml. *iso*heptane), 0·0475 g.; and fraction 6 [500–700 ml. *iso*heptane : ethanol (80 : 20, v/v)], 0·0454 g.

A twin band near 5·8 and 5·9 μ in the infra-red spectrum showed that fraction 6 was still a mixture of ketones and αβ-unsaturated ketones. This fraction was not investigated further.

Alcohols

Fraction 2 (Fig. 2) was made up of alcohols only, as indicated by its infra-red spectrum. In order to resolve it further, it was acetylated and the acetate (0·48 g.) distilled at 1 mm. pressure in a spinning band column (Horn & Hougen[10]). The distillation curve obtained is shown in Fig. 3. Only one plateau was found, showing that most of fraction 2 was made up of one alcohol. The hold-up of the column was 1·97 g.

Fractions 8 to 12 of Fig. 3 were combined and crystallized once from *iso*heptane to give *n*-octacosanol acetate, m.p. 64·4–64·6° (Piper *et al.*,[11] m.p. 64·6–64·8°) (Found: C, 79·7; H, 13·5; acetyl, 9·5. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·4; acetyl, 9·5%). Part of this material was saponified to give *n*-octacosanol, m.p. 83·4–83·6°, long spacing (pressed) 61·9 Å (Piper *et al.*,[11] 62·15 Å) (Found: C, 81·6; H., 14·2. Calc. for $C_{28}H_{58}O$: C, 81·9; H, 14·2%).

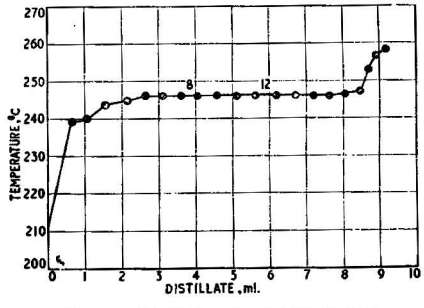

FIG. 3.—*Distillation of acetylated alcohols*

Hydrocarbons

Fraction 4 (Fig. 2) was rechromatographed on acid-washed alumina to give only one peak. The material obtained did not char on treatment with H_2SO_4 at 120°, and after one crystallization from ethanol it had a melting point of 62·7–63·0° and setting point of 62·5° (Found: C, 85·2; H, 14·8%).

The infra-red spectrum showed only the expected aliphatic hydrocarbon bands, and the *X*-ray long spacing (few reflexions only) was 39·5 Å.

αβ-Unsaturated ketones

Fraction 5 of Fig. 2 (0·335 g.) was rechromatographed on a column of acid-washed alumina (30 g.), using *iso*heptane as eluting solvent. The first peak, eluted with 350 ml. of *iso*heptane and representing 77% of material, was crystallized from ethanol–benzene to m.p. 71–72°, setting point 70·5° (Found: C, 83·6; H, 12·9%).

The infra-red spectrum of the crystallized material showed strong bands near 5·9 and 6·1 μ, due to αβ-unsaturated ketone grouping, as well as a band near 13·2 μ. In the ultra-violet, well-defined maxima at 320 mμ and 227·5 mμ ($E^{1\%}_{1\,cm.}$ 154) were detected. The maximum at 227·5 mμ was shifted to 300 mμ when the spectrum was determined in ethanol.

Chromatography of the distillation residue

The residue obtained on molecular distillation of the acetylated unsaponifiable material (Fig. 2) was saponified and worked up as described before. The saponified material (14·0 g.) was chromatographed on acid-washed alumina (1000 g.) using benzene as eluting solvent, and the eluate collected in 200-ml. aliquots. Three fractions (Fig. 2), numbered 7, 8 and 9 respectively, were obtained, viz. fraction 7 (0–3000 ml. benzene), 6·5 g.; fraction 8 [3500–5900 ml. benzene : ethanol (90 : 10, v/v)], 3·7 g.; fraction 9 [6000–8400 ml. benzene : ethanol : acetic acid (89 : 10 : 1, v/v)], 0·9 g.

Fraction 7 (Found : C, 83·7; H, 14·0%; molecular weight, 900) had in its infra-red spectrum fairly strong bands near 5·8, 5·9 and 6·1 μ, as well as a band near 13·2 μ, but no alcohol bands near 2·7 and 9·5 μ. In the ultra-violet, a maximum at 227·5 mμ ($E^{1\%}_{1\,cm.}$ 54) and an inflexion at 280 mμ were detected. On rechromatographing this fraction with *iso*heptane as solvent, two fractions were obtained of which the first (66%) appeared from infra-red evidence to be made up of $\alpha\beta$-unsaturated ketones, and the second (20%) of saturated ketones.

Fraction 8 had in its infra-red spectrum, in addition to alcohol bands near 2·7 and 9·5 μ, weak bands in the carbonyl region (5·8 μ). Only an inflexion at 227·5 mμ was recorded in the ultra-violet (Found : C, 82·5; H, 14·0 %; molecular weight, 796; acetylated material : acetyl, 7·4%).

The infra-red spectrum of fraction 9 had a strong band near 5·8 μ and a weak one near 13·2 μ. The ultra-violet spectrum had a maximum at 270 mμ and an inflexion at 280 mμ (Found : C, 81·8; H, 13·4%; molecular weight, 1258).

The effect of heat and alkali on the cuticular wax

The total cuticular wax was heated at 130° *in vacuo* (water pump). Samples were removed at different times and their ultra-violet absorption at 227·5 and 270 mμ measured. The results, together with molecular weights of some fractions, are given in Table I.

Table I

Effect of heating cuticular wax at 130° in vacuo

Time of heating, h.	$E^{1\%}_{1\,cm.}$ at 270 mμ	$E^{1\%}_{1\,cm.}$ at 227·5 mμ	Molecular weight
0	20·9	17·5	509
½	20·8	18·9	
1	20·7	20·9	
2	21·7	24·1	
4	21·5	27·8	
6	21·1	29·4	536
8	21·0	31·4	
12	20·1	33·1	586

On molecular distillation of the wax at 215° (see Methods), 70% was recovered as distillate and 28% as residue. When the material heated for 12 h. at 130° was distilled under the same conditions, 43% was recovered as distillate and 55% as residue.

The total wax was saponified under the same conditions as described previously. After 1, 3 and 6 h. of saponification, samples were taken, acidified with H_2SO_4, and after addition of water, extracted with hot *iso*heptane. After removal of the solvent, the ultra-violet absorption at 270 and 227·5 mμ was measured. The results obtained and the molecular weights determined are shown in Table II.

Discussion

A spectroscopic examination of the wax extracted from scrapings of sugar cane with *iso*-heptane indicated that it contained compounds having $\alpha\beta$-unsaturated ketone groupings as well as about 1% of material (calculated as elaeostearic acid) with three conjugated double bonds. The latter material, after saponification of the wax, was present in the acid fraction. The unsaponifiable part of the wax contained a large proportion of higher-molecular-weight material (molecular weight 800–1200) in addition to the expected compounds of about 30 carbon atoms in

Table II

Effect of time of saponification on total fatty matter in cuticular wax

Time of saponification, h.	$E^{1\%}_{1\,cm.}$ at 270 mμ	$E^{1\%}_{1\,cm.}$ at 227·5 mμ	Molecular weight
0	20·9	17·5	509
1	24·6	120	710
3	24·1	129	
6	24·8	91	752

chain length. The higher-molecular-weight material was separated by means of molecular distillation. Further resolution of both lower- and higher-molecular-weight materials was achieved by chromatography on acid-washed alumina at 50°.

The lower-molecular-weight material, obtained as a distillate by molecular distillation of the acetylated unsaponifiable fraction, was saponified and separated by chromatography into three groups of compounds, viz. (i) hydrocarbons, (ii) $\alpha\beta$-unsaturated ketones and (iii) alcohols. Saturated ketones were also present in this material but were not obtained in a state of purity. Both hydrocarbons and $\alpha\beta$-unsaturated ketones were minor components (about 3% of the wax) and were not investigated in detail.

The hydrocarbon fraction was a mixture of homologues, probably odd and even numbered (cf. Wanless, King & Ritter[12]), and no attempt was made to isolate pure compounds from it. It is suggested, however, on the grounds of the melting point, elementary analysis and *X*-ray long spacing, that the hydrocarbons are probably in the C_{27}–C_{31} range (cf. Piper *et al.*[13]). The fraction containing $\alpha\beta$-unsaturated ketones was also a mixture, as shown by its broad melting point, and no pure compound could be isolated from it, but as these compounds are a part of the distillate, they are possibly also in the C_{30} range. The position of the maximum in the ultra-violet (230 mμ in ethanol) was half-way between those expected for mono- ($\lambda_{max.}$ 225 mμ) and di-substituted ($\lambda_{max.}$ 235 mμ) $\alpha\beta$-unsaturated ketones (cf. Gillam & Stern[14]).

From the alcoholic fraction, which represented the bulk of the distillate, the main component was isolated by distillation of its acetate. It was identified, by means of its melting point, elementary analysis and *X*-ray long spacing, as *n*-octacosanol (6–7% of the wax). Its lower and higher homologues were also present in small amounts, and the probable composition of the alcoholic fraction is as follows: alcohols below C_{28}, 9%; C_{28} *n*-alcohol, 65%; alcohols above C_{28}, 26%. Kreger's[5] claim that the C_{28}-alcohol is present in sugar-cane cuticular wax is thus confirmed.

Treatment of the original cuticular wax with either heat or alkali brought about a substantial increase in both the percentage of polymer and the specific extinction coefficient at 227·5 mμ in the ultra-violet absorption spectrum. Thus most or the whole of the higher-molecular-weight material in the unsaponifiables is an artefact. Some information about the nature of this polymer has been obtained and is summarized below.

The higher-molecular-weight material can be partially separated by chromatography on acid-washed alumina into $\alpha\beta$-unsaturated ketones, alcohols and saturated ketones. Hydrocarbons are apparently absent from this fraction. From the analytical evidence it is concluded that the higher-molecular-weight substances have two or three times the molecular weight of the original wax components and are of similar structures. For example, in the case of the alcoholic fraction, the analytical data obtained are in fairly good agreement with those expected for a diol of about 56 carbon atoms. The nature of the reaction which occurs on heating or on treatment with alkali has not been elucidated. It is clear, however, that the compounds having conjugated triene groupings do not participate in it, but it is not clear what rôle the $\alpha\beta$-unsaturated ketones play in this reaction.

Politzer[15] reported that a certain fraction of sisal wax apparently polymerizes on heating, and Wanless, King & Ritter[12] suggested that the hydrocarbon portion of pyrethrum cuticular wax contains some higher-molecular-weight fractions. These observations suggest that the occurrence of higher-molecular-weight materials, or their precursors, in plant waxes may be more widespread than was previously suspected.

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References

[1] Chibnall, A. C., Piper, S. H., Pollard, A., Williams, E. F., & Sahai, P. N., *Biochem. J.*, 1934, **28**, 2189
[2] Balch, R. T., ' Wax and Fatty By-products from Sugar Cane ', Technological Report Series, 1947, No. 3 (New York : Sugar Research Foundation Inc.)
[3] Whyte, D. E., & Hengeveld, B., *J. Amer. Oil Chem. Soc.*, 1950, **27**, 57
[4] Rindl, M., *S. Afr. J. Ind.*, 1922, **5**, 513
[5] Kreger, D. R., *Rec. Trav. bot. néerl.*, 1948, **46**, 606
[6] Wijnberg, A., ' Over rietwas en de mogelijkheden zijner technische gewinnning ', 1909, Dissertation, Delft
[7] Ray, N. H., *Trans. Faraday Soc.*, 1952, **48**, 809
[8] Evelyn, S. R., *J. Soc. Leath. Tr. Chem.*, 1954, **38**, 142
[9] Smith, H., *Trans. Faraday Soc.*, 1956, **52**, 402
[10] Horn, D. H. S., & Hougen, F. H., *J. chem. Soc.*, 1953, p. 3533
[11] Piper, S. H., Chibnall, A. C., & Williams, E. F., *Biochem. J.*, 1934, **28**, 2175
[12] Wanless, G. G., King, W. H., & Ritter, J. J., *Biochem. J.*, 1955, **59**, 684
[13] Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, A., Smith, J. A. B., & Williams, E. F., *Biochem. J.*, 1931, **25**, 2072
[14] Gillam, A. E., & Stern, E. S., ' An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry ', 1954 (London : Edward Arnold Ltd.)
[15] Politzer, W., *Chem. & Ind.*, 1948, p. 408

THE CAKING OF GRANULAR FERTILIZERS: AN INVESTIGATION ON A LABORATORY SCALE

By A. L. WHYNES and T. P. DEE

Preliminary consideration suggested a technique for studying the caking of granular fertilizers on a laboratory scale similar to that used in soil mechanics. An apparatus and technique were devised, and details of these are given. Time of storage of the fertilizer is found to be an important factor, and caking is rapid in the first few days. Preliminary investigations on the effect of chemical composition showed setting to be more serious when ammonium sulphate (1), superphosphate (2) and muriate of potash (3) were all present than when only (1) and (2), or (2) and (3) were included. Free acid content seemed to have little effect nor had light ammoniation of the superphosphate. Moisture content is related to caking, which has been reduced to negligible amounts by drying down to less than 1% free moisture. Caking increases with the temperature, and this indicates the desirability of cooling. The correlation between the test developed and the results obtained on the large scale is discussed, and is shown to be sufficiently good for the test to be of considerable value.

Introduction

The ' condition ' of a fertilizer is a term used to cover a range of different meanings. For example, some fertilizers tend to pick up water vapour rapidly and become difficult to distribute in a farmer's drill. Others, when stored, cake badly, particles adhering firmly to each other,

again making drilling in the field less easy. This paper is concerned with the latter aspect of the problem. The granulation of mixed fertilizers does not eliminate their caking, although the extent of the trouble is difficult to evaluate.

Investigation of caking on a scale larger than that of the laboratory is very expensive. Owing to the large number of variables, the number of samples to be tested and therefore the quantity of material to be dealt with is large, and new types of fertilizer are not always available in sufficient quantity. Experiments on a full scale are obviously necessary ultimately, but it is desirable to have a laboratory test by means of which various aspects can be studied.

A direct comparison between results on the laboratory apparatus and full-scale experiments would be ideal, but this is difficult as conditions are much less under control on a large scale. From co-operative tests with the Production Department of our organization, it can be said that the test described correlates reasonably well with those done on a large scale (see in summary of results).

The problem of caking is a complex one and the aim was not only to find a simple solution to it, but to investigate the effect of the variables.

Experimental

Preliminary considerations and development of apparatus

It was decided, at the commencement of the experiments, to rule out as a variable the effect of atmospheric humidity on the caking for two reasons:

(*a*) The development of paper sacks, in which the fertilizer is generally stored and which are resistant to diffusion of water vapour.

(*b*) In regard to heaps of granular material, calculation shows that a very large volume of air must come into contact with the material to bring about even a small increase of moisture content.

Any apparatus by which the material was contained in a rigid tube with the pressure applied at one end was rejected, as it has been shown by Shaxby & Evans[1] that, with powdered or granular material, the pressure is not uniformly distributed throughout its length.

Such an apparatus was used by Pierrain & Mercier[2] in which pressure was transferred by a lead weight to fertilizer in a split tube. Previous workers, e.g. Adams & Ross,[3] have used comparatively large pressures for a short time (e.g., 12 p.s.i. for 7 days). Hardesty & Kumagai[4] prepared their specimens in a similar way to Adams & Ross, but, after storage for 7 days, the material was dried in an air oven for 72 h. at 50°. The moisture content of the cake was thus reduced to less than 0·5% w/w and this ensured ' maximum cementation '. The cake was then ' sanded to a uniform thickness of 1 in. and its crushing strength determined '. These conditions are too drastic to correlate with actual practice, and the sanding of specimens would certainly affect their strength.

Consider a pile of 1 cwt. bags stored 12 high; the area of contact between bags being taken as 28 in. × 16 in., the pressure on the bottom bag in the pile will be:

$\frac{12 \times 112}{28 \times 16}$ p.s.i. = 3·0 p.s.i., which was chosen for the tests.

The method used for storing the material under pressure is a modification of one developed by the Building Research Station (Department of Soils Mechanics). Pressure is applied by air to the outside of an elastic container in which a sample of granules is tightly held. The air inside the container is given access to the atmosphere, so that the applied pressure is transmitted from granule to granule through the mass, as in a sack of fertilizer.

The container is cylindrical. In order to obtain consistent results in the breaking test, it is important that the height shall be greater than the diameter, and a proportion of height equal to two diameters was adopted.

The filled container is referred to here as a ' specimen '. In general, eleven specimens of each batch of granular fertilizer for test are prepared. One of these is ' broken ' at once to give a ' blank ' value, the others are stored under a given pressure for a given time, after which the breaking strength of each is measured.

Equipment used for making fertilizer cakes is shown in Figs. 1 and 2. Two rubber O-rings (Fig. 1, No. 3) are rolled on to the mild steel support (No. 5), the rubber sleeve (No. 4) is placed inside, and the ends turned back over the support. Any unevenness in the rubber is avoided by applying gentle suction to the tube, and the sleeve is pressed to the wall (A in Fig. 2). With the vacuum still on, this assembly is placed on the metal bottom (Fig. 1, No. 1) and the tube filled with fertilizer to within $\frac{3}{8}$ in. of the top. (The first bases and discs were of mild steel, but these suffered some corrosion and have been replaced by others of stainless steel.) Segregation of the granules is minimized by rotating the beaker containing the fertilizer while the tube is being filled. The tube is tapped three times to consolidate the bed of granules; the metal

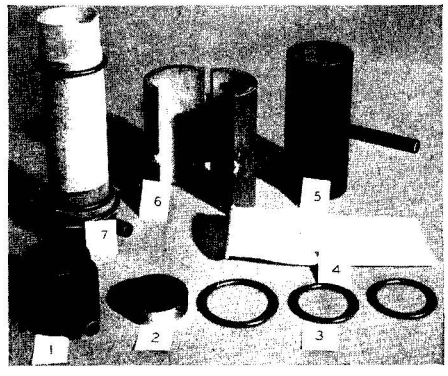

FIG. 1. *Components for making specimens*

top (No. 2) is next put in place, the rubber sleeve at the bottom is rolled down over the base, and the two bottom O-rings slipped down from the support over the rubber to hold it to the base. The top of the rubber sleeve is now rolled up, and the support (No. 5) removed. A $1\frac{1}{4}$-in. diameter O-ring secures the top of the disc; this is rolled down while supporting the cylinder by the hinged split tube (No. 6). The disc has, in a later modification, a groove at the circumference to locate the rubber O-ring.

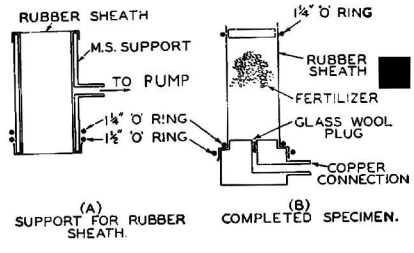

FIG. 2

The specimen, ready for storage, is seen in section in B of Fig. 2 and No. 7 in Fig. 1; it is connected to a $\frac{3}{8}$-in. copper manifold by pressure tubing; 10 specimens of the same material can be connected up in this way.

The rubber sleeves used in the work reported here were $5\frac{1}{2}$ in. long and 2·3 in. wide (when flat), and had an average weight of 4·4 g. In more recent work, the sleeves have been found to suffer some chemical attack, and a heavier sleeve has been used, $5\frac{1}{2}$ in. long, 2·2 in. wide, average weight 7·25 g.

The arrangement to keep the pressure difference between the outside and inside of the specimen at 6 in. mercury (= 2·94 p.s.i.) is shown in Fig. 3.

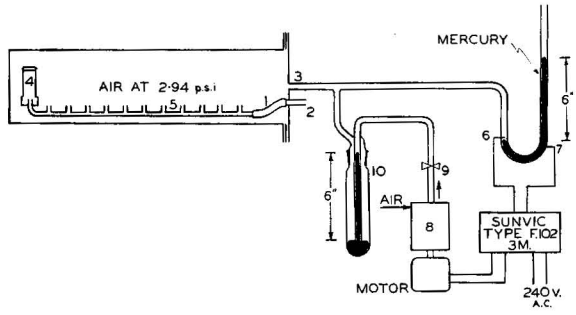

FIG. 3.—*General arrangement of apparatus*

Stout Perspex tubes, 2 ft. long, closed at one end and fitted at the other end with flange and rubber gasket, each house 10 specimens. A disc to fit the flange carries two tubes, one (2) to enable any air diffusing into the specimens to escape, and the other (3) to enable the air inside the cylinder to be maintained at constant pressure. The fertilizer containers are connected, by means of the manifold (5), with tube 2. After placing the specimens in the Perspex tube and bolting on the front disc, the pressure is controlled as follows:

The pressure in the Perspex cylinders is indicated and controlled by a mercury manometer, carrying platinum contacts (6) and (7); these are connected to a Sunvic Hot Wire Switch, which controls the electric motor of the compressor (8). Compressed air is fed through the reducing valve (9); the bubbler (10), containing mercury, acts as a non-return valve. At the commencement, the mercury levels in the manometer are the same, and contacts (6) and (7) complete the circuit for the relay. The small compressor is therefore switched on, and air bubbles through the mercury of the non-return valve (10) to compress the air inside the tube to 2·94 p.s.i. As the pressure increases, the mercury level falls in the left-hand limb of the manometer until the platinum contact (6) leaves the surface, when the circuit is broken and the pump switches off. Mercury rises in the non-return valve (10) to the same height as that in the manometer, i.e. 6 in. Due to imperfections in the rubber, etc., air leaks slowly into the manifold and to the atmosphere (connexion 2, Fig. 3), the mercury level rises in the left-hand limb of the manometer until the contact is made again, and the pump switched on. By this means the pressure in the Perspex cylinder is maintained at $6 \pm 0{\cdot}1$ in. Hg. Each compressor with its accessories can serve 3, 6 or 9 cylinders. Care must be taken to ensure good impermeable rubber sleeves, otherwise some drying out of the fertilizer may occur; alternatively, hygroscopic fertilizers can pick up water and, to prevent this, the incoming air can be dried by a 3 ft. × 2 in. vertical column of silica gel.

The whole apparatus has been used in a constant-temperature room at 25°, except for the preliminary experiments. The apparatus has been working in this form for 3 years, and has given little mechanical trouble. After an appropriate storage time, we have a caked specimen 3 in. high and $1\frac{1}{2}$ in. in diameter, and this is tested without removing the rubber or the steel top and base.

The other problem was to find a suitable means of testing the specimens to give a measure of their caking.

In soil mechanics, engineers are concerned with the result of loading a soil, for example, when it is carrying buildings; it can be regarded as a study of the cohesive properties of materials, which may be plastic, semi-plastic or brittle. Measurement of the caking of granular fertilizers appears to be a similar problem, for here the granules correspond to the soil particles and the force holding them together (the caking) can be measured in a similar way.

The apparatus used for the determination of strength under compression is shown diagrammatically in Figs. 4 and 5. This is a slightly modified version of that described by Cooling & Golder[5, 6] and referred to as an ' Unconfined Compression Apparatus '.

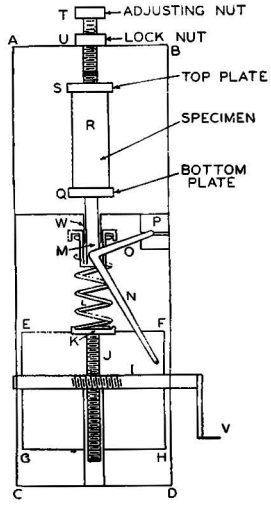

FIG. 4.—*Unconfined compression apparatus*

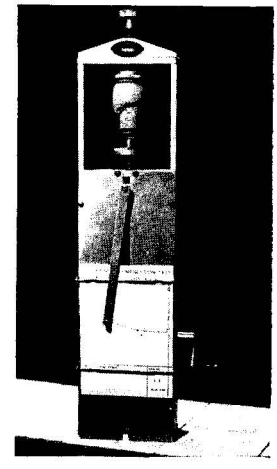

FIG. 5.—*Testing machine, showing failure of specimen*

The machine (Fig. 4) consists essentially of an aluminium framework, ABCD, through which is fixed a spindle carrying a cross-tooth gear, I. By means of a handle, V, this can be made to raise the screw thread, J, which carries the platform, K. The chart, EFGH, is also attached to K, i.e. turning V raises or lowers the platform, K, and the chart plate, EFGH. A compression spring, L, fits on to the base plate, K ; the top of the spring carries part M, which is steadied by the guide tube, W. The top of M forms the bottom platen, Q, on which the specimen, R, rests. An arm, N, carrying a pencil point, is pivoted to M, and another arm, O, fixed rigidly to N, carries a small tip which can only move in the slot, P.

The procedure is as follows. A spring, having a suitable spring factor, is selected and placed between M and K. The stylus of arm N is then at zero on the chart, EFGH. The specimen, R, is set up on the platen, Q, and the adjusting nut, T, screwed down until the top platen, S, is just in contact with the specimen. Locknut U is then clamped into place and handle V wound to raise K. The chart moves upward with the lower end of the spring, so that the movement of the stylus relative to the chart is equal to the compression of the spring and hence proportional to the load. Movement of the bottom platen, Q, upwards, is shown by the stylus moving across the paper. The lateral movement in the arc of the pencil is proportional to the compressive strain in the specimen. As the specimen is compressed, its cross-sectional area increases, so that for stress to be read directly from the chart a transparent mask with constant stress lines is used (Fig. 6).

Consideration has been given to control of the rate of raising the platform. The construction is such, however, that the speed tends to be low, and it is felt that no further control is necessary.

Two typical results obtained from the test are shown in Fig. 7. Curve A is that of an uncaked granular fertilizer ; a spring with a factor of 0·97 was used, so that the maximum reading multiplied by 0·97 gave the maximum compressive strength. This value includes the

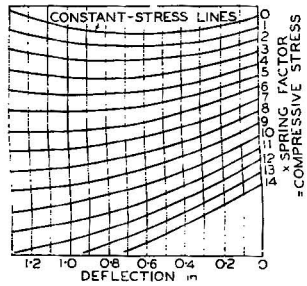

FIG. 6.—*Constant stress lines*

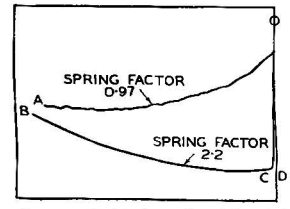

FIG. 7. *Typical results with caked and free-flowing granules*

small effect of the rubber sleeve. With a sample of granular caked fertilizer the stylus traced out the curve OCB ; the part OC records the compression of the spring and the small distance, CD, measures the deformation induced. At C the specimen shears, and the stylus traces out CB. The maximum value, read from the chart and multiplied by the spring factor (2·2 in this case), gives a measure of the caking. Since the specimen is unsupported at the sides, the other two principal stresses are zero, and the shear stress at failure occurs on a plane at 45° to the plane on which the principal stress acts.

Fig. 5 shows the type of failure found with a caked specimen. On examination, it was found that the top part of the sleeve contained loose granular material and the bottom part caked granules (Fig. 8A). No powder was formed due to the shearing of the granules themselves *so that the test measures the strength of the bonding between the granules rather than the strength of the granule itself.*

Fig. 8 shows examples of the failure of specimens ; A shows the type of failure to be expected with caked material and B with free-flowing granular fertilizer. From C it is seen that cakes with a small ratio of height to diameter should not be used, since the plane of failure would not completely cut the circumference of the specimen. This is probably a fault of several of the previous designs of apparatus, and the cause of inconsistent results.

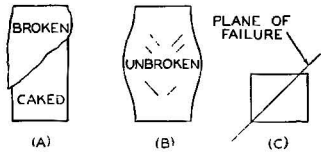

FIG. 8.—*Types of failure in specimens*

Some experiments were carried out to estimate the effect of the rubber sleeve on the final breaking strength. Although results obtained with sleeves were more consistent than those without, the average maximum strengths agreed well. In cutting the rubber sheath away, slight breakdown of key granules may have occurred ; this resulted in a crumbling in some cases when subjected to compression, rather than a clean shear.

Design of the experiments

Some of the variables affecting caking are as follows : (1) pressure ; (2) moisture content ; (3) granule size ; (4) fertilizer composition ; (5) temperature of storage ; (6) atmospheric humidity ; (7) hardness of granules ; (8) free acid content of single or triple superphosphate, and of the granular fertilizer made from it. Some of these variables are now discussed with particular reference to the present work.

(1) *Pressure.*—This was standardized at 6 in. Hg, as described above, except in a few experiments in which specimens were stored at atmospheric pressure.

(2) *Moisture content.*—The free moisture content of fertilizers is difficult to estimate accurately; it was found that reproducible results were obtained in most of the cases dealt with here by drying a 5-20-g. ground sample for 3 h. at 50° under 27 in. Hg vacuum.

(3) *Granule size.*—It was expected that particle size would be important. The sieve fraction lying between 5- and 18-mesh BSS was used, sieve analyses being carried out in practically all cases. Although some of the results departed a long way from the ideal curve, consideration shows that particle size would have to have a very large effect on the caking tendency for this to be important.

In one experiment, three distinct sieve fractions were taken from a batch of material and tested separately, $\frac{3}{16}$ to $\frac{1}{8}$ in., 6-7 mesh, 8-18 mesh. The caking results were almost identical. Chemical analyses (N, P_2O_5, K_2O) and moisture content, however, vary considerably with granule size, and it would appear that the variations tend to balance one another.

(4) *Temperature.* The first experiments were carried out at the temperature of the laboratory, later ones in a constant-temperature room at 25°. Separate experiments were made to determine the effect of temperature on caking.

(5) *Humidity.*—Experiments were not carried out over a range of humidities for the reasons given earlier.

(6) *Hardness of granules.* It is unlikely that plasticity plays an important part in the caking of the granules as no setting is observed in granular superphosphate, which is the most plastic of the materials used.

(7) *Free acid.* The effect of free acid on the caking was investigated, also the effect of partial neutralization with ammonia.

Granulation of mixtures.—Whenever possible, granular mixtures from the production plant were used; otherwise samples were prepared in a small laboratory granulator. There is no evidence that granular mixed fertilizers from the plant are essentially different from those made in the laboratory, and it was shown that batches made at different factories and in the laboratory differed little in their response to the test.

Summary of results

(1) *Effect of time of storage on caking*

A batch of granular fertilizer (9% N, 9% P_2O_5, 15% K_2O) was received from the production plant, and 90 specimens were prepared in the way described, as 9 groups of 10. The breaking strength was estimated after various periods of storage under 6 in. Hg pressure; after 1, 2, 3, 4, 7, 10, 15, 30 and 49 days.

The compressive strength of the cake is plotted against the caking time in days in Fig. 9. It is seen that the strength rises rapidly in the first 10 days, but continues to rise even after a month. A plot of log(days + 1) against the strength gave a straight line for the 10 points (9 stored in the apparatus and 1 of fresh material). From the latter it was decided that a period

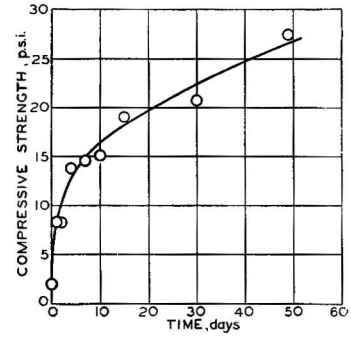

FIG. 9. *Time vs. caking strength*

of 28 days could be adopted as the usual duration of a test. Later it became necessary to compromise between reliability of test and the time taken, and a period of 14 days is now usual.

No definite information is available on full-scale caking tests to confirm these results, but it is agreed that caking does occur rapidly in the first few days and reaches an almost steady value after some weeks.

(2) *Effect of chemical composition on caking*

Consideration has been given to NPK fertilizers made from: (*a*) triple superphosphate, (*b*) single superphosphate, (*c*) potassium chloride and (*d*) ammonium sulphate. Since the representation and design of experiments with all four components is complex, two groups of experiments were carried out, using: (1) varying amounts of (*b*), (*c*) and (*d*) at approximately constant moisture content; (2) varying amounts of (*a*), (*c*) and (*d*) at approximately constant moisture content. The experiments are not comprehensive but give a lead to the effect of composition on caking.

The results obtained can be depicted on a triangular diagram for two or three components as shown in Figs. 10 and 11, the numbers shown being the breaking strength of the specimens in p.s.i. (Free moisture contents of the specimens when put on for caking were 1·0–2·7% in both series of experiments.)

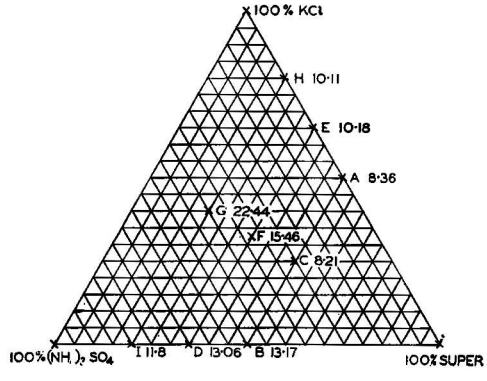

FIG. 10.—*Composition vs. caking strength with single superphosphate present*

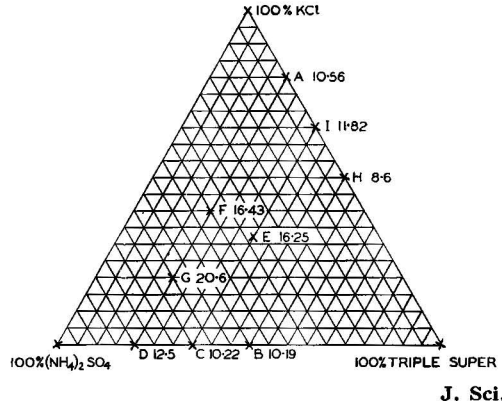

FIG. 11.—*Composition vs. caking strength with triple superphosphate present*

The results of Series 1, with single superphosphate, potassium chloride and ammonium sulphate, can be summarized as follows. A small amount of caking occurs with mixtures of potassium chloride and superphosphate, and more with ammonium sulphate–superphosphate, possibly due to the reaction

$$(NH_4)_2SO_4 + CaH_4P_2O_8 \rightarrow 2NH_4H_2PO_4 + CaSO_4$$

Monoammonium phosphate and calcium sulphate are doubtless formed during the granulation process, and caking may occur as a result of further reaction at the points of contact of granules. The reaction between ammonium sulphate and potassium chloride

$$(NH_4)_2SO_4 + 2KCl \rightarrow 2NH_4Cl + K_2SO_4 \quad . \quad . \quad . \quad . \quad (1)$$

is apparently also important, as mixtures falling within the triangle have a greater breaking strength than those represented along the sides. Mitchell[7] has identified ammonium chloride crystals in granular fertilizer. Granulation was not found to be possible in binary mixtures of ammonium sulphate and potassium chloride.

In Series 2, mixtures of triple superphosphate, potassium chloride and ammonium sulphate were investigated. To facilitate granulation, the triple superphosphate was ground in a laboratory mill before use. The results are summarized in Fig. 11. Breaking strengths are very similar to those of the previous experiment, in spite of the exchange of $CaH_4P_2O_8$ for $CaSO_4$ and the lack of dilution by the latter, consequent on the change from single to triple superphosphate. Crystals of monoammonium phosphate were again recognized on the granule surfaces before and after storage. Caking occurs in the NPK part of the diagram, and, assuming little set with triple superphosphate alone, it appears that the reaction (1) may be largely effective in causing the caking (if the moisture content is approximately 2%). Certainly the results suggest that either single or triple superphosphate tends to act as a diluent and reduce the strength of cake.

There appears to be no general correlation between the ease of granulation of a mixture and its caking properties, but NPK mixtures low in P_2O_5 are subject both to difficult granulation and strong caking.

(3) *Effect of free acid on the caking of a* 9 : 9 : 15* *compound*

Some free phosphoric acid is present with the monocalcium phosphate in superphosphate, and the possibility that this might affect the caking was investigated by measuring the caking strength of mixtures (*a*) prepared from superphosphate of different ages (and so of different free acid contents) and (*b*) prepared from superphosphate which had been ammoniated to various degrees.

(*a*) Here a 9 : 9 : 15 granular fertilizer was prepared using superphosphate of various ages, prepared in the laboratory from Morocco rock (70% through 100-mesh BSS) and 70·2% w/w H_2SO_4 with an acid : rock ratio of 60 g. of H_2SO_4 per 100 g. of rock, and kept in an oven at 90° for 45 min. to imitate den treatment. Six specimens were granulated, using superphosphate of various ages, i.e. 1 h., 1 day, 3, 7, 14 and 28 days. The fertilizer prepared was in other respects practically the same, i.e. the same ammonium sulphate and potassium chloride used, granules −5- to +18-mesh BSS, and free moisture content within the range 0·9 to 2·2%. With free acidity falling from 1·6 to 0·7% and water-soluble P_2O_5 fraction rising correspondingly from 87·5 to 93·8%, the average breaking strength remained the same within the limits of experimental accuracy. Ten specimens were made at each free acid content, i.e. a total of 60.

(*b*) In this series, superphosphate was ammoniated to various degrees and then made into 9 : 9 : 15 compounds : (1) sufficient aqueous ammonia was added to neutralize the free H_3PO_4 in the superphosphate ; (2) sufficient ammonia was added to give an excess of 0·5 mol. of free NH_3 per mol. of P_2O_5 ; (3) sufficient ammonia was added to give an excess of 1 mol. of free NH_3 per mol. of P_2O_5. Results obtained are summarized in the Appendix. They show no decrease in caking with ammoniation.

From the results of these two series of experiments it can be said that the free acid content of the granules has no effect on the caking.

* A mixture of superphosphate, $(NH_4)_2SO_4$ and KCl

If the reaction between monocalcium phosphate and ammonium sulphate is one of the reactions which is important in caking, the use of one of the reaction products, monoammonium phosphate, as a source of nitrogen and phosphorus should reduce the caking. In the first experiment of this type, some of the triple superphosphate was replaced by monoammonium phosphate and in the second, triple superphosphate was completely replaced by monoammonium phosphate. It was found that this made no difference to the caking at the normal moisture level.

(4) *The effect of moisture content on the caking of a* 9 : 9 : 15 *mixture*

A 9 : 9 : 15 granular fertilizer was prepared in the laboratory from triple and single superphosphates, $(NH_4)_2SO_4$ and KCl. The material was then dried and the moisture content estimated ; a set of 10 specimens was prepared and stored for 1 month under 6 in. Hg pressure difference. From the results of this and similar experiments, the curve in Fig. 12 was constructed, which shows that the breaking strength decreases with decreasing free moisture content.

A run was carried out at this stage on a production plant, the final moisture content being 0·63%. Some of this material was stored in 1-cwt. waterproof paper sacks 20 high, and a sample of the low-moisture-content material and a control (at about 5% moisture content) were sent for test in the laboratory apparatus. The material stored on a large scale was tested after one month, using a drop test, cf. Adams & Ross.[3] It was found that the control had caked but the material dried to a low moisture content had not. Very similar results were found in the laboratory apparatus.

Details of a typical experiment are given in the Appendix. Curves of the type shown in Fig. 12 have been found when ammonium sulphate in the fertilizer has been replaced by other sources of nitrogen. It is seen that a low moisture content is required if granular fertilizers are not to cake when stored in piles.

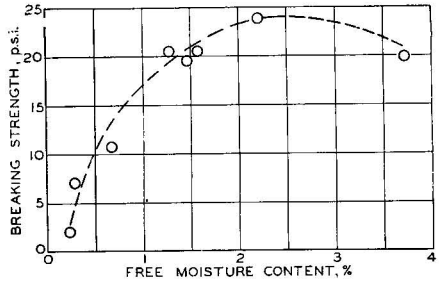

FIG. 12.– *Caking of No.* 31 *with various moisture contents*

Analytical determinations showed that no loss of water-soluble P_2O_5 occurred on drying to low moisture content under the conditions of the experiment.

A batch of fertilizer was sub-divided to permit of experiments on the effects of drying to low moisture content, time of storage at two moisture contents, and pressure with the higher moisture level. (See Appendix for experimental details.)

Results showed that (*a*) material (a 9 : 9 : 15 mixture at 1·5% free H_2O) not stored under pressure was not caked at all after 1 month ; (*b*) material dried down to 0·6% free water set but lightly even when stored for 6 months at 25°.

Hardesty & Kumagai[4] found that the crushing strength of a 10 : 10 : 10 fertilizer decreased with decreasing moisture content.

(5) *Effect of temperature on caking*

In order to investigate the effect of temperature on caking, samples of 9 : 9 : 15 compound were each divided into two and stored at different temperatures in an air thermostat. The results are shown in Fig. 13, in which the compressive stress in p.s.i. in the breaking test is plotted against the temperature. During storage for 1 month, some drying out of the fertilizer occurred, but a similar experiment in which the material contained nitrate as the source of nitrogen, in

which there was very little loss of water, gave similar results. Translation of these results to large-scale storage conditions is difficult. It is known from measurements on piles of unbagged granular fertilizer that the inside of a heap cools relatively slowly, so that the effect of temperature is an important one. With material having about 2% free moisture content, a cooler after the drier is undoubtedly a help.

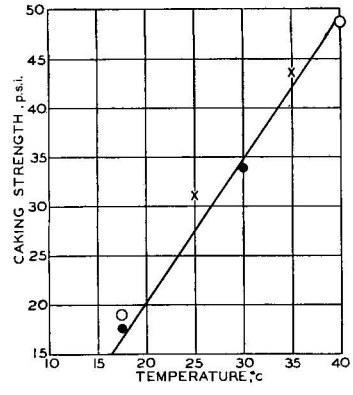

FIG. 13.—*Variation of caking with temperature*
A given symbol represents a batch of material, and it will be seen that each batch was investigated at two different temperatures

(6) *Use of wetting agents and a dye*

Wetting agents have been extensively tried in the United States to improve storage qualities, and their use was considered for granular fertilizers. Of those tried, only sodium lauryl sulphate gave an appreciable reduction, namely from 31·5 p.s.i. to 10·5 p.s.i. with 3 lb./ton of wetting agent; it is seen that this is not as good a reduction as can be obtained by drying the material to low moisture content.

Buckley[8] has found that solutions of Trypan Red are capable of modifying the crystal structure of potassium sulphate, one of the reaction products in an NPK fertilizer, and several patents have been granted for the use of dyes in order to modify the crystal structure of ammonium nitrate and reduce the caking in storage. It was thought that, if caking was due to recrystallization, dyes might prove effective as anti-caking agents. Here the proportion used had to be kept low on account of the cost of large-scale application; a 9 : 9 : 15 mixture sprayed with Trypan Red showed no reduction in caking in the laboratory apparatus.

(7) *Slurry granulation of a fertilizer*

If the setting of a granular fertilizer is due to double decomposition reactions occurring during storage, it would be thought that, by completing the reactions as far as possible before granulation, setting could be avoided. The method of this experiment was to react the components as completely as possible in a slurry stage, then granulate, measure the moisture content, and determine the caking strength.

The components for a 9 : 9 : 15 mixture were ground to pass No. 60 mesh, and mixed. Water was heated to 70°, and the mixture added with stirring to form a fluid slurry. The temperature of the mixture was maintained at about 60° for about 4 hours with continuous agitation. The material was dried with hot air, ground to pass an 18-mesh B.S. sieve, wetted, granulated, and dried. The granules were uniform and seemed to harden on standing.

An average caking strength of 30·0 p.s.i. was attained, one of the highest reached with a 9 : 9 : 15 mixture. It seems evident that chemical reactions continuing during storage are not the main cause of caking in granular mixtures. Details of the analyses are given in the Appendix.

(8) *Correlation between laboratory tests and plant experiments*

Large-scale tests are made by storing 1-cwt. bags of the material in piles about 20 bags in height for periods of one or more months, subjecting individual bags to a standardized drop on

to a concrete floor, cutting the bag open with a sharp knife, pouring the contents on to a screen of 2-in. mesh, and weighing the lumps retained.

Rough correlation with the laboratory results was obtained in some co-operative tests with the Production Department, and this is illustrated by Fig. 14. Up to a certain crushing strength, all the bonds will be destroyed by the dropping of the bags and the caking index will be zero. Above a certain crushing strength, none of the bonds will be destroyed in the drop test, and the caking index will be 100.

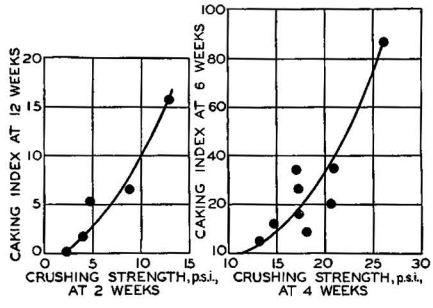

FIG. 14. *Correlation with large-scale results, in two sets of tests*

Further indications of correlation are given by the following:

(*a*) A pile of bagged fertilizer (5% moisture content) set hard, and a laboratory test on the same material gave 22·5 p.s.i. breaking strength; drying to low moisture content (0·6%) gave no set on a large scale and 4·4 p.s.i. in the laboratory test.

(*b*) Replacement of some of the nitrogen as monoammonium phosphate was carried out on a plant scale and samples immediately tested in the laboratory apparatus. Controls and treatment gave average breaking strengths of 18·7 and 18·1 p.s.i. respectively and both set in the plant scale tests.

(*c*) Sodium lauryl sulphate: from laboratory work it was suggested that by applying 3 lb./ton the caking could be halved; almost the same ratio was found when the plant run was carried out.

(*d*) Several tests, over a period of months, using dusting agents on ammonium-nitrate-containing fertilizers, showed good correlation with laboratory experiments, the latter indicating the most promising materials to use.

Discussion

Causes of caking

There are a number of causes of caking which operate in different cases. It is clear that, in the experiments reported here, moisture content and pressure were important variables, so that a suggestion by Sir Robert Robertson[9] as to a possible cause of caking in Oppau salt (ammonium sulphate–nitrate) is relevant: increased pressure would locally raise the solubility of the salt, and the saturated solution, flowing into neighbouring interstices where the pressure is less, would give rise to crystals which would bind the whole together.

Acknowledgments

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References

[1] Shaxby, J. H., & Evans, J. C., *Trans. Faraday Soc.*, 1923, **19**, 60
[2] Pierrain, J., & Mercier, O., *Chim. et Industr.*, 1954, **71**, 281 ; *C.R. 27e Congr. int. chim. Ind., Brussels*, 1954, **2**, 560
[3] Adams, J. R., & Ross, W. H., *Industr. Engng Chem.*, 1941, **33**, 121
[4] Hardesty, J. O., & Kumagai, R., *Agric. Chemic.*, 1952, **7**, 38, 55 ; *J. agric. Fd Chem.*, 1956, **4**, 132
[5] Cooling, L. F., & Golder, H. Q., *Engineering, Lond.*, 1940, **149**, 57
[6] ' Soil Mechanics for Road Engineers ', 1952, p. 369 (London : H.M.S.O.)
[7] Mitchell, W. A., *J. Sci. Fd Agric.*, 1954, **5**, 455
[8] Buckley, H. E., ' Crystal Growth ', 1951, p. 549 (London : Chapman & Hall)
[9] Robertson, (Sir) R., *Trans. Faraday Soc.*, 1924, **20**, 54

APPENDIX

Effect of ammoniation of the superphosphate (Expt. 3)

	Neutralization of free acid	Neutralization of free acid + 0·5 mol. excess NH_3/mol. P_2O_5	Neutralization of free acid + 1 mol. excess NH_3/mol. P_2O_5	Neutralization of free acid + 1 mol. excess NH_3/mol. P_2O_5
Analysis				
Total P_2O_5, %	8·9	9·19	9·93	10·16
Water-sol. P_2O_5, %	8·29	7·28	6·84	7·23
Free P_2O_5 or CaO, %	0·21 P_2O_5	0·13 CaO	0·17 CaO	0·16 CaO
Ammonium-citrate-insol. P_2O_5 (A.O.A.C. method), %	0·1	0·15	0·23	0·25
K_2O, %	15·0	16·96	16·66	17·6
N, %	9·26	8·45	9·72	7·89
Free water before caking, %	1·83, 1·84	2·38, 2·15	4·46, 4·65	3·39, 3·36
Free water after caking, %	0·84	1·30	4·46, 4·51	3·35, 3·39
Breaking strength before caking, p.s.i.	2·0	2·3	2·6	2·9
Breaking strength after 1 month's storage at 6-in. Hg, p.s.i.	14·4 18·3	19·6 21·8	21·2 28·5	28·2 36·2
	15·5 19·6	20·7 22·0	23·8 30·6	29·4 39·8
	16·6 19·6	21·2 21·5	24·1 23·9	30·2 30·2
	17·2 19·6	21·4 22·7	28·5 23·3	31·0 35·0
	17·5 18·5	21·4		31·4
Average breaking strength, p.s.i.	17·7	21·4	25·5	32·4
Standard deviation	1·8	0·9	3·3	3·8

Effect of moisture content on caking (Expt. 4)

9 : 9 : 15 fertilizer made in the Boston Plant	Two passes through dryer at normal temp.	One pass through dryer (Control)
Chemical analysis		
Ammoniacal N, %	9·26	8·26
K_2O, %	16·14	14·44
Total P_2O_5, %	8·37	8·9
Water-sol. P_2O_5, %	7·68	8·1
Free P_2O_5, %	0·64	0·72
Ammonium-citrate-insol. P_2O_5 (A.O.A.C. method), %	...	—
Free water before caking, %	0·62, 0·63	5·04, 5·0
Free water after caking, %	0·77, 0·79	4·8, 4·8
Breaking strength before caking, p.s.i.	1·9	1·8
Breaking strength after 1 month's storage at 6-in. Hg at laboratory temperature, p.s.i.	3·8 4·5	19·0 21·9
	3·9 4·6	19·7 22·6
	4·0 4·7	20·8 24·1
	4·2 4·7	20·8 26·0
	4·4 5·6	21·4 29·0
Average breaking strength, p.s.i.	4·4	22·5

Effect of time of storage, moisture content and pressure on the caking of a 9 : 9 : 15 fertilizer

Conditions	Undried 1 month at atm. pressure and laboratory temp.	Undried 1 month, 3 p.s.i. at 25°	Undried 3 months, 3 p.s.i. at 25°	Dried 1 month, 3 p.s.i. at 30°	Dried 1 month, 3 p.s.i. at 25°	Dried 3 months, 3 p.s.i. at 25°	Dried 4·5 months, 3 p.s.i. at 25°	Dried 6 months, 3 p.s.i. at 25°
Free water before caking, %	1·49, 1·52	1·49, 1·52	1·49, 1·52	0·61, 0·56	0·61, 0·56	0·61, 0·56	0·61, 0·56	0·61, 0·56
Free water after caking, %	1·22, 1·18	0·71, 0·64	0·23, 0·23	0·40, 0·5	0·6, 0·6	0·29, 0·29	0·21, 0·18	0·22, 0·24
Breaking strength before caking (p.s.i.)	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6
Breaking strength, p.s.i., after storage at 6-in. Hg except in first experiment. 'Temperature indicated under 'Conditions', also time of storage	3·1 3·1	10·3 12·7	10·5 15·1	6·6 8·2	4·9 6·1	4·9 5·3	6·3 7·8	4·4 4·4
	3·1 3·1	10·3 13·2	11·6 15·3	7·3 8·4	5·1 6·8	4·7 5·0	6·9 7·8	4·4 4·9
	3·1 3·1	11·0 14·0	11·8 16·4	7·3 8·7	5·2 7·2	4·8 5·0	6·8 8·8	4·4 5·1
	3·1 3·1	12·3 14·2	13·2 21·0	7·8 11·6	5·8 5·8	4·8 5·8	6·8 8·8	4·4 5·8
	3·1 3·1	12·3 14·7	13·2 28·3	7·8 13·6	6·0 5·8	6·0 6·5	7·1 12·1	4·4 10·0
Average breaking strength, p.s.i.	3·1	12·5	15·6	8·7	5·9	5·2	7·9	5·2
Analysis								
Ammoniacal N, %	8·82	8·82	8·82	8·61	8·61	8·61	8·61	8·61
Total P_2O_5, %	9·42	9·42	9·42	9·65	9·65	9·65	9·65	9·65
Water-sol. P_2O_5, %	8·85	8·85	8·85	8·90	8·90	8·90	8·90	8·90
Free P_2O_5, %	1·23	1·23	1·23	1·19	1·19	1·19	1·19	1·19
K_2O, %	13·04	13·04	13·64	13·80	13·80	13·80	13·80	13·80
Ammonium-citrate-insol. P_2O_5 (A.O.A.C. method), %	0·28	0·28	0·28	0·29	0·29	0·29	0·29	0·29

Effect of pressure on caking

Analysis	
Total P_2O_5, %	11·1, 11·1
Water-sol. P_2O_5, %	10·0, 9·78
K_2O, %	16·35
N, %	6·27, 6·23
Free water before caking, %	3·67
Free water after caking, %	3·41
Free P_2O_5, %	1·3
Wt. of each cake 3 in. × 1½ in., g.	90·1
Breaking strength before caking, p.s.i.	2·2
Breaking strength after storage for 1 month at 6 in. Hg, p.s.i.	18·35 18·50 19·20 20·25 21·20 21·80 22·85 26·00 23·25 30·80
Average breaking strength, p.s.i.	22·22
Standard deviation	± 3·83
Breaking strength after storage for 1 month at atmospheric pressure, p.s.i.	3·69 4·85 5·05
Average breaking strength, p.s.i.	4·53

Preparation of 9 : 9 : 15 fertilizer by slurry granulation

Analysis	%
Total P_2O_5	8·81
Water-sol. P_2O_5	8·36
Free P_2O_5	0·43
Citrate-insol. P_2O_5	<0·01
K_2O	14·84
N	9·16
Free water before caking	2·36, 2·38
Free water after caking	1·85, 1·9
Breaking strength before caking, p.s.i.	1·94
Breaking strength after 1 month's storage at 6 in. Hg, p.s.i.	25·7 30·6 27·3 31·4 27·3 33·8 27·3 41·5 28·5 26·6
Average breaking strength, p.s.i.	30·0
Standard deviation	± 4·8

SOIL FUMIGATION. VI.*—The Distribution of Ethylene Dibromide Round an Injection Point†

By F. CALL

The distribution of ethylene dibromide vapour round an injection point has been measured experimentally in a number of soils. It is concluded that diffusion is the most important factor controlling distribution. The concentration–time products (C.T.) have been calculated at various distances from the injection point and an LD_{50} range has been derived from the C.T.–distance curves. These LD_{50} ranges were found to have a linear relationship with the soil porosity for all soils at two temperatures. The implications of these findings are discussed.

The diffusion patterns of fumigants in soil during soil fumigation have been investigated by biological, chemical and physical methods. The biological method (Allen & Raski ;[1] Thorne[2]) involves assessment of the toxic effects of the fumigant at various points in the soil and can thus lead only to qualitative or semi-quantitative results. The chemical methods have usually required removal of samples of the soil followed by chemical determination of the contained fumigant (Higgins & Pollard ;[3] Hanson & Nex[4]). This method thus leads to average values

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† Part of a thesis approved for the degree of Ph.D. in the University of London

of the concentration over a range of distances and does not differentiate between fumigant in the vapour or sorbed phases. Siegel, Erickson & Turk[5] used a radioactive tracer technique which overcomes these disadvantages but is difficult to apply to soils in the field and to interpret quantitatively.

In the present work, the concentration distribution of ethylene dibromide vapour in soil is measured by withdrawing samples of soil air and analysing them by the micro-sampling apparatus (Call[6]). This technique has many advantages, e.g., the structure of the soil is not disturbed during an experiment so that a single fumigation can be studied in entirety. Furthermore, the concentration determined is that of the vapour phase only and since the total volume of soil air withdrawn for a single determination is of the order of 2–3 ml., there is little disturbance of existing vapour-concentration gradients. Call[7] has shown that at least 97% of the total fumigant in the soil is in the sorbed state so that ethylene dibromide withdrawn in a small sample of soil air will be replaced largely from the sorbed phase with minimal change in the vapour phase distribution.

Experimental

Soils were lifted from the field during the late autumn and stored in airtight dustbins until required. Each soil was rubbed through a sieve of about 1-cm. mesh in order to remove the larger stones. Care was taken to lift soils during a fine period following rain so that they were approximately at field capacity. Moisture determinations at intervals showed little change in moisture content during the 3 to 6 months' storage period.

The following soils have been used in these experiments:

Reference	Soil	Type
A1	Ashurst Garden	Sand
A2	Ashurst Field	Sand
C	Woburn Greensand	Coarse sand
U	Auchincruive	Loam
H	Kirton Silt	Silt
V	Whittlesey Black Fen	Peat
Y	Pondersbridge	Peaty clay loam

A full description of these soils has been published earlier (Call[7]).

Fumigations were carried out in a large cylindrical bin 60 cm. in diameter and 60 cm. deep which required seven or eight hundred kg. of soil to fill it. The dimensions of the bin were chosen so as to allow ample space round the injection point and to minimize possible wall effects. A number of small holes, each about 1 mm. in diameter, were drilled in the wall of the bin at 5-cm. intervals so as to allow samples to be taken through 30-cm. lengths of No. 20 s.w.g. stainless steel hypodermic tubing each fitted with a No. 21 s.w.g. steel wire in order to clear the bore of soil. A 3-cm. length of brass tubing was sweated near one end of each sample tube to enable the micro-sampling apparatus to be connected.

Fumigations were carried out in a constant-temperature room maintained at $20° \pm 0{\cdot}1°$. Before starting each fumigation, the storage bins required were taken into the constant-temperature room and left for at least three days in order to come into temperature equilibrium.

Soils were packed to constant bulk density as follows. Sufficient soil to form a layer, 10 cm. deep at the required bulk density, was weighed into the bin and, after levelling, the soil was compacted to form a layer 10 cm. deep by means of a rammer. Care was taken to allow the rammer to fall through the same height for each blow so as to compact the soil evenly. If necessary, a large pressure board was placed on the soil layer and further compaction carried out by adding heavy weights. Another layer of soil was added and compacted, the process being repeated until the bin was filled to within 5 or 10 cm. of the top. The bin was now covered with a close-fitting lid to prevent drying out of the upper layers and set aside for another two to three days. This technique resulted in fairly uniform packing as is shown by the figures in Table I for core samples taken after the fumigation. Porosities of cores were measured by the technique of Torstenssen & Erickson.[8]

The hypodermic sample tubes were placed in position, each one being carefully aligned by eye before pushing it into the soil. Samples were taken in the centre of the bin on a line vertically

Table I

Packing of core samples of soil

Depth, in.	Bulk density	Porosity	Moisture content, %
0–3	1·285	0·388	18·3
3–6	1·285	0·384	18·7
6–9	1·288	0·390	18·5
9–12	1·288	0·391	18·9
12–15	1·298	0·386	18·7
15–18	1·320	0·380	18·9

above and below the injection point and at the level of the injection point at 2-cm. intervals radially. Sample tubes for points vertically above the injection point were not pushed home until after the injection had been made. The radial sampling points were staggered on a spiral to avoid 'screening' of one point by a nearer one. Each sampling tube was fixed in position by means of plasticine moulded to the outside of the bin.

Injections were made at 6 in. (15 cm.) depth. Attempts to inject the liquid by means of a hypodermic syringe proved unsuccessful owing to leakage of liquid back along the hole made by the needle. A technique was therefore adopted which resembled that used in practice. First, a thin-walled metal tube was used to remove a core of soil 1 cm. in diameter and 15 cm. long. A little loose soil was dropped into this hole and 1 ml. of ethylene dibromide was carefully introduced at the bottom of the hole by means of a glass pipette. The hole was now filled with portions of soil, each portion being carefully tamped with a rod. Finally the surface was once more compacted with a rammer. It is obviously very difficult to reproduce the original packing of the soil by this technique, but an attempt was made to gauge the resistance offered to the rod by the soil and it is probable that the packing of the injection hole was not markedly different from that of the soil mass.

Zero time was counted from the instant the ethylene dibromide was added and samples were taken at all points at 4, 12 and 24 hours, thereafter at 24-hourly intervals until the concentrations were too small to measure accurately. Samples were taken in the order which was anticipated would lead progressively from the smallest to the highest concentration. Before taking each sample, the inner wire was moved backwards and forwards several times to ensure that the tube was free from soil. The wire was then withdrawn and the micro-sampling apparatus was connected to the tube. Two to three ml. of air were now drawn slowly through the apparatus by means of a hypodermic syringe connected to the bottom of the furnace tube. This not only ensured that the dead space was filled with vapour of the concentration being sampled but also brought all sampling tubes into sorption equilibrium with the vapour. The maximum volume of air from each sample point was thus about 5 ml. and, for a soil porosity 0·300, this volume represents a sphere of radius 1·5 cm. round each sample point. It has been pointed out that only about 3% of the ethylene dibromide is in the vapour phase, the remaining 97% being sorbed. The ethylene dibromide removed in sampling will thus be only a small fraction of that actually present and will cause negligible interference with concentration gradients.

When concentrations were too small to measure accurately, the sampling tubes were withdrawn and the bin was emptied, core samples being taken at 3-in. intervals of depth. These core samples were weighed to determine the bulk density, the porosity was measured by means of the porosimeter described by Torstenssen & Eriksson[8] and samples of the soil were weighed out for determination of moisture content.

Results

Concentration–time curves for four experimental fumigations are shown in Fig. 1. These relate to concentrations measured at the depth of the injection point (6 in.) and at various radial distances from this point. The curves are all of similar shape, a rise to a peak concentration being followed by a more gradual decay to zero concentration. The initial stage roughly corresponds to the period during which the liquid fumigant is evaporating. When evaporation is complete, concentrations fall gradually as the fumigant vapour diffuses away. It is interesting

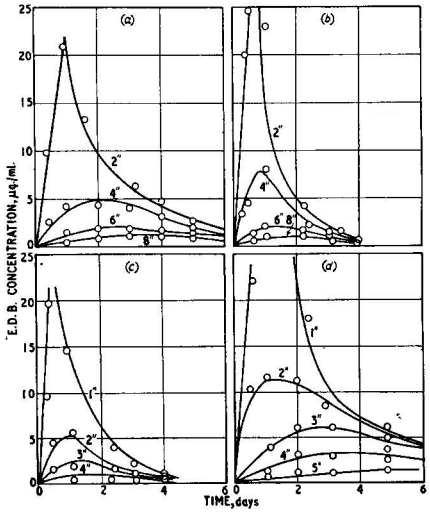

FIG. 1.—*Concentration time curves at 6 in. depth at different distances from injection point*
E.D.B. = ethylene dibromide
(*a*) Ashurst Field Soil A2
(*b*) Woburn Greensand C
(*c*) Whittlsey Black Fen V
(*d*) Kirton Heavy Silt H

to note that the maximum concentration occurs a little later in time as the distance from the injection point increases. Thus the peak concentration travels through the soil with a finite velocity being rapidly damped out.

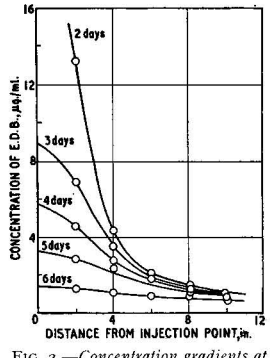

FIG. 2.—*Concentration gradients at 6 in. depth at different times for Ashurst soil*
E.D.B. = ethylene dibromide

Fig. 2 shows the horizontal concentration gradients at the depth of the injection for Ashurst Field soil. Concentration gradients are at first very steep but gradually become flatter as diffusion proceeds.

Table II shows the concentrations at various depths along a vertical line through the injection point for all soils 24 hours after injection.

It will be seen that, in general, the concentrations at points below the point of injection are lower than concentrations at points the same distance above this point. The only exceptions are the peat soils, Whittlesey and Pondersbridge, and it might be assumed that liquid ethylene dibromide was able to percolate downwards a short distance into these very open, light soils. The results do not show the downward gravity flow of vapour reported by Higgins & Pollard.[3] On the contrary, there appears to be an upward movement of vapour towards the open surface of the soil where it can escape into the air.

The dose of fumigant to which an organism at any point in the soil would be subjected, is usually expressed as the product of the mean concentration at that point and the time of exposure (concentration–time product or C.T. product). This assumes that the toxic effect is independent of the concentration which is not always true.

The C.T. product (μg. h./ml.) for each distance from the injection point was obtained by graphical integration of the appropriate curve. The results, when plotted against the distances from the injection point, were found to give smooth curves for each soil as shown in Fig. 3. Parallel straight lines were obtained by plotting the log(C.T. product) against porosity.

Table II

Concentration, μg./ml., of ethylene dibromide at various depths along a vertical line through the injection point, 24 h. after injection

Soil	Depth in inches					
	2	4	6	8	10	12
Ashurst Field	5·4	10·6	Injection point	7·3	1·4	1·3
Woburn	8·1	23·5	,, ,,	13·1	6·9	4·2
Whittlesey	1·7	2·8	,, ,,	11·2	0·8	0·5
Auchincruive	1·3	35·3	,, ,,	12·1	1·1	0·4
Pondersbridge	0·6	8·1	,, ,,	20·7	2·3	0·3
Ashurst Garden	7·7	12·7	,, ,,	1·4	0·9	0·6
Kirton Medium	0·7	14·5	,, ,,	9·7	0·2	0·1
Kirton Heavy	2·1	26·1	,, ,,	4·7	3·1	0·3

No reliable data are available for calculating the median lethal dose (LD_{50}) of ethylene dibromide for nematodes or other soil pests, but a C.T. product of 300 μg. h./ml. was assumed to be a reasonable value. The argument that follows is not vitiated by any error in this assumption. If through the curves of Fig. 3 a line is drawn parallel to the abscissa at 300 μg. h./ml., the intercepts with the curves give the distances at which this C.T. product is just attained. For convenience this distance is called the LD_{50} range. The LD_{50} ranges were then plotted against various soil properties such as the unsteady state diffusion coefficient in the soil (Call[9]), the sorption coefficient (Call[7]) and the porosity. No obvious correlation was found with either of the first two coefficients but there was high correlation with soil porosity. Fig. 4 shows the LD_{50} range plotted against soil porosity for fumigations at 20° and at 10°. The relationship is seen to be linear.

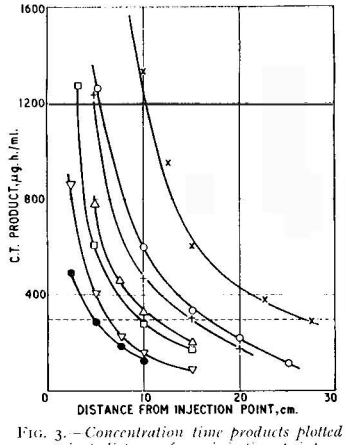

FIG. 3.—*Concentration time products plotted against distance from injection point*

Soil		Soil	
×	H	△	Y
○	A2	□	C
+	U	▽	V
		●	A1

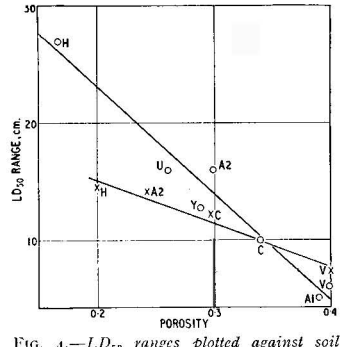

FIG. 4.—LD_{50} *ranges plotted against soil porosity*

○ 20° × 10°

LD_{50} ranges vertically above the injection point were similarly obtained and Table III lists the horizontal and vertical ranges for four soils at the two temperatures.

It will be noted that the superior vertical ranges are always less than the horizontal ones, the differences being much more marked at low porosities and at high temperatures.

Discussion

This work strongly suggests that the movement of ethylene dibromide vapour through soils

Table III

Vertical and horizontal LD_{50} ranges

Soil	Range (cm.)					
		20°			10°	
	Porosity	Horizontal	Vertical	Porosity	Horizontal	Vertical
H	0·172	27·0	12·6	0·200	14·2	11·4
A2	0·302	16·0	10·6	0·242	14·0	11·0
C	0·340	10·0	7·2	0·295	11·6	8·8
V	0·398	6·0	5·3	0·400	7·5	7·3

during soil fumigation is a pure diffusion process and that downward gravity flow of the vapour plays a negligible part.

The work has been carried out under ideal conditions of uniform porosity, compaction and constant temperature, as of course is essential in any physical study. It is appreciated that, in the field, soils will be far from uniform, while the temperature will vary periodically during the time of fumigation, and this variation will depend on the depth from the surface. These factors will increase the complexity of the vapour distribution but, since the fluctuations will be around an average value, the vapour distribution will probably not be far from the distribution achieved by holding this average value constant.

Two main points emerge from the work. First, the low concentrations near the surface of the soil are due to loss of fumigant into the air and arise from the geometry of the system. The concentration–time product falls to zero at the soil surface and organisms lying in the surface layer will thus escape effective treatment. It would seem that the only method of obtaining adequate concentrations in these surface layers is by altering the geometry, for example, by sealing the soil surface by water or by an impervious covering. Decreasing the porosity by rolling the soil may also be of some value.

The second point is the unexpected simplicity of the empirical relationship between the LD_{50} range and porosity. It would thus seem preferable to fumigate a field when the soil is well compacted before cultivation as a seed bed. Unfortunately such a soil has usually a very uneven surface and possesses many fissures due to lifting of the previous crop.

Probably the most important variable controlling the air spaces of a soil is the water content. It has been found by taking core samples of undisturbed soils some days after rain that the air porosities of the layers down to 6 or 9 in. are between 50% and 100% greater than porosities below this depth, an effect clearly due to drainage of water as shown by the moisture contents. The higher porosity in the surface layers will of course contribute to loss of fumigant vapour into the air leading to low concentrations in these layers.

The reduction of porosity following rainfall may perhaps be advantageous for fumigation but such a technique will always be uncertain in countries with an erratic rainfall such as Great Britain.

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References

[1] Allen, M. W., & Raski, D. J., *Phytopathology*, 1950, **40,** 1042
[2] Thorne, G., *Proc. helm. Soc. Wash.*, 1951, **18,** 18
[3] Higgins, J. C., & Pollard, A. G., *Ann. appl. Biol.*, 1937, **24,** 895
[4] Hansen, W. J., & Nex, R. W., *Soil Sci.*, 1951, **76,** 209
[5] Siegel, J. J., Erickson, A. E., & Turk, L. M. *Soil Sci.*, 1951, **72,** 333
[6] Call, F., *J. appl. Chem.*, 1957, **7,** 210
[7] Call, F., *J. Sci. Fd Agric.*, 1957, **8,** 137
[8] Torstenssen, G., & Eriksson, S., *Soil Sci.*, 1936, **42,** 406
[9] Call, F., *J. Sci. Fd Agric.*, 1957, **8,** 143

MERCURY RESIDUES IN SPRAYED CROPS. I.—Tomatoes

By A. S. BEIDAS and D. J. HIGGONS

Mercury residues have been determined on glasshouse crops of tomatoes which have been treated with mercury aerosols. The results show that in some cases 0·5 p.p.m. (as metallic mercury) may be present on the fruit as it is harvested. This mercury contamination is situated mainly in the pulp of the tomato and is a potential health hazard to the consumer.

Introduction

The presence of mercury residues in harvested crops which have been sprayed with organomercury fungicides has given rise to considerable concern in some quarters. This concern has been emphasized by the recent inclusion of mercury vaporizing solutions within the terms of the Agricultural Poisonous Substances Act.

Very few data (published or unpublished) exist on mercury residues likely to be found in treated crops at harvest. The only published work of which we are aware, which deals with the subject of mercurial residues in tomatoes is by Stone, Clark & Jacks[1] from New Zealand. In this paper it is claimed that the residues appearing from the use of mercury aerosols did not exceed 0·05 p.p.m. as metallic mercury, which was considered a satisfactory tolerance level. Some doubt is cast on the value of this work, however, as mercury was determined only on the skins of treated tomatoes.

The scope of the present investigation is to provide figures for total mercury residues in tomatoes which have been treated with mercury vaporizing solutions under normal user conditions. These aerosols usually contain about 0·2% of organically combined mercury, and are applied to growing tomato crops. Because fruit in all stages of development is likely to be present at the time of application, it is usually impracticable to defer picking treated crops of tomatoes for more than three days after application.

For the analytical determinations, samples of about 1 lb. of fruit were picked at random across the glasshouse. In all cases only fruit ready for marketing was picked so that the results express the true mercury residue at the time of harvesting.

Experimental

Treatment of samples

In order to study the distribution of residues in tomatoes the mercury was determined on :

(1) The surface washings obtained by soaking 100 g. of tomatoes in hot 3N-nitric acid, then in hot water and finally in hot 3N-nitric acid.
(2) The skin separated after treatment as in (1).
(3) The residual pulp.

For determination of total mercury residues, 500 g. of tomatoes were macerated and 100-g. aliquots were used for analysis.

Analytical procedure

The tomatoes were subjected to wet oxidation by the method of Klein[2] and the following technique used in the isolation of the mercury. This has been used for some years in this laboratory and has been proved by recovery experiments to be satisfactory.

Reagents. Solutions of dithizone.

(*a*) Extracting solution (10 mg. in 200 ml. of carbon tetrachloride).
(*b*) Strong solution (50 mg. in 100 ml. of chloroform).
(*c*) Titrating solution (5 ml. of *b* in 250 ml. of chloroform), freshly prepared.

The sample solution, after wet oxidation and adjustment of acidity to 1·0 N with ammonia, was transferred to a 250-ml. separator and 0·5 g. of hydroxylamine hydrochloride was added. The mercury was extracted with 2 × 5 ml. of dithizone solution (*a*) each with shaking for 30 sec.

The dithizone solutions were bulked in a 150-ml. separator and extracted with 20 ml. of 1·0N-sulphuric acid and 5 ml. of 0·1N-potassium permanganate, shaking the separator vigorously for 1 minute. The sulphuric acid/permanganate extraction was repeated twice, with rejection of the carbon tetrachloride layer. The aqueous phase was washed with 10 ml. of carbon tetrachloride and the latter rejected.

The aqueous phase was decolorized with a few crystals of sodium nitrite, 0·5 g. of hydroxylamine hydrochloride and 3 ml. of 33% acetic acid were added and the solution was titrated with dithizone solution (*c*). Near the end-point, the titration solution was added in 0·2-ml. quantities, shaking the separator for 30 sec. after each addition and rejecting the chloroform layer (golden orange in colour). The solution was titrated until the chloroform layer remained a definite green.

The dithizone titrating solution (*c*) was standardized by titrating a solution containing a standard quantity of mercury approximately equivalent to the amount extracted in the experiment.

A blank determination was carried out on all the reagents used.

Results

The first trial was carried out in a 4000-cu. ft. glasshouse containing a crop of tomatoes (var. Potentate). Applications of mercury vaporizing solution (solution of phenylmercuric chloride in acetone containing 0·2% Hg) were commenced on 7 August and were carried out weekly according to normal commercial practice. The rate of application was 3 fl. oz. per 4000 cu. ft. for each application. The results are shown in Table I.

The results are very variable and appear to bear no relation to the number of applications. This occurrence was noticed by Stone and co-workers, and is probably associated with the fact that the fruit is in all stages of development during the course of the trial and also with the large sampling error which is inevitable in any work of this nature.

The second trial was carried out by giving a single application of 1 pint of mercury vaporizing solution to a crop of E.S.1 tomatoes in a 28,000-cu. ft. glasshouse, the mercury residues being followed to zero level. The results are in Table II.

The results again show considerable variation. The nil values for the first two days are difficult to understand, but are believed to be due to the fact that fruit in these samples was picked from the bottom trusses heavily screened by leaf, whereas later samples were picked from higher trusses.

In order to gain some idea of the distribution in the fruit, the mercury in two samples from Trials I and II respectively was determined as surface, skin and pulp residues. The results are shown in Table III.

It would appear that penetration is rapid with up to 50% of the residual mercury appearing in the pulp three days after application. On the long-term trial (see Table I) 90% of the residual mercury was found in the pulp 34 days after the beginning of treatment.

To confirm these results (Tables I and II), which were carried out under carefully controlled conditions, an assessment was made of the residual mercury in crops from commercial holdings

Table I

Total mercury residues appearing in crop

Date	Sampling time	p.p.m. as metallic mercury	
		A	B
7 Aug.	Before treatment	Nil	—
8 Aug.	1 day after first treatment	0·30	0·30
9 Aug.	2 days ,, ,, ,,	0·30	0·25
10 Aug.	3 ,, ,, ,, ,,	0·25	0·25
13 Aug.	6 ,, ,, ,, ,,	0·20	0·20
14 Aug.	1 day after second treatment	0·50	0·50
17 Aug.	4 days ,, ,, ,,	0·30	0·10
21 Aug.	1 day after third treatment	0·10	0·10
24 Aug.	4 days ,, ,, ,,	0·05	0·05
28 Aug.	1 day after fourth treatment	0·04	0·04
31 Aug.	4 days ,, ,, ,,	0·15	0·15
7 Sept.	11 ,, ,, ,, ,,	0·17	—
11 Sept.	1 day after fifth treatment	0·14	—

Table II

Persistence of mercury residues from a single application

Date	Sampling time after treatment, days	Residue, p.p.m. Hg	Date	Sampling time after treatment, days	Residue, p.p.m. Hg
3 Sept.	Before treatment	Nil	11 Sept.	8	0·05
4 Sept.	1	Nil	12 Sept.	9	Nil
5 Sept.	2	Nil	13 Sept.	10	0·03
6 Sept.	3	0·08	14 Sept.	11	0·05
7 Sept.	4	0·12	17 Sept.	14	0·25
10 Sept.	7	0·16	25 Sept.	22	Nil
			2 Oct.	29	Nil

Table III

Distribution of mercury residues in tomatoes

Sample	Surface		Skin		Pulp		Total (direct)
	p.p.m. Hg	% of total	p.p.m. Hg	% of total	p.p.m. Hg	% of total	
Trial I – 1 day after fifth treatment	0·004	3	0·009	7	0·125	90	0·14
Trial II – 3 days after first treatment	0·01	12	0·017	20	0·042	50	0·083

to which mercury vaporizing solution had been applied as a standard practice. Samples were collected the morning after application and three days later to give an indication of initial deposit and persistence. It would be normal practice to pick the crop for marketing on the third morning. The results are shown in Table IV.

Throughout all this work, frequent blanks from untreated glasshouses were examined. In all cases these were free from mercury.

Table IV

Total mercury residues in tomatoes from commercial houses

Centre	Location	Commercial product	Mercury residue (p.p.m.)	
			Morning after application	Four days after application
A	Thames Valley	I	0·20	0·05
B	Wisbech	I	0·05	0·05
C	Worthing	II	0·50	0·40
D	Worthing	II	0·40	—
E	Guernsey	I	0·55	Nil

Discussion

Throughout all the trial work reported, the mercury residues show considerable variation, although the residues from duplicate samples, taken at any one time in the house, are reasonably close. This occurrence was also noticed by Stone *et al.* and either their explanation of the relative age of fruit from progressive trusses seems to be feasible or the protection of fruit in lower trusses by foliage may be the explanation.

Despite the variation of results obtained, it is clear that samples of treated crops from experimental and commercial houses may contain residues up to 0·5 p.p.m. of mercury. It also appears that these residues are persistent and that a large proportion is to be found after a short time in the pulp of the fruit.

It is beyond the scope of the present paper to discuss the detailed pharmacological significance of the residues found. Stone and co-workers suggest that 0·05 p.p.m. would be satisfactory as the permissible maximum for residual mercury, but this figure seems to be based more on the level of residues found in practice than from practical pharmacological work. The data presented above on penetration of mercury into the pulp also casts doubt on the validity of the results obtained from the analysis of the skins only.

In the United States under the terms of the Miller Act, a ' nil ' tolerance for residues from mercury products is specified. The levels of mercury reported in this work would therefore seem to constitute a potential consumer hazard.

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References

[1] Stone, H. M., Clark, P. J., & Jacks, H., *N.Z. J. Sci. Tech.*, 1954, **35**, [B], 301

[2] Klein, A. K., *J. Ass. off. agric. Chem.*, 1952, **35**, 537

THE STORAGE OF GROUNDNUTS UNDER TROPICAL CONDITIONS. I.—The Effects of Prolonged Storage on Undecorticated and Decorticated Groundnuts

By J. C. DUERDEN and J. R. CUTLER

In a study of the extent of insect damage and determination of quality of groundnuts stored in sacks for 16 months in a warehouse in N. Nigeria, there was found little difference between undecorticated, hand-shelled and ' pestle-and-mortar '-shelled nuts, in the loss of weight and production of powder, as a result of attack by insects (mainly *Tribolium castaneum*), but there were large differences in the build-up of free fatty acids. The insects are shown to cause breakage of the nuts, but under the conditions of the experiment an unbroken shell provides complete protection of the kernels against the species used.

Introduction

The annual crop of decorticated groundnuts in Northern Nigeria usually exceeds 300,000 tons and prolonged storage is essential. In some years when the new season's crop is harvested, much of the preceding crop remains at the railheads and a storage period of up to 20 months has been known, during which time considerable losses occur. These are in three principal forms: (*a*) direct loss of weight due to the activity of insects, (*b*) powdering of nuts by insects and (*c*) rise in the free fatty acid (F.F.A.) content of the oil. It has been shown[1] that both the damage by insects and the rate of increase of F.F.A. are greater when a high proportion of the groundnuts is broken into fragments.

The groundnuts are decorticated in the growing areas by means of a wooden pestle and mortar followed by winnowing. This method produces whole, half and broken nuts in approximately equal proportions by weight.

The desirability of increasing the proportion of unbroken kernels has long been appreciated but the traditional method of shelling is difficult to change and it is not known accurately to what extent the ultimate losses would be reduced on a field scale. The work described here was carried out to determine these losses.

Between the commencement and completion of this investigation a special marketing scheme incorporating a price incentive has been introduced in an attempt to increase the proportion of whole nuts in Nigerian groundnuts. Preliminary figures indicate that the response has been small.

Experimental

Methods

Normal pestle-and-mortar-shelled groundnuts were compared with hand-shelled and unshelled groundnuts stored in a warehouse in Kano, Northern Nigeria. The latter category was included for the purpose of comparison. The nuts were harvested at the end of 1953, the stacking carried out in May, 1954, and the first assessments done 10 months later. Before stacking, all the nuts were fumigated with methyl bromide and sieved to remove dust. The sieve was of sufficient size to take the contents of a whole bag of nuts and was fitted with a perforated sheet having eight holes per inch, each approximately $\frac{1}{12}$ in. in diameter. The groundnuts were re-bagged in numbered, standard size, hessian sacks weighing approximately 180 lb. dry weight in the case of the hand- and pestle-shelled nuts and about 85 lb. for the unshelled nuts. The bushel weight of every bag was determined as it was filled. Each bag was accurately weighed and small replicated stacks of each type of nuts were built, each stack containing twelve bags. The storage period commenced just before the onset of the rains.

Before weighing, a homogeneous sample of each type of groundnuts was withdrawn from every sixth bag and determinations of moisture, oil and F.F.A. contents carried out. The proportions of whole, half, and broken nuts (less than half a kernel in size) were determined for every sample and the degree of post-harvest insect damage shown by each of the above fractions was recorded. An arbitrary scale of insect damage was devised as follows:

Nil—no evidence of attack by stored products pests.
Slight—kernel or pieces of kernel 'nibbled', less than one-quarter consumed.
Medium—kernel or piece showing indications of between one-quarter and one-half eaten away.
Heavy—over one-half eaten away.

From the samples of undecorticated nuts the percentage of perforated pods was assessed. These holed and broken pods were further examined for evidence of post-harvest insect attack. This took the form of frass seen through or issuing from the holes or fractures, presence of webbing in the vicinity of the holes, and cast larval skins adhering to the nuts, etc.

As the store used was reasonably distant from other groundnut storage centres and the building had fairly close-fitting doors and no windows, several lots of about 500 *Tribolium castaneum* Hbst. insects were liberated at different points in the store periodically to ensure adequate infestation. Apart from this and occasional inspections, the groundnuts were untouched for an initial period of 10 months.

In March, 1955, four bags were removed from each stack and weighed. The frass was sieved out and weighed, the bushel weight of each bag was determined and samples for laboratory analyses taken. The 3-lb. samples taken were made up of handfuls taken at random from the entire contents of one bag as they lay exposed in the large sieve. From these samples similar data to those taken before storage were obtained. Oil, moisture and F.F.A. contents, proportions of whole, half and broken nuts, holed pods and degree of insect damage were determined. This procedure was repeated in June and September, 1955, giving storage periods of 13 and 16 months respectively.

Results

To assist in making direct comparisons between different times of sampling, all weights have been converted to dry-weights on the basis of moisture contents determined at the time of sampling. The summarized physical and chemical changes in the nuts are given in Table I, while Table II shows the changes in extent of insect damage and proportions of whole, half and broken nuts.

Classification of the degree of damage to broken fragments was difficult, and it was impossible in many cases to say with accuracy whether a particular fragment represented a quarter or a half of the original piece, but in the main, damage to the broken pieces shown in Table II appears to maintain established trends. Where the results appear ambiguous it is probable that the difficulties in classification have caused errors.

Table I

Physical and chemical changes in three types of stored groundnuts

Category of nuts	Time of storage, months	Weight in lb. Loss in dry weight/ 100 lb. of nuts	Dry weight of frass/ 100 lb. of nuts	Bushel weight, lb. dry weight	Moisture content, %	Oil content as % of dry weight	Free fatty acids, %
Unshelled	Before storage	—	—	24·7	3·8	50·7	0·3
	10	1·1	1·1	25·7	3·4	50·4	1·0
	13	1·8	0·9	25·0	4·6	50·0	0·6
	16	0·8	1·1	25·3	6·0	50·6	1·2
Hand-shelled	Before storage	—	—	49·9	3·7	51·1	0·6
	10	0·1	0·3	51·6	3·3	51·3	2·5
	13	0·5	0·6	51·3	4·2	51·2	2·5
	16	0·7	0·9	50·9	5·8	51·8	5·6
Normal Kano-type nuts	Before storage	—	—	51·6	3·6	52·2	3·0
	10	0·0	0·9	52·2	3·1	52·4	9·7
	13	0·3	1·1	51·9	4·0	51·9	10·3
	16	0·5	1·1	51·0	5·5	51·8	13·8

In order that direct comparisons may be made between the proportions of broken nuts and the degree of insect damage, the percentages of whole, half and broken nuts at each sampling date in Table II are based on a numerical assessment. The numbers of whole, half and broken nuts in a sample from each bag were counted. The number of half nuts was divided by two to give the equivalent number of whole nuts. From a series of observations it was concluded that four broken pieces were approximately equivalent to one whole nut. Consequently the number of fragments was divided by four. Thus the figures in columns four and five of Table II express the proportion of whole nuts which was split or broken into the respective categories.

The percentages of insect-damaged nuts have been calculated from the actual numbers of whole nuts, half nuts and broken pieces in the sample.

During inspections and sievings the following species of stored products pests were recorded :

Tribolium castaneum Hbst., *T. confusum* J. du V., *Oryzaephilus mercator* Faw. and *Xylocoris flavipes* Reuter.

Of these species *T. castaneum* was by far the most numerous and important.

Discussion and conclusions

Direct losses, both as weight lost and powder produced, tended to fluctuate. By the end of the storage period, no large differences were apparent between any of the categories. It appears that, with prolonged storage, upwards of half a pound of nuts per 100 lb. stored will be lost and that approximately one pound of powder will be produced. Thus from the point of view of weight lost alone, no advantage would be gained by storing groundnuts decorticated by other than the traditional methods.

Hall[2] reports that bagged, decorticated Nigerian groundnuts on arrival in the United Kingdom contain 0·3–1·6% of dust after 6 months' storage and 1·0–2·0% of dust after 20 months' storage. The percentages of the frass sieved from Kano-type nuts in the present work agrees reasonably closely with Hall's figures and such higher values as are given by this author can readily be ascribed to the development of infestation in the groundnuts during transit from the dry conditions of Northern Nigeria.

Similarly, the insignificant variations in both bushel weight and oil content showed no category superior to another.

The changes in the F.F.A. content of the nuts, however, showed very important and economic differences. The ultimate figure of 14% for the normal Kano-type nuts was over ten times as great as that of the nuts in shell and over twice that of the hand-shelled nuts. This latter category maintained a low level of F.F.A. content until after the second rainy season, that is

Table II

Changes in proportion of, and damage to, whole, half and broken nuts

Category of nuts	Time of storage, months	% of whole nuts	% of half nuts	% of broken (less than ¼ kernel)	Whole nuts				Insect damage Half nuts				Broken pieces			% of pods with holes	% of holed pods showing external signs of insect damage
					% of heavy damage	% of medium damage	% of slight damage	% of un-damaged	% of heavy damage	% of medium damage	% of slight damage	% of un-damaged	% of heavy damage	% of medium damage	% of slight damage	% of un-damaged	
Unshelled	Before storage	98·2	1·4	0·4	0·0	0·2	0·8	99·0	0·0	9·2	15·4	75·4	0·0	15·4	15·4	69·2	13·4	1·2
	10	98·6	0·9	0·5	1·1	0·6	1·3	97·0	4·5	9·1	6·1	80·3	4·6	10·8	5·5	35·1	13·9	6·3
	13	98·7	0·2	0·1	3·5	0·6	1·8	94·1	26·7	0·0	0·0	73·3	46·7	6·7	13·3	33·3	18·9	8·6
	16	99·8	0·1	0·1	3·7	0·6	2·1	93·6	40·0	0·0	0·0	60·0	80·0	20·0	0·0	0·0	14·9	8·3
Hand-shelled	Before storage	89·6	8·6	1·8	0·9	0·2	3·5	96·3	0·4	2·2	21·3	76·1	0·5	4·9	34·6	60·0	—	—
	10	78·0	16·6	5·4	0·3	0·7	13·5	85·5	1·6	3·5	44·4	50·5	3·9	9·6	39·4	47·1	—	—
	13	81·6	15·1	3·3	0·6	1·1	39·2	59·1	3·6	7·1	72·6	16·7	17·2	8·5	55·2	19·1	—	—
	16	68·2	19·1	12·7	1·9	2·9	57·8	37·3	9·3	12·8	72·0	5·9	14·4	6·9	66·6	12·1	—	—
Normal Kano-type nuts	Before storage	44·4	29·3	26·7	0·1	0·4	25·7	73·9	0·0	0·3	36·5	63·2	0·1	0·8	32·9	66·2	—	—
	10	39·2	23·4	37·4	0·1	2·0	65·8	32·1	0·3	2·7	85·3	11·7	0·3	1·0	84·6	14·1	—	—
	13	27·9	24·2	47·9	0·4	2·6	84·0	13·0	0·4	2·5	90·6	6·5	0·2	0·8	87·3	11·7	—	—
	16	39·2	26·2	34·6	3·8	5·9	81·8	8·5	4·2	9·0	84·5	2·3	4·0	4·9	82·1	9·0	—	—

between the thirteenth and sixteenth month of storage. Almost a threefold increase in percentage of F.F.A. in Kano-type nuts between 6 and 20 months' storage is recorded by Hall[2] and it is likely that this interval covered two separate periods of high atmospheric humidity. The role of moist conditions has previously been established[3] and the comparable figures in the present investigations show the same degree of F.F.A. rise in pestle-and-mortar-shelled nuts.

The fatty acid content of Nigerian groundnuts has been studied by others, notably Howe[1] and Raymond *et al.*[4]

Table III gives a comparison of the various results obtained.

Table III

Percentage of free fatty acid in Nigerian groundnuts before and after storage

	Storage period	Kano-type nuts	Whole nuts	Unshelled nuts
Howe[1]	7 months (May to December)	5·5–17	3·0–9·6	—
Raymond *et al.*[4]	Sampled at harvest	0·9	—	0·4
Present work	10 months (May to March)	3–10	1–2·5	0·3–1·0
,, ,,	16 months (May to Sept.)	3–14	1–6	0·3–1·2

The desirability of reducing the proportion of split and fragmented kernels of groundnuts for storage is clearly illustrated, as is the degree of protection afforded by the shell.

This protection is emphasized by the low rate of increase in insect damage to unshelled nuts. Insect infestation was concentrated into those pods which already had incomplete shells and the kernels within suffered heavy damage. Penetration of undamaged shells by stored-products pests either did not occur, or was so slight as to be undetectable by the sampling methods used. Variation in the percentages of pods with holes (Table II) can be ascribed partly to the breakage of shells during handling and partly to sampling errors.

The increase in damage to kernels with incomplete or holed shells can be detected only partly by examination of the undecorticated nuts. The percentage of holed pods which clearly indicated insect damage within, rose with increased storage but not in the same proportions as when the shells were removed and the kernels examined.

In both types of decorticated nuts, insect attack is particularly directed against broken pieces, and in the hand-shelled nuts, such half and broken nuts as are present are selected by the insects for food. Thus the ultimate damage to half and broken nuts in the hand-shelled category is, in the main, greater than that in the normal Kano-type nuts.

From the foregoing it may be concluded that the quality of groundnuts after storage is considerably influenced by whether the shell is removed or not and if removed, by which method. The importance of the method of decortication lies in the proportion of whole to broken nuts produced. The storage and transport of the groundnut crop of Northern Nigeria in the unshelled state is not economically possible and the conclusions from this work are in no sense a recommendation to this method of storage. The storage of groundnuts is necessitated by the seasonal nature of the crop and excessive quantities of produce which are handled by the existing transport facilities.

As unshelled groundnuts have over twice the volume of decorticated nuts the difficulties and delays in transport would be doubled.

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References

[1] Howe, R. W., *Bull. ent. Res.*, 1952, **43**, 111
[2] Hall, D. W., *Dept. Sci. industr. Res.*, Rep. colon. Liaison Officer, 1953
[3] *Colon. Res. Publ.*, 1952, No. 12. (H.M.S.O.)
[4] Raymond, W. D., Squires, J. A., & Ward, J. B., *Colon Pl. Anim. Prod.*, **4**, (3), 1954, 206

JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE

ABSTRACTS

OCTOBER, 1957

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.

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JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE

ABSTRACTS

OCTOBER, 1957

I.—AGRICULTURE AND HORTICULTURE

General : Soils and Fertilizers

Remarks on soil science. L. Sody (*Agricultura*, 1956, **4**, 315—328).—A review covering the solubility of soil phosphates, the determination of the solubility of agricultural phosphates, and the part played by humus in promoting the uptake of N and P. The value of the active peat, Tourbac, as an org. soil constituent is pointed out. P. S. ARUP.

Sampling of natural soil profiles. R. Rataj and I. Lieberoth (*Z. PflErnähr. Düng.*, 1957, **77**, 52—58).—Use of a core sampler, halved longitudinally to permit easy subdivision of the core into successive depth samples, is described. M. LONG.

Clay mineralogy and particle size. J. S. Hosking, M. E. Neilson and A. R. Carthew (*Aust. J. agric. Res.*, 1957, **8**, 45—74).—In 24 soils examined the clay minerals were distributed through all particle size fractions. In granitic and other soils characterized by kaolinite, with mica, illite or montmorillonoids sometimes present, the clay mineral content of the silts averaged about 50% of that in the clay fraction ; in the sands, clay minerals are negligible. In basaltic soils characterized by halloysite and/or nontronite, with other types subsidiary, the clay mineral content is rather less than in granitic soils, but persists at about 20% in the sands. The higher concn. of kaolinite in the silt reflects its larger particle size. The concn. of halloysite or nontronite in the sand, and even the concn. reached in the silts of soils containing them, reflects their fibrous nature which allows the formation of stable interlaced aggregates. The two types of mineral, altered (authigenic) and residual (allogenic) vary with particle size ; the former constituting the bulk of the colloids, decrease to small amounts in the coarse sand, while the latter show the reverse effect. The silts contain both types of mineral and thus represent the intermediate particle size of mechanical breakdown and chemical alteration. (32 references.) R. H. HURST.

Evaporation—an introductory survey. H. L. Penman (*Neth. J. agric. Sci.*, 1956, **4**, 9—29).—A general survey of evaporation as an agricultural phenomenon. A. H. CORNFIELD.

Evaporation at night. J. L. Monteith (*Neth. J. agric. Sci.*, 1956, **4**, 34—38).—Direct measurements of evaporation from a short grass surface were compared with humidity gradients in the grass. At nights, when the air in the cover was unsaturated, evaporation took place by diffusion of water vapour from the soil surface through a thin layer of air in which the transfer coeff. was seldom $> 2 \times$ mol. value. The rate of evaporation was $\sim$0·04 mm. per hr. A. H. CORNFIELD.

Actual evapotranspiration as a function of potential evapotranspiration and the soil moisture tension. G. F. Makkink and H. D. J. van Heemst (*Neth. J. agric. Sci.*, 1956, **4**, 67—72).—The real (actual) evapotranspiration of grassland fell below the potential evapotranspiration when the soil was drying. The rate of reduction depended on the moisture tension of the soil and on the intensity of the potential evapotranspiration as a measure of evaporation. The real evapotranspiration may keep up with the potential evapotranspiration of a definite intensity ; the wetter the soil the higher the intensity at which reduction begins to occur. A. H. CORNFIELD.

Evaporation from soil and vegetation. W. J. Staple (*Neth. J. agric. Sci.*, 1956, **4**, 39—42).—Results of 28 years' measurements of moisture conservation and use in soil tanks and field plots are described. Most of the rainfall in S. Sasketchewan is soon returned to the atm. by evaporation from bare soil or transpiration from crops. During 21 months summer fallow only 21% of the precipitation was conserved. A. H. CORNFIELD.

Measuring soil moisture content and evaporation by the neutron scattering method. J. W. Holmes (*Neth. J. agric. Sci.*, 1956, **4**, 30—34).—The neutron scattering method gave fairly reliable results for soil moisture content over five months. A. H. CORNFIELD.

Soil moisture and yield. K. Kreeb (*Ber. dtsch. bot. Ges.*, 1957, **70**, 121—136).—Field experiments made with barley in Iraq during winter show decreased yields of grain (but not of the 1000-grain wt.) when the optimum watering is exceeded. In comparison with irrigation, sprinkling is more economical of water, causes less caking of the soil, and removes salt from the soil more efficiently. Determination of optimum watering has been simplified and modified by the use of refractometric values, which (generally) show a correlation with optimum watering values. (23 references.) P. S. ARUP.

Degree of salinity of upper soil strata as dependent upon depth of ground water. V. V. Egorov and G. V. Zakhar'ina (*Dokl. Akad. Nauk SSSR*, 1956, **109**, 851—853).—In Eastern Transcaucasian valley soils, contrary to the general assumption, there is no complete parallelism between the process of concn. of soil solutions and of saline accumulation in the system soil–ground level–ground water, on the one hand; and the salinification of the upper level of the soil, on the other ; the nearer is ground water to the surface the smaller is the amount of salt sedimentation from soil solutions. Z. N. PREEV.

Effects of tractor-traffic compaction on the physical properties of an irrigated soil in Southwestern Puerto Rico. M. A. Lugo-Lopez and G. Acevedo (*J. Agric. Puerto Rico*, 1956, **40**, 235—244).—The soil in the tractor row of a clay soil had a higher bulk density and lower hydraulic conductivity, quick drainage value and porosity than had non-compacted soil. Water retention at pF 1·78 was not affected by compaction. A. H. CORNFIELD.

Study of soil stability by a volumetric test. J. Livens (*Agricultura*, 1956, **4**, 431—451).—The soil stability test made according to Hénin *et al.* on conc. soil suspensions can be supplemented usefully by measurement of the vol. of the sediment, which, for loams, varies appreciably with the clay and humus content and with the soil-pH. An approx. relationship found exists between the vol. of the sediment and the micro-structure of the soil. (8 references.) P. S. ARUP.

Problems of soil testing on calcareous soils. D. H. Yaalon (*Plant & Soil*, 1957, **8**, 275—288).—The effect of variation in CO_2 concn. on the pH of calcareous soils is discussed. The pH of calcareous soils of Israel ranged from 7·60 to 8·30 when measured in water which had been aerated with normal air, from 7·45 to 7·80 in 0·01M-$CaCl_2$, and from 7·25 to 7·80 in saturated $CaSO_4$ ($\sim$0·015M). Particle size distribution of $CaCO_3$ in soils, particularly in the smaller size ranges, may be important in indicating their susceptibility to lime-induced chlorosis. Determination of particle size distribution before and after treatment of the soil with acid is a satisfactory method of indicating the contribution of $CaCO_3$. A chemical method, based on the amount of oxalate pptd. when the soil is shaken with 0·2N-NH_4 oxalate (pH 7·0), is described for diagnosing susceptibility to lime-induced chlorosis. A. H. CORNFIELD.

Determination of available nitrogen in soils. G. Lenhard (*Z. PflErnähr. Düng.*, 1957, **77**, 59—61).—The mineralization of org. N in soil is investigated. The determination of NH_3-N is considered essential. The suggested method is to extract the soil with $CaSO_4$, incubate at 30° for 14 days, extract with $CaSO_4$ and determine NH_3-N and NO_3-N in the extract. (Cf. *ibid.*, 1956, **74**, 186). M. LONG.

Calibration of soil test methods for the determination of phosphate and potash status. F. van der Paauw (*Plant & Soil*, 1956, **8**, 105—125).—The relationship between chemically extractable P and K and yields of permanent grass and arable crops for a variety of soil types is presented. A. H. CORNFIELD.

Potassium Symposium, 1956. (*III Congr. Int. Potash Inst. London*, 1956. *Annu. Mtg, Bd tech. Advisors* (iv sessions)).—The symposium comprised the following 11 papers : (i) Selective absorption of alkali cations by storage tissues and intact barley plants. J. F. Sutcliffe 1—11 ; Potassium in tissue culture. R. Hellier 13—38. (28 references.) ; Potassium in the cell. Y. Coïc 39—52. (26 references.) ; (ii) Potassium deficiency in plants. F. J. Richards 59—73. (55 references.) ; Potassium content of plants. E. Welte 75—107. (17 references.) ; Physiological basis of the effect of potassium on crop yield. D. J. Watson 109—119. (11 references.) ; Visual symptoms of potassium deficiency in crops and relation of potassium to magnesium in plant nutrition. T. Wallace 121—131. (25 references.) ; (iii) Effect of potassium on crop yield. D. A. Boyd 143—154. (10 references.) ; Influence of potassium on the quality of food plants under special survey of biological values. W. Schuphan 155—178. (22 references.) ; Effect of potassium on parasitic plant diseases. F. T. Last 179—188. (34 references.) ; a discussion followed each of the three sessions ; (iv) Review of modern British farming. J. A. Scott Watson 201—211 ; and Closing address. E. J. Russell 213—218. E. M. J.

Comparative influence of two legumes on nitrogen content of a chalky soil. P. Duchaufour and F. Jacquin (*C. R. Acad. Sci., Paris*

1957, **244,** 1256—1258).—When used as green manures, lucerne produced a substantial increase of mineral N but did not improve the C/N ratio of the soil; clover produced mineral N less rapidly but improves the C/N ratio and, while having a less marked immediate effect on the N nutrition of crops, effected a more permanent improvement in the humic content of the soils by building up a stock of org. N. J. S. C.

Behaviour of iron chelates in calcareous soils. I. Laboratory experiments with ferric-iron chelates of ethylenediaminetetra-acetic acid and *N*-hydroxyethylethylenediaminetriacetic acid. D. G. Hill-Cottingham and C. P. Lloyd-Jones (*Plant & Soil*, 1957, **8,** 263—274).—The decrease in water solubility of Fe from a clay soil (28% $CaCO_3$) treated with two Fe chelates (labelled with ^{59}Fe) and then stored for 1—15 days was studied. The initial decrease in concn. of sol. Fe was rapid for both chelates, but was greater for Fe *N*-hydroxyethylethylenediaminetriacetate (Fe-HEEDTA) than for Fe ethylenediaminetetra-acetate (Fe-EDTA). The amount of each chelate absorbed changed little with time and was proportional to the quantity applied (Fe 10—100 p.p.m.). HEEDTA was sorbed to the greater extent. The decrease in sol. Fe was attributed to both sorption of chelate anions by the clay and to replacement of Fe by Ca in the chelate mol. Pptn. of Fe from sol. Fe-HEEDTA was slower than from Fe-EDTA. Water-sol. Fe was greater when the treated soils were stored in sealed than when stored in unsealed containers, the effect being greater with Fe-EDTA than with Fe-HEEDTA. Isotopic exchange of ^{59}Fe with natural soil Fe was greater where 10 than where 100 p.p.m. of chelated Fe had been applied. Isotopic exchange of the Fe in HEEDTA was greater than that of Fe in EDTA. A. H. CORNFIELD.

Metabolic activity of the soil microflora. H. Katznelson and I. L. Stevenson (*Canad. J. Microbiol.*, 1956, **2,** 611—622).—The technique of the manometric method is examined using various substrates. Using casamino acids variations of soil moisture content between 60 and 80% of the moisture-holding capacity did not affect the O_2 uptake. N-free substrates (sugars, disaccharides, org. acids) produced variable results. The respiratory activity of soil decreased markedly with fall in pH to 3·5—4·5. Soils differing in org. matter or N contents or in fertility showed considerable differences in gaseous exchange. A. G. POLLARD.

Production of antibiotics in soil. V. Breakdown of griseofulvin in soil. J. M. Wright and J. F. Grove (*Ann. appl. Biol.*, 1957, **45,** 36—43).—When added to a garden loam griseofulvin disappeared rapidly after an initial lag period. The rate of disappearance of further added amounts indicated that it was degraded biologically. A *Pseudomonas* sp. increased in soil after addition of griseofulvin. Griseofulvin disappeared rapidly when soil was added to a liquid culture containing griseofulvin as the sole source of C. At pH 7·0 the *Pseudomonas* sp. was identified, whilst at pH 5·0 a dematiaceous fungus was responsible for the breakdown of griseofulvin. An amine and a dechloro-analogue of griseofulvin were also degraded by the *Pseudomonas* sp. A. H. CORNFIELD.

Rapid colorimetric estimation of magnesium in soil using a single, self-compensating reagent. S. N. Edson and R. H. Mills (*Chem. Anal.*, 1957, **46,** 4—5).—Taras' method for determining Mg in soil (*Analyt. Chem.*, 1948, **20,** 1157) has been modified by using saturated aq. $Ca(OH)_2$ to adjust the pH and compensate simultaneously for the error due to Ca. The self-compensating agent is prepared by adding 9 vol. of clear limewater to 1 vol. of a 0·01% solution of Brilliant yellow in MeOH–water (1 : 1). The Mg is extracted from the soil by 0·5% aq. Na acetate. Beer's law is valid for 2—30 p.p.m. of Mg. W. J. BAKER.

Determination of small amounts of magnesium in agricultural chemistry. K. Scharrer and K. Mengel (*Z. PflErnähr. Düng.*, 1957, **77,** 18—36).—The oxyquinoline technique is examined and a flame spectrometric technique for determining Mg in plant and biological matter and soil extracts is developed. pH 10·2—10·8 is optimal for the pptn. of Mg in Na tartrate in the oxyquinoline method. Interfering anions are removed by an ion-exchange resin, Na, K and Ca as sulphates in ethereal solution. The method described permits the determination of 2—10 mg. of Mg with a scatter of 3%, whilst the flame spectrometric method permits the determination of 0·25—10 mg. with a max. error of 4%. Comparison of the methods gave an average deviation of 3·4%. $CaCl_2$ extracts of soil for determining available Mg are suitable for the flame spectrometric method. M. LONG.

Field plot technique with a number of crops. J. F. Moore and J. G. Darroch (*Washington agric. Exp. Sta.*, 1956, Tech. Bull. 21, 30 pp.).—The precision of various types of designs in field tests with pole beans, bush beans, carrots, sweet maize and autumn cauliflower is presented. A. H. CORNFIELD.

Effect of size of plot, experimental design and replication on efficiency of potato fertilizer experiments. G. L. Terman, M. R. Covell and C. E. Cunningham (*Amer. Potato J.*, 1957, **34,** 59—68).—Results with various designs using P and K at varying rates are presented. A. H. CORNFIELD.

1955—56 fertilizer and plant nutrient consumption in the U.S. W. Scholl, H. M. Wallace, E. I. Fox ..nd F. B. Crammate (*Farm Chem.*, 1957, **120,** No. 7, 50—57).—A critical consideration of a mass of official statistics. A. G. POLLARD.

Use of ^{32}P in the determination of phosphorus fertilizer utilization. G. Michael and O. Machold (*Z. PflErnähr. Düng.*, 1957, **77,** 1—18).—The exchange of ^{32}P from sol. to insol. P in soils is found to lead to errors. The order of magnitude of these errors can be determined and can give rise to figures for the utilization of P not exceeding 20% and very often less. Even though errors of these magnitudes arise, tracer techniques can be used to compare fertilizers under the same conditions. M. LONG.

Surface properties of phosphate materials by isotopic exchange. I. Rock phosphate. J. Cano Ruiz and O. Talibudeen (*J. Sci. Fd Agric.*, 1957, **8,** 305—308).—Preliminary data on surface areas determined by tracer methods are presented and compared with values obtained by gas absorption and values obtained by different workers are compared. When ^{32}P was used in the determination of surface phosphate of apatite rock, surface areas of these materials calculated from these determinations are smaller than those derived from gas-adsorption methods. Less than 2·5% of the total P exists as surface P in the 100-mesh size fraction of these materials. E. M. J.

Influence of water-soluble phosphorus on agronomic quality of fertilizer mixtures containing two phosphorus compounds. M. A. Norland, R. W. Starostka and W. L. Hill (*J. agric. Fd Chem.*, 1957, **5,** 217—219).—The yield and P uptake of maize and vetch on slightly acid soil treated with N–P fertilizer containing 5, 10 and 20% and 5, 20 and 40%, respectively, of water-sol. P increased significantly with increasing % of water-sol. P in the fertilizers. With the highest level of water-sol. P results with vetch were comparable to those given by triple superphosphate and $(NH_4)H_2PO_4$. (20 references.) S. C. JOLLY.

Fertilizer placement experiments. J. Prummel (*Plant & Soil*, 1957, **8,** 231—253).—Results of over 100 field tests over a number of years comparing band-placed with broadcast applications of superphosphate, K_2SO_4 and Nitrochalk on yields of a variety of crops are reported. Band-placed N was ~1·2 times as effective as broadcast N for cereals, potatoes and beets. Band-placed P was 7·5 times as effective as broadcast P for pulses, 2·9 times for maize, 2·45 for cereals, 1·9 for potatoes and 1·2 for beets. K on river clay was 3·65 times as effective when band-placed than when broadcast for cereals, 1·6 for potatoes on soils of high pH, but no more effective for potatoes on soils of low pH or for beets. A. H. CORNFIELD.

Lime and minor-element fertilizer trials in Puerto Rico, 1949—50. P. Landrau, jun. and G. Samuels (*J. Agric. Puerto Rico*, 1956, **40,** 224—234).—Application of lime to soils of pH $<5{\cdot}5$ increased the yields of most of the crops studied. Yields of sugar cane were not increased by liming soils of pH >6. No consistent yield increases were obtained by applying $MnSO_4$, NaCl, S, $ZnSO_4$, mixtures of trace elements, MgO, or borax, although yields of sweet potatoes were increased by MgO and borax. Pineapple yields were increased by foliage sprays of $FeSO_4$ or Fe ethylenediaminetetra-acetate, or by soil treatment with a mixture of fritted trace elements. A. H. CORNFIELD.

Plant nutrition on "fly-ash". W. J. Rees and G. H. Sidrak (*Plant & Soil*, 1956, **8,** 141—159).—Physical properties and chemical composition of fly-ash (residue from combustion of pulverized coal) are presented. A wide range of plants grown on the ash accumulated Al and Mn and exhibited toxicities of these metals. P deficiency, probably induced by Al, also occurred in some cases. *Atriplex hastata* var. *deltoidea*, which establishes itself readily on fly-ash deposits, also accumulated Al and Mn, but did not exhibit toxicities of the elements. Barley yields were reduced when soil contained more than 10% of fly-ash. Mangold yields increased with 12·5% of ash present in the soil and were not reduced even with 50% ash present. Cabbage and sprout yields were unaffected by 25% ash but were reduced somewhat by larger amounts. A. H. CORNFIELD.

Plant Physiology, Nutrition and Biochemistry

Transpiration of glasshouse tomatoes, lettuce and carnations. F. E. Neale (*Neth. J. agric. Sci.*, 1956, **4,** 48—56).—The relationship between transpiration from glasshouse tomatoes, lettuce and carnations and total incoming radiation is examined. A. H. CORNFIELD.

Determination of the nitrogen balance of oats. H. Roschach (*Z. PflErnähr. Düng.*, 1957, **77**, 37—52).—Plant tissue is dried at 60° for 16 hr. Total N in the nutrient solution is determined after removal of water by vac. distillation. The oats are grown in purified air under cloches, and the N content of the complete plants and the nutrient solution are determined. With 1 mg. N per plant the N balance is zero whilst with higher applications the tendency is negative. M. LONG.

Preferential assimilation of nitrate ion by *Haematococcus pluvialis*. V. W. Proctor (*Amer. J. Bot.*, 1957, **44**, 141—143).—Of six algae given NH_4NO_3, $(NH)_2SO_4$ or KNO_3 as N source, four preferred NH_4'–N, whilst *Pandorina morum* and *H. pluvialis* preferred NO_3'–N. *Chlamydomonas reinhardi* assimilated NH_4'–N almost exclusively from NH_4NO_3 (while available), whilst *H. pluvialis* assimilated NO_3'–N twice as rapidly as NH_4'–N. (12 references.) P. S. ARUP.

Chromatography as a means of selecting effective strains of *Rhizobia*. K. T. Wieringa and J. A. Bakhuis (*Plant & Soil*, 1957, **8**, 254—262).—Aspartic acid was the only amino-acid detected in chromatograms of bleeding sap of pea plants inoculated with ineffective strains of *Rhizobia*. Aspartic acid, arginine, glutamine, hydroxyproline, threonine and possibly valine and leucine were found in the sap of plants inoculated with effective strains. Water uptake by plants inoculated with effective strains was higher than by uninoculated plants or plants inoculated with ineffective strains. Effective strains could be selected in three weeks by this technique. A. H. CORNFIELD.

Effect of mineral nutrition on content of free amino-acids and amides in tomato plants. II. Effect of molybdenum nutrition. J. V. Possingham (*Aust. J. biol. Sci.*, 1957, **10**, 40—49).—Tomato plants cultured in the absence of Mo were then provided with MoO_4''. Within 4 hr. the concn. of aspartic acid, glutamic acid, glycine, glutamine and asparagine, measured by paper chromatography, increased markedly, and then steadily declined. β-Alanine and γ-aminobutyric acid decreased in concn. soon after MoO_4'' was applied. The way in which the products of NO_3' reduction are incorporated into proteins is discussed. (13 references.) R. H. HURST.

Effect of sulphur deficiency on free amino-acids of some plants. R. G. Coleman (*Aust. J. biol. Sci.*, 1957, **10**, 50—56).—White clover and four other species were cultured with and without S. Free arginine increased greatly in S-deficient *Desmodium uncinatum* DC., white clover, tomato and flax. The glutamic acid content of all except flax was much reduced and some amide accumulated. Asparagine predominated among amides which accumulated in the S-deficient legumes, while in tomato glutamine predominated; barley contained about equal amounts of both. The amide in greatest amount in the deficient plants was that which occurred in greatest amount in the normal plants. Glycine and serine increased in all species where S was in short supply. Citrulline (not previously noted in flax) occurs in moderate amount in the S-deficient plant. (18 references.) R. H. HURST.

Manganese deficiency in peach tree induced by excess of phosphorus in nutrient solution. J. Delmas, J. Bats and P. Rémy (*C. R. Acad. Sci., Paris*, 1957, **244**, 1971—1974).—Hydroponic studies in a greenhouse included observation of a deficiency in Mn induced by increased phosphate uptake. Chlorosis of the leaves was caused which could be cured in 8—10 days by painting the limbs affected with 1% aq. $MnSO_4$. J. S. C.

Presence of manganese in fungi. G. Bertrand and L. Silberstein (*C. R. Acad. Sci., Paris*, 1957, **244**, 1685—1687).—The Mn contents of 42 fungal species, expressed as mg. of Mn/kg. of dry matter, are reported and discussed in comparison with values previously reported for phanerogams (cf. J.S.F.A. Abstr., 1956, i, 302). J. S. C.

Manganese toxicity in standard culture solutions. D. E. Williams and J. Vlamis (*Plant & Soil*, 1957, **8**, 183—193).—Atlas barley plants grown in water cultures with standard Hoagland solution (0·5 p.p.m. each of Mn and B) developed dark brown necrotic spots on the older leaves. Extent of necrosis increased with higher Mn or B concn. and nearly disappeared when 0·025 p.p.m. Mn or B were present. The Hoagland concn. of Mn or B were only slightly toxic to lettuce and non-toxic to tomatoes. Barley plants growing in the winter tolerated higher concn. of Mn and B than did those grown in summer. Optimum concn. of Mn and B depended also on vol. of the culture solution, no. of plants present and concn. of macro-salts. A. H. CORNFIELD.

Use of chelates for controlling iron chlorosis in soya-beans grown under greenhouse conditions. E. Hernandez-Medina (*J. Agric. Puerto Rico*, 1956, **40**, 245—254).—When grown in solution cultures at pH 5·0 soya-bean plants showed no Fe deficiency symptoms when the solution contained 0·5 p.p.m. Fe as $FeSO_4$ or Fe sequestrene. At pH 7·0 only Fe sequestrene was effective in preventing chlorosis of the upper leaves. At both pH levels the presence of 0·01 p.p.m. chelated Fe was ineffective in preventing chlorosis of the upper leaves. Yields of tops and roots at both pH levels were higher with 0·5 p.p.m. chelated Fe than with 0·01 p.p.m. chelated Fe or 0·5 p.p.m. inorg. Fe. A. H. CORNFIELD.

Colorimetric determination of β-aminopropionitrile in mature legume seeds. J. T. Garbutt and G. M. Strong (*J. agric. Fd Chem.*, 1957, **5**, 367—370).—The toxic principle, β-aminopropionitrile, occurring in *Lathyrus odoratus* caused bony deformities and connective tissue breakdown when incorporated in the diet (0·2% of the ration) of rats. On paper chromatograms, the substance when treated with ninhydrin produced a green colour. Concn. as low as 50 p.p.m. in the sample were detected by this method, but in samples of *L. latifolius*, *L. sylvestris* and *L. splendens* which are toxic to rats, no β-aminopropionitrile was indicated. (11 references.) E. M. J.

Determination of zinc in plants and soils. E. T. Verdier, W. J. A. Steyn and D. J. Eve (*J. agric. Fd Chem.*, 1957, **5**, 354—360).—The dithizone and polarographic methods are critically examined and a modified proceeding, based on the dithizone photometric method of Cowling & Miller (*Industr. Engng Chem., Anal. Ed.*, 1941, **13**, 145) is described. The influence of pH on Zn extraction, transmittance curves and accuracy of technique are studied. The speed of analysis was increased. All measurements were made at a wavelength of 520 mμ. A modified polarographic method is described which could be adapted to the simultaneous determination of Cu, Ni, Mn and even Co, although the presence of phosphate might interfere with the determination of Mn. (26 references.) E. M. J.

Flame photometric estimation of copper in plant tissue. H. F. Massey (*Analyt. Chem.*, 1957, **29**, 365—366).—Concn. $\geq$200 μg. of Cu in the liquid from acid digestion of ~5 g. of plant tissue can be determined accurately by extraction from 0·1N-HCl with a 0·5% solution of dithizone in $CHCl_3$–liquid paraffin (1 : 1), followed by direct flame photometry of the org. extract. Results agree well with the standard spectrophotometric method used in agricultural laboratories. W. J. BAKER.

Plant growth-regulating substances. II. Auxin antagonism in relation to a theory on mode of action of aryl- and aryloxy-alkanecarboxylic acids. R. L. Wain and F. Wightman (*Ann. appl. Biol.*, 1957, **45**, 140—157).—A study was made of the antagonistic effects of a range of phenoxy and other acids on the growth-promoting activity of a number of auxins as assessed by the Avena cylinder and pea curvature tests. The compounds examined were selected on the basis of not possessing the structural requirements considered necessary for growth-regulating activity, yet possessing groupings which might allow them to accumulate at a site of action from which the growth response by auxins might be initiated. Inactive stereoisomers of α-aryloxypropionic acids competitively inhibited the activity of their active enantiomorph. A similar antagonism was found with other inactive aryloxy acids. A. H. CORNFIELD.

Effects of growth-substances on development of apricot seeds and seedlings. M. V. Bradley and J. C. Crane (*Amer. J. Bot.*, 1957, **44**, 164—175).—Varying reductions in seed germination result from spraying the trees with growth-substances at the time of pit-hardening. Germination is completely inhibited by 2 : 4-D in all the concn. used, and partly inhibited (in descending order) by 2 : 4 : 5-trichlorophenoxy-propionic and -acetic acids or naphthylacetic acid (NAA). Viable seeds showed occasional abnormalities but the surviving seedlings (except from trees treated with NAA) show inhibited radicle and epicotyl growth, proliferation and adventitious rooting. Treatment of normal seeds or of seedlings with 2 : 4 : 5-T causes inhibition of germination (0—100%) and abnormalities of the type caused by tree-treatment. (31 references.) P. S. ARUP.

Survey of fungi and actinomycetes for compounds possessing gibberellin-like activity. R. W. Curtis (*Science*, 1957, **125**, 646).—About 1000 fungus and 500 actinomycete culture filtrates were examined for the presence of substances having the same effect as gibberellin on growth. Maize seedlings were used as the test plant. No active compounds were discovered. T. G. MORRIS.

Effect of gibberellin on germination of lettuce seed. A. Kahn, J. A. Goss and D. E. Smith (*Science*, 1957, **125**, 645—646).—Two types of lettuce (*Lactuca sativa* L.) were used. The first (*A*) had a "primary" light requirement, induced by brief exposure to red light which increases germination. The other (type *B*) had a "secondary" light requirement induced by (i) storing imbibed seeds at 35° or (ii) by including an osmotically active material in the medium. Both (i) and (ii) reduce germination in the dark, this being restored by light. Gibberellin (100 mg./l.) was as effective in raising the germination of *A* as was 3-min. exposure to red light. When gibberellin (50 mg./l.) was present during the pretreatment of *B* at high temp. no secondary light requirement is apparent.

Gibberellin promotes germination in darkness, after a dependency on red light has been established by pretreatment at high temp. It also reduces or destroys the dark osmotic inhibition when it is given simultaneously with the inhibiting solution, or as a pretreatment. T. G. MORRIS.

Influence of gibberellin on stem elongation and flowering of endive. J. F. Harrington, L. Rappaport and K. J. Hood (*Science*, 1957, **125**, 601—602).—The interaction of vernalization and gibberellin treatments on endive has been studied. Gibberellin treatment of seedlings hastened stem elongation regardless of vernalization. Repeated gibberellin treatments enhanced the effect, increased the percentage of incipient flowers and hastened flowering, although some flowers were abnormal and sterile. When the gibberellin treatment was stopped the flowers became normal. T. G. MORRIS.

Effect of gibberellic acid on growth of Kentucky bluegrass. C. Leben and L. V. Barton (*Science*, 1957, **125**, 494—495).—Kentucky bluegrass (*Poa pratensis*, L.) was fertilized in Oct. and sprayed once with freshly made aq. gibberellic acid three days later. After four days the sprayed grass showed signs of growth. After 15 days treated plants contained more water and those given gibberellic acid (**I**) alone were yellowish green. With fertilizer + **I** the foliage was normal in colour and similar to spring herbage. The **I**-treated grass later became spindly and chlorotic with dead tips, possibly because of low temp. T. G. MORRIS.

Effect of kinetin on protein content and survival of detached *Xanthium* leaves. A. E. Richmond and A. Lang (*Science*, 1957, **125**, 650—651).—Fully expanded detached *X. pennsylvanicum* leaves were kept for 10 days with their petioles in either water or solutions of kinetin (1 or 5 mg./l.). Water-treated leaves lost most of their chlorophyll but the kinetin-treated leaves retained their green colour with much reduced losses of protein. The amount of sol. N in the blades was much the same in both control and treated leaves. T. G. MORRIS.

Trials of fruit-setting sprays on glasshouse tomatoes. R. M. Davison (*N.Z. J. Sci. Tech.*, 1957, **38, A**, 544—547).—Sprays of β-naphthoxyacetic acid, *p*-chlorophenoxyacetic acid, and some commercial prep. increased the yield and mean fruit wt. on early crops which developed under adverse weather conditions. Sprays of β-naphthoxypropionic acid (5 and 10 p.p.m.) and one commercial prep. were unsatisfactory. Most treatments gave heavier early pickings, and fruit of good quality. R. H. HURST.

Crops and Cropping

Effect of ferrous sulphate on the yield and manganese uptake of oats on sandy soil fertilized with pyrolusite. E. Boken (*Plant & Soil*, 1956, **8**, 160—169).—In pot tests with oats on a sandy soil of low Mn status the response to quinol-reducible Mn in added pyrolusites (β-Mn dioxides) was slightly less than that to an equiv. amount of water-sol. Mn ($MnSO_4$). When $FeSO_4$ was added the response to the pyrolusites was 2—3 times as high as that to water-sol. Mn, indicating that Fe^{++} can reduce the higher Mn oxides in soil. Two samples of pyrolusite varied somewhat in their ability to be reduced by $FeSO_4$ in soil. A. H. CORNFIELD.

[A] **Productivity of Belgian loam-loess soils.** [B] **Wheat yield as function of pH and K content [of soil].** J. Livens (*Agricultura*, 1956, **4**, 33—62, 81—98).—[A] Yields of wheat and other crops on the same soil-types, are appreciably influenced by the nature of previous crops and cultivation, and by soil-pH and -structure. For wheat, the optimum pH range is 7·1—7·6. A survey is given of soil-pH in the Hisbaye district. (9 references.)

[B] Inferior wheat yields on these soils at pH <6·5 and on soils not rich in K when the pH exceeds 7·9, are probably due to the increased proportion of exchangeable K (extracted by N-NH_4 acetate) to water-sol. K found at high and low pH. The availability of the former appears to be much inferior to that of the latter. The optimum pH range for wheat is 7·0—7·4. Practical applications of these findings are considered. P. S. ARUP.

Situation and expectations of beet culture. G. Fazio (*Rev. int. Agric., Milano*, 1956, **1**, [8/9], 5—17).—The beet situation in Italy and other countries is examined exhaustively, and compared with the various sugar consumption rates, with many statistics. Beet culture and the sugar industry in Italy are in a particularly strong position, due to favourable production costs. Some suggestions for winter beet production in southern Italy are discussed. C. A. FINCH.

Interaction of temperature and moistening agents in the germination and early development of potato seedlings. G. P. Steinbauer (*Amer. Potato J.*, 1957, **34**, 89—93).—A germination temp. near 20° was most suitable for recently harvested seed. Substitution of water by 0·1—0·5% KNO_3 increased the % germination in one of two tests and also increased the velocity of germination at 20°, but not at 20—30°. The NO_3^1 treatment increased the size and stem/root ratio of all lots at all temp. A. H. CORNFIELD.

γ-Irradiation of potatoes. Effects on sugar content, chip colour, germination, greening and susceptibility to mould. S. Schwimmer, H. K. Burr, W. O. Harrington and W. J. Weston (*Amer. Potato J.*, 1957, **34**, 31—41).—In comparison with controls total sugars and sucrose content of γ-irradiated tubers first increased and then decreased with time of storage. Reducing sugars and glucose contents behaved similarly, but changes were of a smaller magnitude. The treatment increased chip colour, delayed sprouting, reduced sprout length, and decreased rate of chlorophyll formation on exposure of tubers to light. A. H. CORNFIELD.

Potato handling equipment for use in experimental work. D. R. Isleib and N. R. Thompson (*Amer. Potato J.*, 1957, **34**, 70—71).—Storage containers, a picking table, and equipment for rapid sp. gr. determinations are described. A. H. CORNFIELD.

Influence of nitrogen fertilizers on water consumption of grassland. G. P. Wind (*Proc. European Grassland Conf., Paris*, [1954], 1956, 195—198).—The consumption of water by grassland was not increased by applications of N fertilizers in amounts which more than doubled the yields of grass. A. G. POLLARD.

Fertilization of grassland with farm-produced manure. F. Brünner (*Proc. European Grassland Conf., Paris*, [1954], 1956, 198—204).—Comparison is made of the composition and manurial efficiency, on pasture, of farmyard manure made with litter and "gülle" (fæces, urine with very small amounts of litter and some added water, stored in pits). Effects of frequency and level of application and yields and botanical composition of the herbage and on milk yields are examined. A. G. POLLARD.

Rôle of clover in grassland. W. Holmes and D. S. MacLusty (*Proc. European Grassland Conf., Paris*, [1954], 1956, 224—228).—Differences in the effects of various levels of application of N fertilizers on the growth and yield of several grass species in clover-dominant swards are associated with effects on the growth-habit of the grasses and with the shading effects of the clover.

Nutritive value of the crop on fertilized grassland. A. Gouere (*Proc. European Grassland Conf., Paris*, [1954], 1956, 217—223).—Data obtained on mountain meadows for the effects of N, P and K fertilizers, in various combinations, on the N, P and K contents of the hay and on milk yields are recorded. A. G. POLLARD.

Effects of using waste water on grassland in Bavaria. O. Schweighart (*Proc. European Grassland Conf., Paris*, [1954], 1956, 204—209).—Sewage, strained from bulky solids, is distributed over grassland by sprinklers or sub-irrigation pipes. Treated areas produce greater yields (starch equiv.) of pasture, and of milk. Effects on various grass species and clovers are noted. Similar trials with industrial wastes are recorded. A. G. POLLARD.

Effect of cold storage on the fluoride content of lucerne. C. P. McCarty and E. Robinson (*J. agric. Fd Chem.*, 1957, **5**, 377—379).—In testing the effect of storage on the F content of crop samples awaiting analysis, no consistent change in the F content of lucerne was found after storage for 4—6 weeks at 0°F. Stored samples gave more variable results than did freshly cut samples. Addition of lime reduced the variation of the stored samples. E. M. J.

Influence of phosphate fertilizers on pineapple yields. G. Samuels, P. Landrau, jun. and S. A. Alders (*J. Agric. Puerto Rico*, 1956, **40**, 218—223).—Application of up to 56 lb. of P_2O_5 per acre four months after planting on an acid clay or sandy clay loam produced no or small yield increases, whilst heavier applications depressed yields. The higher levels hastened fruiting and produced more culls. The depressing influence of P on yields is probably due to its action in lowering NO_3' intake when carbohydrate and P reserves are ample. A. H. CORNFIELD.

Effects of temperature and nitrogen nutrition on flower formation in the tomato. S. H. Wittwer and F. G. Teubner (*Amer. J. Bot.*, 1957, **44**, 125—129).—Tomato seedlings exposed during 2—3 weeks following cotyledonary expansion, to night temp. of 10—13°, and especially those kept continuously at 10—13°, show appreciably increased flowering in the first cluster (and fewer leaves preceding this cluster) in comparison with plants maintained at 18—21°. Vernalization of the seed has no such effect, but exposure of the plants to 10—13° at a later stage improves the flowering of subsequent clusters. Increases in the supply of N (55—440 p.p.m.) in solution cultures greatly enhance the effect of the low-temp. treatment. (15 references.) P. S. ARUP.

Nutrient interactions and deficiency diagnosis in the lettuce. II. Effects of nutrition on water content. D. W. Goodall, W. G. Slater and A. E. Grant Lipp (*Aust. J. biol. Sci.*, 1957, **10**, 57—65).—Sand-cultured lettuces received five levels of N, P and K, and the water

contents of the aerial parts were measured. The higher levels of N decreased the water content, while increases in P had the reverse effect. Plants deficient in K had a higher water content than had those receiving adequate K, unless P was also deficient. (17 references.) R. H. HURST.

Utilization of applied nitrogen by sugar cane. G. Samuels (*J. Agric. Puerto Rico*, 1956, **40**, 209—217).—Fall and spring plantings utilized applied N more efficiently than did ratoon canes. N was utilized more efficiently in humid than in irrigated areas. Canes utilized about the same amount of applied N irrespective of sugar yields. Sugar yields were highly correlated with cane yields. Where sugar yields were high, a ton of cane required 3 lb. and a ton of sugar 23 lb. of N. A. H. CORNFIELD.

Effect of fertilizers on groundnut yields and vegetative development. A. Huber (*Plant & Soil*, 1956, **8**, 126—131).—Pot tests with groundnuts using a red sandy loam subsoil receiving varying levels of N, P and K were carried out. Pod yields, hay yields and nodule no. were all positively correlated with each other, whilst nodule no. were negatively correlated with root length. Application of N reduced, of P increased, and of K had no effect on, nodulation. Application of N reduced, whilst application of P increased, yields of pods and hay. N increased yields when applied with P. K had no effect on yields when applied alone or with N and P. A. H. CORNFIELD.

Culture of sorgo for syrup production. I. E. Stokes, O. H. Coleman and J. L. Dean (*U.S. Dep. Agric.*, 1957, Fmrs' Bull. No. 2100, 32 pp.).—The " sorgo " plants, or those varieties of sorghum which have an abundance of sweet juice, and the nature of the syrup obtained, are described. Varieties of sorgo, the diseases and insect pests to which it is liable, cultural practices, harvesting, and the processes of syrup manufacture, are also described. J. S. C.

Beneficial effect of cobalt on growth of rubber plant (*Hevea brasiliensis*). E. W. Bolle-Jones and V. R. Mallikarjuneswara (*Nature, Lond.*, 1957, **179**, 738—739).—Evidence is presented in summary form to show that a minute amount of Co supplied in nutrient solution to rubber plants grown in sand significantly improved growth. J. S. C.

Photoperiod and chilling control growth of hemlock. J. S. Olson and H. Nienstaedt (*Science*, 1957, **125**, 492—494).—Seedlings (2 yr.) of Eastern hemlock (*Tsuga canadensis* (L.) Carr.), placed in pots and chilled during winter under various conditions, began growing when placed in favourable temp. Unchilled plants did not open their buds except under short-night (4 hr.) conditions. Effects of temp., variation in photoperiod and of continuous and interrupted photoperiod on bud-break and rate of shoot elongation are examined. T. G. MORRIS.

Magnesium treatment for solanum. Anon. (*The Grower*, 1957, **47**, 1524).—The effects of Mg deficiency in *Solanum capsicastrum* are described briefly. Spraying with $MgSO_4$ solution is without effect on this disorder. Addition of $MgSO_4$ to composts and its inclusion in nutrient dressings prevents the deficiency. O. OWEN.

Pest Control

Common names of insecticides. H. L. Haller (*J. econ. Ent.*, 1957, **50**, 226—228).—Common names of insecticides, their chemical definition, and other names sometimes given to them are listed. A. A. MARSDEN.

Phytopharmacy. II. Fungicides and herbicides. G. Speroni (*Chim. e Industr.*, 1957, **39**, 184—205).—The use of agricultural fungicides and herbicides is discussed. The principal uses of 125 fungicides (org. Hg compounds, phenols, quinones, chlorinated and dinitro-aromatic compounds, 8-hydroxyquinoline deriv., quaternary ammonium salts, dithiocarbamic acid derivatives, and antibiotics, and of 50 herbicides (acids, salts, nitro- and chloro-phenols and compounds with auxinic action) are listed. L. A. O'NEILL.

Comparison of yellow cylindrical, flat and water traps, and of Johnson suction traps, for sampling aphids. G. D. Heathcote (*Ann. appl. Biol.*, 1957, **45**, 133—139).—The performance of the different types of traps are described. A. H. CORNFIELD.

Comparison of glasshouse and laboratory methods for testing fungicides against *Botrytis cinerea*. P. J. Brook (*N.Z. J. Sci. Tech.*, 1957, **38, A**, 506—511).—The main discrepancy between laboratory and glasshouse results was that the standard slide germination method gave Cu fungicides a high rating, whereas in practice these materials did not effectively control grey mould on tomatoes. This was because spores of *B. cinerea* can germinate on heavy deposits of Cu in the absence of free water. R. H. HURST.

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Particle size of insecticidal suspensions and their contact toxicity. VI. Effect of temperature on relative toxicity. A. H. McIntosh (*Ann. appl. Biol.*, 1957, **45**, 189—205).—A study was made of the toxicities of aq. suspensions of uniform-size crystals and of colloidal particles of seven solid contact poisons to three species of insects held at 28° and at 11—20° after treatment. In contact tests the colloid was nearly always more toxic than the crystals. There was a negative temp. coeff. of relative toxicity (colloid : crystal) for all materials except dieldrin (**I**), which had a positive temp. coeff. Two DDT analogues, DDT, rotenone and endrin (**II**) had negative temp. coeff. of kill by contact action. Temp. coeff. was greater for colloid than for crystals. **I** and 2-bromomercurithiophen (**III**) had positive temp. coeff. of kill. The temp. coeff. was greater for colloid than for crystals with **I** but the reverse was true with **III**. The temp. coeff. of kill by injection of colloidal suspensions was negative for DDT, but positive for **I** and **II**. An explanation of the results based on a number of assumptions about the penetration of insect cuticle by solid poisons is presented. A. H. CORNFIELD.

Application equipment for granulated insecticides. W. G. Lovely, H. C. Cox and T. A. Brindley (*J. econ. Ent.*, 1956, **49**, 839—846).—Experiments using five machines with different types of metering mechanisms and five different carriers of several sizes for the application of granulated insecticides are reported. Little apparent difference was found amongst the machines tested whilst residue analyses of stalks and axils were the same. The general requirements for an application of granulated insecticides to control European maize borer are given. A. A. MARSDEN.

A flow meter for spray machines. P. Garman (*J. econ. Ent.*, 1957, **50**, 223).—The principle involved in the instrument (known as a linameter) is described and an illustration given. This flow meter provides a quick method of determining the rate of flow for users of spray machines. A. A. MARSDEN.

New organic fungicide : 1-chloro-2 : 4-dinitronaphthalene. A. Soenen and L. Werotte (*Agricultura*, 1956, **4**, 241—271).—In laboratory tests against nine common fungi, the new fungicide shows equal or superior efficiency in comparison with the best fungicides in common use. The fungicide resists wetting, functions well at 6—25°, and has given promising results in field experiments with various crops. P. S. ARUP.

Fungicides : 2-trichloromethanesulphenyl-6-nitrosaccharin and related compounds. G. H. Hamor (*J. Amer. pharm. Ass., Sci, Edn.*, 1957, **46**, 207—208).—2-Trichloromethanesulphenyl-6-nitrosaccharin (**I**) is prepared in yields of 79% by treating a solution of trichloromethanesulphenyl chloride in CCl_4 with an aq. solution of Na 6-nitrosaccharin at room temp. The antifungal aictivity of **I**, when assayed by the inhibiting action of spore germinaton of *Stemphylium sarcinæforme* (14) and *Sclerotinia fruticola* (seven days old) shows it to be more active than 2-methylsaccharin and considerably more so than *N*-methylphthalimide. G. R. WHALLEY.

Fungicides. II. Aryloxy- and arylthio-alkanecarboxylic acids and their activity as fungicides and systemic fungicides. C. H. Fawcett, D. M. Spencer and R. L. Wain (*Ann. appl. Biol.*, 1957, **45**, 158—176).—A wide range of aryloxyacetic acids and corresponding acids with alkyl groups in the side chain, their arylthio-analogues and the antibiotic griseofulvin were assayed in the plate test for fungistatic effect on six fungi, and as systemic fungicides against *Botrytis fabæ* in broad beans and *Alternaria solani* in tomatoes. In general, arylthio-derivatives were more fungicidal than their aryloxy-analogues. The systemic fungicidal activity of α-(2-chlorophenylthio)propionic acid in the tomato test at 1—100 p.p.m. was similar to that of griseofulvin at 50—500 p.p.m. Griseofulvin gave variable results in the tomato test and poor results in the bean test. A. H. CORNFIELD.

Fungistatic properties of plant tissues. I. An antifungal substance from tissues of *Vicia faba*. D. M. Spencer, J. H. Topps and R. L. Wain. **II. Fungistatic properties of leaf exudates.** J. H. Topps and R. L. Wain (*Nature, Lond.*, 1957, **179**, 651—652, 652—653).—I. Segments of the stems and roots of broad bean (*V. faba*) seedlings were found to exert a marked inhibitory effect on the growth of *Aspergillus niger*, the antifungal activity being much greater in immature than in mature plants. The activity was not present in fluid expressed from the plant tissue nor in extracts made with various solvents but was shown by extracts of the cut tissue with agar. The properties of the antifungal extract, examined by paper chromatography, indicated that the substance is phenolic and has reducing properties, but its exact chemical nature has not yet been determined.

II. Verdant leaves of 12 spp. of woodland trees were washed with distilled water and the washings examined for their inhibitory effect on the germination of *Botrytis cinerea*. Intact leaves of some spp.

can yield small quantities of water-sol. fungitoxic substances, the extracts from elder (*Sambucus nigra*) and privet (*Ligustrum vulgare*) being the most active of those studied. J. S. C.

Small-plot trials of griseofulvin as a fungicide. A. Rhodes, R. Crosse, R. McWilliam, J. P. R. Toothill and A. T. Dunn (*Ann. appl. Biol.*, 1957, **45**, 215—226).—Fair control of grey mould, *Botrytis cinerea*, of lettuce was obtained by applying 0·022—0·088% griseofulvin foliage sprays 2—4 times from June 28 to July 6 or 29. Good control of tulip fire, *Botrytis tulipæ*, was obtained with 1·75% griseofulvin dusts or 0·022—0·088% sprays applied four times between March 31 and April 26. Satisfactory control of chrysanthemum mildew, *Oidium chrysanthemi*, was obtained with foliage sprays of 0·025—0·050% griseofulvin, but better control was obtained when 0·1% griseofulvin was watered to the roots periodically. A. H. CORNFIELD.

Use of griseofulvin against dollar spot, *Sclerotinia homœocarpa*, Bennett, and *Fusarium* patch, *Fusarium nivale*, Fr. Ces., diseases of turf. J. Drew Smith (*Ann. appl. Biol.*, 1957, **45**, 206—208).—Application of griseofulvin in aq. solution at 220—880 µg. per ml. (liquid-concentrate form) to turf decreased the extent of dollar spot and *Fusarium* patch in proportion to the amount applied, in tests in which the disease was started by inoculation with liquid cultures. In practical tests on bowling greens griseofulvin (wettable powder) showed some protective activity against dollar spot infection. A. H. CORNFIELD.

Toxic fluorine compounds. III. ω-Fluoroalkyl ethers. F. L. M. Pattison, W. C. Howell and R. G. Woolford (*Canad. J. Chem.*, 1957, **35**, 141—148).—Representative ω-fluoroalkyl ethers were synthesized, e.g., 5-fluoroamyl methyl ether (b.p. 127—128°/740 mm., n_D^{25} 1·3879) by slow addition of sodium naphthalene to 5 fluoropentanol and treatment of the resultant alkoxide with MeI. 6-Fluorohexyl methyl, 4 : 4′-dichlorodibutyl, 4 : 4′-difluorodibutyl, 4-fluoro-4′-chlorodibutyl, 4-fluoro-4′-cyanodibutyl, 2-fluoro-2′-*n*-butoxydiethyl and 2-fluoro-1′ : 2′ : 2′ : 2′-tetrachlorodiethyl **ether (I)** were also prepared. The toxicities of these compounds are reported; they show that the ether link ruptures *in vivo*. **I** shows outstanding activity as a systemic insecticide. O. M. WHITTON.

Insecticidal phosphoric esters. G. Schrader (*Angew. Chem.*, 1957, **69**, 86—90).—The mol. structure of org. phosphoric esters developed in the last 10—12 years and recent tendencies towards using compounds having systemic action, are discussed. (45 references.) G. F. PENNY.

Organophosphorus insecticides: *OO*-diethyl β-ethylmercaptoethyl dithiophosphate (M-74) and its analogues. M. I. Kabachnik, T. A. Mastryukova, M. F. Shostakovskii, E. N. Prilezhaeva, D. M. Paĭkin, M. P. Shabanova and N. M. Gamper (*Dokl. Akad. Nauk SSSR*, 1956, **109**, 777—780).—M-74 was tested as a contact and systemic insecticide and acaricide, having been prepared as an emulsion based on a concentrate containing 30% of M-74 and 70% additive "OP-7." As standard for contact tests Thiophos was used, and for systemic tests, Mercaptophos (Systox). In 0·0005% concn. M-74 used as contact toxin (immersion) on *Eurigaster integriceps*, Put., destroyed 100% of females (84% destroyed by Thiophos). In 0·005% concn., used as spray on older larvæ and adults of *Pseudococcus maritimus*, Ehrh. 98·5% were killed or paralysed (72·7% by Thiophos of like concn.); similar results were obtained on *Coccus esperidum*, *Tetranychus* sp., *Metatetranychus ulmi* Koch., *Myzodes persicæ* Schulz., *Hyeaopterus pruni* F. and *Calliptamus italicus* L. in systemic tests. Z. N. PREEV.

Organophosphorus insecticides: analogues of *OO*-diethyl β-ethylmercaptoethyl dithiophosphate (M-74), less toxic to warm-blooded [animals]. M. I. Kabachnik, T. A. Mastryukova, Yu. M. Polikarpov, D. M. Paĭkin, M. P. Shabanova, N. M. Gamper and L. F. Efimova (*Dokl. Akad. Nauk SSSR*, 1956, **109**, 947—949).—Further investigations of M-74 (cf. previous abstract) show that those of its analogues which are less toxic to the warm-blooded animals display at the same time a high degree of insecticidal and acaricidal activity and can be used with advantage for plant protection. Z. N. PREEV.

Systemic behaviour of *OO*-diethyl *S*-2 (diethylamino)ethyl phosphorothiolate and its salts. R. L. Metcalfe, E. M. Stafford, T. R. Fukuto and R. B. March (*J. econ. Ent.*, 1957, **50**, 205—210).—Comparisons between the rates of uptake and the translocation of this material (thiol-isomer base), its oxalate and the demeton thiol isomer in cotton and lemon plants by using ^{32}P radiotracers are reported. The thiol-isomer base penetrated more rapidly than did its oxalate salt. After spray applications at 40 g. per 100 gal. no thiol-isomer oxalate was detected in citrus pulp and only 0·08 to 0·32 p.p.m. occurred in the peel. As cotton-seed treatments, the thiol-isomer base accumulated in the seedlings up to 10 times as rapidly as did the oxalate, and the demeton thiol isomer was more rapid than the thiol-isomer base. The thiol-isomer base and its oxalate are apparently endolytic systemic toxicants. A. A. MARSDEN.

Metabolism and selectivity of *OO*-dimethyl 2 : 2 : 2-trichloro-1-hydroxyethyl phosphonate and its acetyl and vinyl derivatives. B. W. Arthur and J. E. Casida (*J. agric. Fd Chem.*, 1957, **5**, 186—192).—*OO*-Dimethyl 2 : 2-dichlorovinyl phosphate (**I**) was generally more toxic but less selectively toxic than were *OO*-dimethyl 2 : 2 : 2-trichloro-1-hydroxyethyl phosphonate (**II**) and its 1-acetyl derivative (**III**); a marked variation in species susceptibility occurred. Antiesterase activity of **I**, **II** and **III** was apparently due to dimethylphosphorylation of the enzymically active sites. **III** may be deacetylated *in vivo* to form **II**, which is a more active antiesterase, possibly due to H bonding between **II** and the esterase. Apparently **II** was not dehydrochlorinated and transformed *in vivo* into the more toxic **I**. The low mammalian toxicity of **II** is apparently due to phosphonate hydrolysis by serum esterases and excretion of the chlorinated portion of the mol. in the urine as trichloroethyl glucuronide. The rate and products of acid and alkaline hydrolysis of **I**, **II** and **III** are reported, and their phytotoxicity, volatility and *in vivo* distribution in certain insects and plants are discussed. (40 references.) S. C. JOLLY.

Metabolism of the systemic insecticide *OO*-diethyl *S*-ethylthiomethyl phosphorodithioate (Thimet) in plants. J. S. Bowman and J. E. Casida (*J. agric. Fd Chem.*, 1957, **5**, 192—197).—When used as a systemic insecticide for the seed treatment of cotton, Thimet (**I**) is metabolized to *OO*-diethyl *S*-ethyl-sulphinyl- and -sulphonyl-methyl phosphorodithioate and *OO*-diethyl *S*-ethyl-sulphinyl- and -sulphonyl-methyl phosphorothiolate, all of which are potent anticholine-esterases, particularly the last metabolite, on which a method of residue analysis is based. Seeds of cotton plants grown for 52 days from seeds treated with **I** on charcoal at a rate as high as 32 lb. of **I** per 100 lb. of seed contained <0·03 p.p.m. of **I** or its metabolites. Some **I** *per se*, however, persisted in beans, beets, cabbage, carrots, lettuce and peas for up to 37 days after soil and foliage application. (18 references.) S. C. JOLLY.

Properties and metabolism in the cockroach and mouse of malathion and Malaoxon. R. D. O'Brien (*J. econ. Ent.*, 1957, **50**, 159—164).—Malaoxon was a product of malathion metabolism in cockroaches and mice. Probably the non-toxicity of malathion to mice is due to vigorous hydrolytic degradation of either malathion or Malaoxon at the carboxylic ester link. This hydrolysis was more rapid than the formation of Malaoxon by oxidation of malathion. In cockroaches, activation was more rapid than hydrolysis, and malathion apparently accumulated to a lethal level. A. A. MARSDEN.

Repellency of homologous series of *cyclo*hexane aliphatic acids and amides. H. K. Gouck, S. A. Hall, C. N. Smith and I. H. Gilbert (*J. econ. Ent.*, 1957, **50**, 175—177).—Repellency tests with six acids showed that increasing the length of the chain by inserting 1, 2 or 3 C increased the initial effectiveness of the repellent progressively, but the addition of 4 and 5 C decreased its effectiveness. The residual effectiveness at equiv. dosages also increased with the length of the chain up to a certain point. With the four amides tested, extending the length of the structural chain by the addition of 1 C increased the initial repellency but addition of 2 and 3 C decreased it. The residual repellency increased progressively with addition of 1 and 2 C and then decreased. A. A. MARSDEN.

Cumulative toxicity of γ-benzene hexachloride and Diazinon applied in small doses to the desert locust, *Schistocerca gregaria*, Forsk. R. D. MacCuaig (*Ann. appl. Biol.*, 1957, **45**, 114—121).—Application of γ-$C_6H_6Cl_6$ or Diazinon [diethyl (2-*iso*propyl-4-methyl-pyrimid-6-yl)-thiophosphate] in oil solutions to the ventral surfaces of the abdomen of desert locusts 2—4 weeks after fledging showed that when doses were applied in two equal portions with a 72-hr. interval, or in four equal portions at 24-hr. intervals, no significant decrease in toxicity, in comparison with a single dose, could be detected with either insecticide. Results indicated that in the field successive spraying will be fully cumulative over a period of 72 hr. Females were considerably more resistant to Diazinon than were males, but the sexes were equally resistant to γ-$C_6H_6Cl_6$. A. H. CORNFIELD.

Use of chlorinated polyphenyls to increase the effective insecticidal life of lindane. E. J. Duda (*J. econ. Ent.*, 1957, **50**, 218—219).—Addition of Arochlor to lindane increased its effective life. Arochlor alone was toxic to the elm leaf beetle, *Galerucella xanthomelæna*; when used in combination with lindane, mortality occurred earlier than when lindane alone was used. A. A. MARSDEN.

Further evidence for autosomal, multiple-factor inheritance of chlordane resistance in the German cockroach. F. E. Jarvis, jun., J. M. Grayson and M. Levitan (*J. econ. Ent.*, 1957, **50**, 185—187).—The inheritance of resistance to chlordane in *Blatella germanica* was

examined. Chlordane resistance is apparently transmitted by the autosomes, with no evidence of material factors or sex-linked inheritance. Resistance factors which exert some form of dominance may be present. A. A. MARSDEN.

Agricultural fungicides. I. Trichloromethyl thiolsulphonates. J. H. Uhlenbroek, M. J. Koopmans and H. O. Huisman (*Rec. Trav. chim. Pays-Bas*, 1957, **76**, 129—146).—Prep. and biological properties of many strongly fungitoxic compounds of the general type $R{\cdot}SO_2{\cdot}S{\cdot}CCl_3$ are described (R is aliphatic, aromatic, or heterocyclic). The nature of R has a relatively small influence on the fungitoxic properties, but does affect the strongly phytotoxic effects shown by many of the compounds. Compounds $R = C_6H_4A$ (where $A = p\text{-}O{\cdot}[CH_2]_2{\cdot}OEt$, $p\text{-}O{\cdot}[CH_2]_2{\cdot}O{\cdot}[CH_2]_2{\cdot}OEt$, *o*- and *p*-$CO_2H$, *o*- and *p*-$CO_2Et$, *m*- and *p*-NHAc, etc.) have lowered phytotoxicity without decrease in fungitoxicity. Two compounds ($R = p\text{-}C_6H_4{\cdot}NHAc$ and $p\text{-}C_6H_4{\cdot}CO_2H$) are being studied in extensive field trials. From preliminary results it appears that they can be used for the control of fungus diseases in fruit. M. DAVIS.

Chemical structures and dissociation constants of amino-acids, peptides and proteins in relation to their reaction rates with 2 : 4-dichloro-6-(o-chloroanilino)-s-triazine. H. P. Burchfield and E. E. Storrs (*Contr. Boyce Thompson Inst.*, 1956, **18**, 395—418).—Aspartic acid was the least reactive compound, on which quant. data was obtained, with a 2nd order velocity constant of $1{\cdot}2 \times 10^{-3}$. With the exceptions of tyrosine and cysteine, the commonly occurring amino-acids react from 2 to 10 times more rapidly than does aspartic acid. The materials most susceptible to alkylation were glutathione, cysteine, *p*-aminobenzoic acid, hydroxyproline, pyridoxamine, proline, tyrosine and pyridoxine. It is assumed that only the $R\text{-}NH_2$ and R-S′ groups can take part in the reactions with the $R\text{-}NH_3^+$ and R-SH groups excluded. (36 references.) E. G. BRICKELL.

Lethal and sterilizing effects of γ-radiation on insects infesting cereal commodities. P. B. Cornwell, L. J. Crook and J. O. Bull (*Nature, Lond.*, 1957, **179**, 670—672).—Seventeen spp. of cereal insect pests were irradiated by γ-radiation (source ^{60}Co). Dosages required to kill and inhibit reproduction were determined. J. S. C.

Temperature–respiration curve of flour beetles exposed to non-optimal temperatures. D. K. Edwards (*Science*, 1957, **125**, 651—652).—Respiratory adaptation to non-optimal temp. does not occur with *Tribolium confusum* but low-temp. survival may be enhanced by low-temp. adaptation. T. G. MORRIS.

Chemical determination of Perthane residues on agricultural crops. J. R. W. Miles (*J. agric. Fd Chem.*, 1957, **5**, 349—350).—The Perthane residues were dehydrochlorinated and the products were treated with conc. H_2SO_4 (96%) at room temp. A characteristic peach colour was obtained (absorption max. at 493 mμ). Perthane residues of 0·1 p.p.m. can be determined on asparagus and maize. E. M. J.

Residues on plants treated with DDT granules and emulsions for European maize borer control. J. E. Fahey, H. W. Rusk and H. C. Cox ((*J. econ. Ent.*, 1956, **49**, 846—849).—DDT emulsion sprays deposited greater residues on maize leaves than did granules but granules deposited equal or greater residues in the plant whorls and leaf axils. Granulated formulations prepared with attapulgite or Celite gave the largest deposits. In a comparison of three machines, the fluted-feed applicator was superior to the chain-type or fluted-shaft seeder. A. A. MARSDEN.

Determination of organic chlorides and residues from chlorinated pesticides by combustion analysis. J. A. Hudy and C. L. Dunn (*J. agric. Fd Chem.*, 1957, **5**, 351—354).—The apparatus comprising a vertical, quartz packed furnace is described. Liquid org. materials may be burnt continuously at rates of 10—20 g. per hr. The chloride resulting from combustion is determined by amperometric titration with $AgNO_3$ after absorption in alkaline solution. In application of the method to toxaphene in various materials, e.g., animal fat butter fat, a sensitivity of 5 μg. of chloride was found. E. M. J.

Effect of date of sowing on the incidence of powdery mildew on spring-sown cereals. F. T. Last (*Ann. appl. Biol.*, 1957, **45**, 1—10).—Delaying the date of sowing of spring-sown barley in 1953 and wheat in 1954 from February to April increased the incidence of powdery mildew, *Erysiphe graminis*, D.C., from May onwards. Before then, conditions did not favour the rapid spread of mildew. From mid-June infected barley produced necrotic lesions. These developed sooner on the early- than on the late-sown crop, and on the lower than upper leaves. Mildew reduced yields of barley to a greater extent when sown on April 28 than when sown on March 30. The no. of ears per m. of row, the wt. of 100 ears, and the 1000-grain wt. were reduced by infection. Varying sowing rate from 1·5 to 2·5 bushels per acre did not affect the incidence, or the effect, of mildew on grain yield. A. H. CORNFIELD.

Experiments on earworm control on sweet maize. W. G. Eden (*J. econ. Ent.*, 1956, **49**, 822—825).—Timing of spray applications, nozzle types, amount of DDT, and use of mineral oil all influenced the degree of control of *Heliothis zea* attacking sweet maize. When sprays were applied at three-day intervals, earworm control increased as DDT was increased from 1·0 to 2·5 lb. per acre. Higher rates of DDT did not give corresponding increase in control. Mineral oil increased earworm control but injured foliage. A. A. MARSDEN.

Control of the European maize borer with granulated insecticides in 1955. H. C. Cox, W. G. Lovely and T. A. Brindley (*J. econ. Ent.*, 1956, **49**, 834—838).—Endrin, heptachlor, aldrin, dieldrin, Isodrin and parathion granules gave better control of *Pyrausta nubilalis* than did granulated or spray formulations of DDT which were equally effective. A 4—7·5% DDT granulated formulation applied at 15 to 20 lb. per acre gave the most practical borer control. Correct timing of insecticidal applications increased yields by almost 10 bushels of maize per acre. A. A. MARSDEN.

Control of maize earworm in sorghum heads by aerial spraying in southwestern Kansas. L. J. DePew (*J. econ. Ent.*, 1957, **50**, 224—225).—The control of *Heliothis zea* in grain sorghum after one and four days, respectively, was: Phosdrin (0·5 lb. per acre) 95 and 100%; DDT (2 lb.) 83 and 92%; and malathion (1 lb.) 81 and 89%. Endrin and parathion gave excellent control after four days, but not after one day. A. A. MARSDEN.

Control of rice stem borer with endrin. G. C. Sengupta and G. D. Rout (*J. econ. Ent.*, 1957, **50**, 221).—An endrin emulsion spray (0·13—0·38 lb. per acre) applied twice to the growing rice crop satisfactorily prevented attack by the rice stem borer, *Schœnapius incertulas*. The importance of correct timing of the sprays is emphasized. A. A. MARSDEN.

Toxicity of DDT in abrasive and non-abrasive dusts to the rice weevil, *Calandra oryzæ*, L. P. A. Harlow (*Ann. appl. Biol.*, 1957, **45**, 90—113).—At high R.H. the toxicity of DDT was not markedly affected by any carrier except C, which reduced the toxicity. Small differences in toxicity of DDT caused by other carriers could not be accounted for by differences in their average particle size, bulk density, amount adhering to the insect, surface area, abrasiveness to the insect, or effect of behaviour of the insect. At low R.H. abrasive dusts killed the insects by desiccation, thus adding to the toxic effect of DDT. Abrasion of the insect's cuticle did not affect the apparent rate of penetration of DDT. Starved insects were more susceptible to DDT poisoning. DDT may be transported to the cuticle as a vapour. A. H. CORNFIELD.

Control of late blight of potatoes with fungicides at Hastings Florida. A. H. Eddins (*Amer. Potato J.*, 1957, **34**, 42—48).—In a severe blight year Dithane D-14–$ZnSO_4$ and Parzate liquid–$ZnSO_4$ were slightly more effective in controlling late blight than were "tribasic Cu–Zn" and much more effective in preventing foliage and tuber infection than were zineb, "tribasic Cu–Zn" and a Cu compound. In a moderate blight year maneb and Cu compound A were more effective than were nabam–$ZnSO_4$, captan or ethylene bisthiuram disulphide in increasing yields.

Carry-over effects of pentachloronitrobenzene (PCNB) applied to the soil for control of potato scab. G. V. C. Houghland and L. C. Cash (*Amer. Potato J.*, 1957, **34**, 85—88).—Soil applications of PCNB (100—200 lb. per acre) greatly reduced the proportion of scabby potatoes in the season of application but had much less effect in the following season. Potato yields were reduced in the season of application, but were unaffected in the following season, when more than 150 lb. of PCNB was applied. A. H. CORNFIELD.

Resistance of the Southern potato wireworm to insecticides. W. J. Reid, jun. and F. P. Cuthbert, jun. (*J. econ. Ent.*, 1956, **49**, 879—880).—In field studies a marked decrease within a few years in the effectiveness of aldrin, dieldrin, heptachlor and chlordane against *Conoderus falli* attacking Irish potatoes was observed. In the laboratory a significant difference was shown in the susceptibility to chlordane of larvæ from potato fields receiving several annual applications of chlordane and wireworms from untreated fields. This high resistance to chlordane and the other three materials tested was not shown by the Gulf wireworm, *Conoderus amplicollis*. No evidence of decreased effectiveness of DDT against *C. falli* was noted. A. A. MARSDEN.

Laboratory toxicity tests against insects affecting sugar beets grown for seed. F. H. Harries and A. C. Valcarce (*J. econ. Ent.*, 1957, **50**, 120—122).—Of 12 insecticides tested against the beet leafhopper, *Circulifer tenellus*, parathion, malathion, Chlorthion and Diazinon were the most toxic materials. One week after dusting most of the dusts had lost their toxicity but chlordane, dieldrin, DDT, malathion and Chlorthion showed significant residual action. The P materials were also highly toxic to *Lygus hesperus*, but only parathion showed

any residual effect against this pest. The systemic insecticides demeton, schradan and Am. Cyanamid 3911 and 12008 had a high toxicity to leafhoppers and lygus bugs for at least a month.
A. A. MARSDEN.

Relative importance of various host plants of the beet leafhopper in S. Idaho. J. R. Douglass and H. C. Hallock (*U.S. Dep. Agric.*, 1957, Tech. Bull. 1155, 11 pp.).—In rangeland the most important host plants to *Circulifer tenellus* (Baker) were flixweed, perfoliate pepperweed and tumblemustard; in sagebrush areas it was green tansymustard. Greenhouse studies showed that curled dock, blistercress, green tanysmustard and perfoliate pepperweed were the most attractive species for egg-laying. E. G. BRICKELL.

Effects of formulations and rates of insecticides on sugar beet. W. L. Gojmerac (*N. Dakota agric. Exp. Sta. Bimonthly Bull.*, 1957, **19,** 97—100).—Applications of aldrin (0·8—2·1 lb.), dieldrin (0·5 lb.) and heptachlor (0·32—6·5 lb. per acre) mixed with fertilizer increased yields of sugar beet. Application of dieldrin (1·9—6·2 lb.) and heptachlor (11 lb. mixed with Attaclay) reduced yields in comparison with controls. Heptachlor (16 lb.) on vermiculite increased yields.
A. H. CORNFIELD.

Streptomycin for control of silvering disease, *Corynebacterium betæ*, of red beet. W. G. Keyworth (*Ann. appl. Biol.*, 1957, **45,** 215).—Considerable reduction in the incidence of silvering disease of red beets followed soaking the seed in 200 p.p.m. streptomycin for 23 hr. prior to sowing. Seed treatment with 1% Hg dust also gave effective control of the disease. A. H. CORNFIELD.

Control of soil insects on turnips. M. W. Stone and F. B. Foley (*J. econ. Ent.*, 1957, **50,** 143—145).—Of seven insecticides tested, dieldrin (2·3 to 3·3 lb. per acre) gave the best and most consistent control of the seed-maize maggot, *Hylemya cilicrura*, the sugar-beet wireworm, *Limonius californicus*, and white grubs attacking turnips. Heptachlor, endrin and aldrin gave only commercial control for one season. Isodrin, toxaphene and DDT gave inadequate protection.
A. A. MARSDEN.

Crown rust of ryegrass. I. A. M. Cruickshank (*N.Z. J. Sci. Tech.*, 1957, **38, A,** 539—543).—Short-rotation ryegrass was highly resistant and perennial ryegrass highly susceptible to the disease. Italian ryegrass and the short-rotation × perennial hybrids were intermediate in reaction. The significance of the data in relation to breeding and selection of ryegrass is discussed. R. H. HURST.

Blackpatch of red clover and other legumes caused by *Rhizoctonia leguminicola*, sp. nov. F. J. Gough and E. S. Elliott (*W. Virginia agric. Exp. Sta.*, 1956, Tech. Bull. 387, 23 pp.).—Characteristics of the disease, which has been reported only on leguminous hosts, are described. The disease is disseminated through infected seed and locally through mycelial growth and by scattering diseased plant parts. Seed treatment, application of foliage fungicides, and application of ground sprays in spring and after the first cutting have not controlled the disease. A. H. CORNFIELD.

Control of the spotted lucerne aphid on lucerne. N. M. Randolph (*J. econ. Ent.*, 1957, **50,** 124—126).—Malathion (0·5 and 1 lb.), parathion (0·25 lb.) and a toxaphene–DDT (2 : 1) (3 lb. per acre) spray gave the most effective control of *Pterocallidium* sp. attacking lucerne. Fair to good control was obtained for 1—2 weeks after treatment. A. A. MARSDEN.

Spotted lucerne aphid occurrence on seedling lucerne as influenced by systemic insecticides and varieties. R. C. Dobson and J. G. Watts (*J. econ. Ent.*, 1957, **50,** 132—135).—As a seed treatment or in granulated form, Thimet and granulated Bayer 23129 were relatively ineffective against injury by *Pterocallidium* sp. to seedling lucerne. Bayer 19639 gave promising results in protecting autumn stands of seedling lucerne for ⩽6 weeks after planting.
A. A. MARSDEN.

Lucerne weevil control in Delaware, 1955, with observations on pea aphid and meadow spittlebug. D. MacCreary (*J. econ. Ent.*, 1957, **50,** 215—216).—Dieldrin gave fair to good control of *Hypera postica* and had better residual toxicity than heptachlor or endrin. Dieldrin and heptachlor were ineffective against the pea aphid, *Macrosiphum pisi*, but endrin greatly reduced this pest. A. A. MARSDEN.

Lucerne weevil control with granulated insecticides in Virginia. A. A. Muka (*J. econ. Ent.*, 1957, **50,** 216—218).—When applied in the winter or spring, heptachlor (1·5 lb. per acre) in granulated form gave excellent control of *Hypera postica* attacking lucerne, and was superior to aldrin, dieldrin, parathion or lindane.
A. A. MARSDEN.

Effects of granular dieldrin and heptachlor on adult weevil populations in red clover. H. L. Hansen and C. K. Dorsey (*J. econ. Ent.*, 1957, **50,** 224).—Granular formulations of heptachlor and dieldrin (0·5 lb. toxicant per acre) applied in April to the ground surface gave >90% kill of *Sitonia hispidula* and *Hypera nigrirostris*. These treatments did not reduce populations of *Hypera meles*.
A. A. MARSDEN.

Concentrate spraying of apple trees. I. Fungicidal efficiency of lime-sulphur. M. H. Moore (*Ann. appl. Biol.*, 1957, **45,** 11—18).—When applied at green cluster, pink bud, petal fall and fruitlet stages with a paint spray gun (compressed air) undiluted lime-S did not cause any damage and was as effective as conventional hydraulically applied dil. sprays in controlling apple scab and mildew. Undiluted lime-S applied as a hydraulic spray caused severe scorching; 50% lime-S applied at increased vol. by spray gun also gave good control, whilst 10% lime-S applied in the same way gave poor control of scab, probably because of reduced dosage. A. H. CORNFIELD.

Resistance of the codling moth to DDT sprays. D. W. Hamilton (*J. econ. Ent.*, 1956, **49,** 866—867).—Laboratory and orchard studies using various strains of codling moths from orchards in which DDT had been heavily or indifferently applied are reported. Strains varied in their resistance to DDT, but favourable weather for codling moth activity, poor spray coverage and the frequent use of other materials which adversely affected the amount and persistence of DDT deposits greatly added to the difficulty in obtaining good codling moth control in mid-western orchards. A. A. MARSDEN.

Field and laboratory evaluations of lead arsenate, wettable sulphur and hydrated lime against the plum curculio. E. H. Smith (*J. econ. Ent.*, 1957, **50,** 177—183).—All field treatments gave some control, the same materials being more effective on cherry than on prune. Curculio beetles tended to desert treated trees: the remaining ones fed at sub-normal levels resulting in reduced oviposition whilst continued feeding resulted in death. A. A. MARSDEN.

Bacterial canker of stone fruit. III. Inoculum concentration and time of inoculation in relation to leaf-scar infection of cherry. J. E. Crosse (*Ann. appl. Biol.*, 1957, **45,** 19—35).—Inoculation tests are described and modification of spray programmes in the light of the results obtained are discussed. A. H. CORNFIELD.

Line-pattern virus disease of plums. A. F. Posnette and C. E. Ellenberger (*Ann. appl. Biol.*, 1957, **45,** 74—80).—Characteristics of the disease are described. A. H. CORNFIELD.

***Pythium* disease of pear trees.** F. J. Newhook (*N.Z. J. Sci. Tech.*, 1957, **38, A,** 533—538).—A species of *Pythium* pathogenic to pears is described. The fungus attacks phloem of trunks, leaders and sometimes small branches (symptoms described). Limbs die, often being attacked secondarily by *Diaporthe peniciosa*, *Stereum purpureum* and *Coriolus versicolor*; within 3—10 years the tree dies. Most varieties of pear are affected. Control measures include avoidance of root wounding and the removal of badly affected leaders or trees. Treating the soil of infected sites before replanting might be beneficial.
R. H. HURST.

Effects of oil spray and of variation in certain spray ingredients on juice quality of citrus fruits in California orchards, 1950—1953. L. A. Riehl, R. T. Wedding, J. L. Rodriguez and J. P. LaDue (*J. econ. Ent.*, 1957, **50,** 197—204).—The % of sol. solids in Valencia and navel orange juice was si nificantly higher in some, but not in all experiments, from fruit treated with parathion than that from oil-sprayed fruit. Reduction in sol. solids due to oil sprays could be avoided if Aug. and Sept. applications were made by recommended procedures. The effect of oil on citrus juice quality was not influenced by variations in formulation. Addition of 2 : 4-D to oil spray mixtures did not influence juice quality except for the % of total sol. solids in navel orange juice which decreased in some experiments. High-paraffin petroleum oils used at half the concn. of the California spray oil reduced the % of sol. solids in most cases. No differences in the effects of a synthetic isoparaffinic hydrocarbon oil and California spray oil were apparent. A. A. MARSDEN.

Effect of soil-type and DDT on ovipositional response of *Chrysopa California* (Coq.) on lemon trees. C. A. Fleschner and G. T. Scriven (*J. econ. Ent.*, 1957, **50,** 221—222).—Green lacewings, *Chrysopa californica*, laid considerably more eggs on lemon trees growing in a loose, sandy soil than on trees in a compact silt soil. Untreated trees in both soils received fewer eggs than trees receiving wettable DDT, whether the DDT material was added to the soil or sprayed on the tree. A. A. MARSDEN.

Control of the carrot weevil attacking parsley. M. Semel (*J. econ. Ent.*, 1957, **50,** 183—184).—Dieldrin or heptachlor emulsion sprays or broadcast treatments gave excellent control of carrot weevils, *Listronotus oregonesis*, attacking parsley when the insecticide was applied to newly emerged plants and repeated after each cutting. Toxaphene and chlordane were unsatisfactory. A. A. MARSDEN.

Control of spider mites on lima beans. J. Wilcox and A. F. Howland (*J. econ. Ent.*, 1957, **50,** 128—132).—The following materials gave the best results against *Tetranychus telarius*: demeton, Am. Cyanamid 12008 and 3911, Rohm and Haas FW-152 and FW-293, Stauffer R-1303, Hercules AC-528, Aramite and Ovex. Against *T. deviatarsus* satisfactory results were obtained from

demeton, Holcomb 326, FW-293, Aramite and parathion. S was ineffective against *T. telarius* but was fairly effective against *T. deviatarsus*: the reverse was true for Ovex and malathion. Demeton, FW-293 and Aramite were the only materials which were toxic to both species of mites. A. A. MARSDEN.

New insecticides to control green June beetle larvæ in tobacco-plant beds. L. B. Scott (*J. econ. Ent.*, 1956, **49**, 868—869).—Of several insecticides tested in baits, dusts and drenches for the control of *Cotinis nitida* in tobacco plant beds, a parathion (1%) dust at 1·5 lb. per 100 sq. yd. gave satisfactory control when night temp. were >15°. Parathion baits and drenches gave similar results. A. A. MARSDEN.

Control of green June beetle adults with insecticides. R. Thurston, K. J. Starks and G. M. Boush (*J. econ. Ent.*, 1956, **49**, 828—830).—Of 18 insecticides tested in $COMe_2$ (1 : 10,000) in the laboratory, lindane, heptachlor, aldrin and endrin were the best materials, giving at least 85% kill of *Cotinis nitida* in 24 hr. None of the P insecticides was very effective. At lower concn., lindane was much more toxic than either heptachlor or aldrin. In a heavily infested vineyard lindane gave excellent, and heptachlor gave good control. Analyses of sprayed grapes showed insignificant residues. A. A. MARSDEN.

Occurrence of iron, copper, calcium and magnesium in tobacco mosaic virus. H. S. Loring and R. S. Waritz (*Science*, 1957, **125**, 646—648).—Ash from virus purified by 3 to 4 ultra-centrifugations contained 30 μg. of Fe, 20 μg. of Cu, 300 μg. of Ca and 600 μg. of Mg per g. of virus. In presence of EDTA the contents of Ca and Mg were reduced but those of Fe and Cu were little affected. Virus recovered from these experiments was still highly active. Fe and Mg occurred in the nucleic acid portion of the virus in concn. about 20 times that in the virus itself. T. G. MORRIS.

Effect of certain acaracides on two species of spider mites on cotton. R. L. Robertson and F. S. Arant (*J. econ. Ent.*, 1956, **49**, 860—861).—Aramite (5%) dust had the longest residual effect against the desert spider mite, *Tetranychus desertorum*. Sprays of Chlorthion, demeton, malathion, methyl parathion, parathion and Ovex effectively reduced both this mite and the strawberry spider mite, *T. atlanticus*. Hercules AC 538 also gave good control of *T. atlanticus*. A. A. MARSDEN.

Phosphorus insecticides for control of pink bollworm and some other cotton pests, 1955. C. A. Richmond (*J. econ. Ent.*, 1956, **49**, 874—875).—Bayer 17147 at 0·98 lb. per acre, and a mixture of 17147 and DDT were equally effective against the pink bollworm, *Pectinophora gossypiella*, and gave the best control. All insecticides gave good control of boll weevils, and of bollworms, *Heliothis zea*. The P compounds, Bayer 17147, 16259, and DDVP, gave satisfactory control of a light infestation of aphids and spider mites. A. A. MARSDEN.

Granulated endrin for white-pine weevil control during hibernation. A. R. Hastings (*J. econ. Ent.*, 1956, **49**, 878).—Cage tests using granulated endrin (1, 2 and 4 lb. per acre) applied in autumn to the surface of the duff in a white pine plantation gave almost complete control of weevils emerging in the spring after hibernation. A. A. MARSDEN.

Anemone mosaic—a virus disease. M. Hollings (*Ann. appl. Biol.*, 1957, **45**, 44—61).—The name anemone mosaic is proposed for a previously unrecorded disease of *Anemone coronaria*, L. Characteristics of the disease, methods of transmission and host plants are described. A. H. CORNFIELD.

Insecticide residues in wireworm control. C. E. Woodworth and M. C. Lane (*J. econ. Ent.*, 1957, **50**, 222—223).—Of five insecticides tested in the field against wireworms, principally *Limonius californicus*, heptachlor at 4 lb. per acre gave the best control, with 94% kill after two years. Dieldrin (4 lb.) gave 90% kill, whilst DDT and chlordane also gave high kills. Aldrin was unsatisfactory. Soil taken from plots 1½ years after being treated with these five insecticides was, in every case, highly toxic to newly hatched wireworms. A. A. MARSDEN.

Small-plot tests for the control of chiggers. J. C. Keller and H. K. Gouck (*J. econ. Ent.*, 1957, **50**, 141—143).—Toxaphene (2 and 1 lb. per acre) emulsion sprays were highly effective against *Eutrombicula alfreddugesi* for 14 and 5—6 weeks, respectively, and a toxaphene (5 lb.) dust was very satisfactory for ≤8 weeks. Dieldrin also gave excellent control but other acaricides were less effective. Endrin, dieldrin, lindane and $C_8H_6Cl_8$ gave good to excellent control of *Trombicula splendens*. A. A. MARSDEN.

Temperature and the action of pyrethrum in the American cockroach. M. S. Blum and C. W. Kearns (*J. econ. Ent.*, 1956, **49**, 862—865).—A negative temp. coeff. of pyrethrum between 15° and 35° was shown for *Periplaneta americana*. Studies with ^{14}C-pyrethrum showed that the rate of penetration at 35° was more than twice that at 15°. Treated roaches transferred from 35° to 15° rapidly became paralysed whilst a return to 35° restored them to an apparently normal state. The absence of radioactivity in the blood of roaches treated with ^{14}C-pyrethrum showed that the toxin was not pyrethrum, the action of which was probably due to its stimulation of the production of a toxic substance in the roach. This toxin was present at 15° but absent in blood removed from treated cockroaches held at 35°. Piperonyl butoxide increased the susceptibility of the cockroach to pyrethrum and the existence of the toxin at higher temp. The toxic agent in the roach blood lost its activity when stored at room temp. A. A. MARSDEN.

Biological control of a soil-borne *Pythium* infection by seed inoculation. J. M. Wright (*Plant & Soil*, 1956, **8**, 132—140).—Disease symptoms on white mustard seedlings grown in a soil infected with *Pythium* sp. were reduced somewhat by dusting the seed with spores of *Trichoderma viride*, *Penicillium nigricans*, *P. frequentans* or *P. godlewski* prior to sowing. Of three strains of *T. viride* tested a gliotoxin-producing strain was more effective than a viridin-producing strain, whilst an antibiotically-inactive strain was the least effective. Disease symptoms were less severe when the soil was treated with acid or $Ca(OH)_2$. Treatment of seed with *T. viride* reduced symptoms even further in the $Ca(OH)_2$, but not in the acid-treated, soil. A. H. CORNFIELD.

Biological control of the wattle bagworm (*Kotochalia junodi*, Heyl.) by a virus disease. I. Small-scale experiments. L. L. J. Ossowski (*Ann. appl. Biol.*, 1957, **45**, 81—89).—A method of purifying and assaying the polyhedral virus of the wattle bagworm is described. Aq. suspensions of 10,000 polyhedra per cu. mm. applied to trees when the larvæ were hatching caused high mortality; no increased mortality occurred with higher concn. Newly-hatched larvæ showed symptoms after 3—4 days' feeding on contaminated food and died two days later. Older larvæ died more slowly but mortality was still high enough to prevent serious defoliation of infected trees. Polyhedra were not washed off the trees by heavy rain and remained infective for long enough to suggest that high mortality could be obtained by spraying before the larvæ emerged. A. H. CORNFIELD.

Effect of erythromycin and other antibiotics on the control of European foulbrood of honeybees. W. T. Wilson and J. O. Moffett (*J. econ. Ent.*, 1957, **50**, 194—196).—Gallimycin (containing 21·1 g. of erythromycin per lb.) was the most effective antibiotic used for controlling European foulbrood and was more successful than Aurefac, MK-65, tetracycline, Penicel, a streptomycin–penicillin combination, or TM-10. The lowest dosage of gallimycin tested (4·5 g. per colony per treatment) gave the best control (91·5% reduction) of this disease. A. A. MARSDEN.

Effects of zinc and amino-acids on cell division in *Ustilago*. E. Spoerl, A. Sarachek and N. Puckett (*Science*, 1957, **125**, 601).—Cultures of *Ustilago spærogena* were grown at 23 ± 1° in a basic medium devoid of Zn or thiamine, with known additions of Zn and either NH_4 acetate, glycine, glutamic acid, proline or ribonucleic acid. After 46 hr. growth ammonium acetate and proline alone produced short cells but those receiving Zn also gave almost entirely long cells. Glycine and ribonucleic acid alone gave long cells. Glutamic acid alone gave mainly short cells but with Zn long cells formed. Zn additions had little effect on growth. T. G. MORRIS.

New chemical product for controlling noxious grass. F. R. Charles (*Rev. int. Agric., Milano*, 1956, **1**, (8–9), 62—64).—The use of γ-(4-chloro-2-methylphenoxy)butyric acid for the control of noxious grass is described. The use of this product depends on the principle of employing a non-toxic substance, which some plants make toxic. The compound is harmless to clover, even in its first phase, and is tolerated by cereals in all phases of their growth. C. A. FINCH.

Animal Husbandry

Rachitogenic effect of vitamin A. A. B. Grant and P. B. O'Hara (*N.Z. J. Sci. Tech.*, 1957, **38, A**, 548—576).—The dead brown leaves of pastures contain appreciable amounts of vitamin D, whereas the green leaves contain a rachitogenic factor, which has been identified as carotene. Equivalent amounts of vitamin A and carotene have the same rachitogenic power. Vitamin A probably has no direct inhibitory effect on vitamin D but appears to exert its rachitogenic influence in some other way, possibly by its local action at the site of bone formation. (29 references.) R. H. HURST.

Preparation of vitamin B_{12} in concentrates and in crystalline form from town sewage subjected to methane fermentation. J. Janicki, J. Pawelkiewicz and K. Nowakowska (*Acta biochim. polon.*, 1956, **3**, 161—170).—The method depends on the liberation of the vitamin from bacterial cells in the fermented sewage by heating to 80—90° at pH 6—7 in presence of NaCN. Colloids are coagulated by K

alum and the vitamin is adsorbed in activated C and eluted with acetone. A concentrate suitable for animal feeding and a cryst. product are prepared (yield 10 mg. of vitamin B_{12} per 100 l. of sewage). Other related products, some being decomposition products of vitamin B_{12}, were isolated. Vitamin B_{12} may be determined spectrophotometrically. A. G. POLLARD.

Feather meal as a source of protein for fattening lambs. R. M. Jordan and H. G. Croom (*J. Anim. Sci.*, 1957, **16**, 118—124).—Replacement of part of the protein of a lamb ration by feather meal did not affect feed consumption, rate of gain in wt. carcass yield or quality. A. G. POLLARD.

Pilot-plant development of alkali-cooking process for cottonseed meals. II. Effect of additional comminution. N. B. Knoepfler, W. H. King, M. F. Stansbury and E. J. McCourtney (*J. Amer. Oil Chem. Soc.*, 1957, **34**, 61—66).—In the alkali-cooking process, comminution lowers the gossypol content of the product. Optimum conditions of temp. and moisture content in relation to gossypol content and N solubility of the meal are examined. Reduced gossypol content without significant loss of N solubility can be achieved by using a mixture having H_2O 18—31%, pH 8·2, at 90°F. G. HELMS.

Value of soya-bean oil-meal, low-gossypol (de-gossypolized) solvent-processed cottonseed meal, low-gossypol expeller-processed cottonseed meal and various blends thereof in the ration of growing fattening swine. C. E. Haines, H. D. Wallace and M. Kager (*J. Anim. Sci.*, 1957, **16**, 12—19).—A de-gossypolized solvent-extracted cottonseed meal (*S*), (free gossypol 0·01 and N-solubility 89%) produced better growth of weanling pigs than did an expeller meal (free gossypol 0·01 and N-solubility 42%). Still better results were obtained by partial replacement (25—75%) of cottonseed (especially *S*) by soya-bean oil-meal. With all rations examined, improved growth rates produced by feeding procaine penicillin were further improved by addition of erythromycin. A. G. POLLARD.

Chemical composition in relation to the nutritive value of coarse fodder for sheep. D. M. Walker (*Proc. European Grassland Conf., Paris*, [1954], 1956, 233—237).—Modern methods of analysis add no extra precision to predictions of digestibility of hay than does the determination of "crude fibre." Current parallel observations on silage are noted. A. G. POLLARD.

Estimation of daily variations in the quality and quantity of herbage consumed by rotationally-grazed cattle and sheep. F. K. van der Kley (*Neth. J. agric. Sci.*, 1956, **4**, 197—204).—The method is described. A. H. CORNFIELD.

Value of herbage concentrates for non-ruminants. K. J. Carpenter J. Duckworth and G. M. Ellinger (*Proc. European Grassland Conf., Paris*, [1954], 1956, 243—248).—Analyses of grass leaf-protein concentrates and feeding trials with chicks are recorded. It is unlikely that such concentrates can replace standard feeding stuffs under present economic conditions. A. G. POLLARD.

The basic principle of rotational grazing. A. Voisin (*Proc. European Grassland Conf., Paris*, [1954], 1956, 209—217).—A critical discussion. The importance of allowing a suitable rest-period for the pasturage, according to seasonal conditions, in which re-growth can occur to a suitable height (12—15 cm.) is stressed. (15 references.) A. G. POLLARD.

Effect of drying temperatures on the quality of the product in dehydrating grass. J. J. I. Sprenger and N. D. Dijkstra (*Proc. European Grassland Conf., Paris*, [1954], 1956, 237—242).—Comparisons of various forms of dryers are recorded. By use of high-temp. dryers for young grass a product of similar value to that from low-temp. dryer can be obtained provided the temp. of the outlet gases is kept low. For this purpose oil fuel was superior to coke. Control of the inlet gas is of less importance under these conditions. A. G. POLLARD.

Studies in silage fermentation at Edinburgh. A. Stirling (*Proc. European Grassland Conf., Paris*, [1954], 1956, 251—253).—A short résumé of recent work. A. G. POLLARD.

Present position of silage in south-east Scotland. J. Nash (*Proc. European Grassland Conf., Paris*, [1954], 1956, 253—256).—Current practices are described and some recent investigations are indicated. A. G. POLLARD.

Effect of feeding certain silages on the relative concentrations of rumen volatile fatty acids. J. M. Elliot, E. Bennett and J. G. Archibald (*J. Dairy Sci.*, 1957, **40**, 356—362).—Replacement of part of the hay in the ration of dairy cattle by either maize silage or hay silage had no significant effect on the total concn. (*C*) or the proportions of volatile fatty acids in the rumen. When fed as sole roughage source, maize silage increased *C* and the proportion of propionic acid and decreased the proportions of acetic, butyric and higher acids to a significantly greater extent than did hay silage. S. C. JOLLY.

Effects of combinations of feedstuffs, with and without aureomycin, on *in vitro* digestion of cellulose by rumen micro-organisms. F. J. Hanold, E. E. Bartley and F. W. Atkeson (*J. Dairy Sci.*, 1957, **40**, 369—376).—The proportion of cereals with poor-quality hay had no effect on the digestion of cellulose *in vitro* by rumen micro-organisms; protein-rich feeds were interchangeable in protein-rich rations without affecting cellulose digestion. In the presence of increasing amounts of aureomycin (0·2 to 2·0 μg. per ml. of rumen liquid), cellulose digestion in all mixtures was increasingly depressed. S. C. JOLLY.

Effect of added sucrose on the digestibility of protein and fibre by swine. C. N. Skipitaris, R. G. Warner and J. K. Loosli (*J. Amer. Sci.*, 1957, **16**, 55—61).—The apparent digestibility of the protein and, notably, of the crude fibre of barley was lowered by addition of sucrose (16%) to a pig ration. The decrease in protein digestibility was not accounted for by "fibre-bound" protein in the fæces; the latter contained increased proportions of bacterial, sol. and "residual" N. A. G. POLLARD.

Effect of potassium orotate and methionine supplementation on feed consumption and growth of dairy heifers. J. M. Wing (*J. Dairy Sci.*, 1957, **40**, 337—339).—Jersey heifers, aged 9—12 months, with well-established rumen function and fed ≯5 lb. daily of a concentrate mixture supplemented with 272 g. each of K orotate and methionine per ton, made significantly greater wt. gains (average) and required significantly less total digestible nutrient per lb. gained than did control animals. Increased activity of internal parasites occurred in the supplemented group. S. C. JOLLY.

Effects of maize treated with fungicides on the performance of fattening steers. T. W. Dawe, J. Matsushima and V. H. Arthaud (*J. Anim. Sci.*, 1957, **16**, 93—99).—Feeding maize treated with Orthocide (captan 75%) or Arasan [tetramethyl thiuram disulphide (**I**) 50%] to steers had no toxic effects but Arasan depressed food consumption and lowered the rate of gain in wt. Treated maize is preferably processed or diluted with untreated material to lower the daily intake of **I** to 125 mg. of captan to 725 mg. per 100 lb. live-wt. A. G. POLLARD.

Plasma 17-hydroxycorticosteroid levels in a dairy cow after intravenous administration of hydrocortisone. J. P. Mixner and W. G. Robertson (*J. Dairy Sci.*, 1957, **40**, 440—442).—Following rapid intravenous infusion, hydrocortisone disappeared from the plasma of a mature lactating Holstein cow in two phases. The first phase, in which hydrocortisone disappeared extremely rapidly (estimated biological half-life of ~0·7 min.), presumably corresponded to the rapid distribution of the steroid into body fluids and tissues, and the second phase, in which the disappearance was slower (half-life 9·01 min.), corresponded to the metabolism and excretion of the steroid. A vol. of distribution of 58·4% of the body wt. was calculated for this steroid. S. C. JOLLY.

Extra-period Latin-square change-over design. H. L. Lucas (*J. Dairy Sci.*, 1957, **40**, 225—239).—An extra period of observation has been added to the Latin-square change-over designs for large-animal experiments in order to estimate carry-over effects more efficiently. Treatments in the extra period are the same as in the last period of the Latin square. The statistical analysis is outlined symbolically and illustrated numerically with uniformity data. S. C. JOLLY.

Continuous drinking-recorder for small animals. M. L. Duffy and G. E. Price (*Amer. J. Psychol.*, 1956, **69**, 664—667).—A description is given of an apparatus designed to obtain direct, continuous records of drinking over prolonged periods. A photo-electric cell is utilized to follow the fluid meniscus in a stoppered vertical tube. Results are recorded on a paper cylinder. J. S. C.

Urine- and fæces-collecting apparatus for heifers and cows. J. Gorski, T. H. Blosser, F. R. Murdock, A. S. Hodgson, B. K. Soni and R. E. Erb (*J. Anim. Sci.*, 1957, **16**, 100—109).—Apparatus described permits the separate collection of urine and fæces from cows maintained under normal herd conditions. A. G. POLLARD.

Effects of various hay–concentrate ratios on nutrient utilization and production responses of dairy cows. II. Ration digestibility and excretion pattern of chromic oxide. S. Bloom, N. L. Jacobson, R. S. Allen, L. D. McGilliard and P. G. Homeyar (*J. Dairy Sci.*, 1957, **40**, 240—251).—Neither genetic ability nor feeding level significantly affected digestibility of feed; observed differences in milk production by cows on similar rations are not attributable to differences in digestibility. Fæcal excretion of Cr_2O_3 used as indicator follows a diurnal pattern, excretion being max. at 5 a.m. and 9 a.m., and min. at 5 p.m. and 9 p.m. This pattern was largely unaffected by wide variations in the physical properties of the ration and of the feeding level. S. C. JOLLY.

Improved determination of chromic oxide in cow feed and fæces. F. T. Kimura and V. L. Miller (*J. agric. Fd Chem.*, 1957, **5**, 216).—

A simple, specific and rapid colorimetric method using HNO_3–$HClO_3$ oxidation with a molybdate catalyst is described for the determination of Cr_2O_3 in feeds and fæces in amounts commonly used as indicator in digestibility experiments with dairy cattle. S. C. JOLLY.

Determination of organic acids in silage. H. G. Wiseman and H. M. Irvin (*J. agric. Fd Chem.*, 1957, **5**, 213—215).—A chromatographic method using a Celite column with internal indicator is described for the quant. separation of silage acids ranging from butyric to succinic. Single-zone collections reduce the no. of titrations to a min. with increase in accuracy. The method eliminates steam distillation or ether extraction of the acids and the need for a mechanical fraction collector. It also separates widely lactic and succinic acid. (16 references.) S. C. JOLLY.

Factors affecting the determination of plasma protein-bound iodine, using the alkaline fusion-ceric sulphate method. H. D. Lennon, jun. and J. P. Mixner (*J. Dairy Sci.*, 1957, **40**, 351—355).—Contribution (25%) to the total variance of the interaction of length and temp. of storage with each other and the animal in the determination of the protein-bound I by alkaline fusion–ceric sulphate method (Barker *et al.*, *J. clin. Invest.*, 1951, **30**, 55; Brown *et al.*, *J. clin. Endocrinol.*, 1953, **13**, 444) can be eliminated by processing and assaying plasma samples immediately after blood collection. The standard error of a single determination (0·46 μg. %) and the coeff. of variation (8·8%) can be reduced by increasing the no. of fusions on each sample. S. C. JOLLY.

Technique for *in vivo* measurement of thyroidal ^{131}I in cattle. G. W. Pipes, B. N. Premachandra and C. W. Turner (*J. Dairy Sci.*, 1957, **40**, 340—350).—Equipment consisting of a scintillation counter mounted on a flexible arm attached to a head holder that immobilizes the neck of the animal enables quantitative changes in thyroidal ^{131}I to be measured in cattle. Data are presented on the normal uptake and release of I by the thyroid; re-utilization of I from metabolized thyroid hormone is inhibited by 1 g. of thouracil per 100 lb. of body wt. The daily thyroxine secretion rate of individual animals may also be measured. S. C. JOLLY.

Preliminary fertility results from the preservation of bovine semen at room temperature. N. L. VanDemark and U. D. Sharma (*J. Dairy Sci.*, 1957, **40**, 438—439).—A method of preserving the motility and fertility of bovine spermatozoa for several days at room temp. is described. The semen is extended to approx. 25 million spermatozoa per ml. by mixing with a diluent prepared by dissolving (by heating nearly to boiling) 20·0 g. of Na citrate dihydrate, 2·1 g. of $NaHCO_3$, 0·4 g. of KCl, 3·0 g. of glucose and 3·0 g. of sulphanilamide in 1 litre of glass-distilled water, cooling, saturating with CO_2 by passing the gas through the solution for 10 min. (or until the pH is reduced to ~6·35), and then adding 1000 i.u. of penicillin and 1000 μg. of streptomycin per ml. of diluent, together with sufficient fresh egg yolk to give a final concn. of 10%. The non-return rate (75·7%) of semen extended with this diluent and stored for six to seven days at room temp. was 9% higher than that of the same semen extended with conventional yolk–citrate diluent and stored at 5° for three days. S. C. JOLLY.

Activation of bovine spermatozoa by sodium carbonate. H. E. Rickard, T. M. Ludwick, E. A. Hess and F. Ely (*J. Dairy Sci.*, 1957, **40**, 203—208).—The livability of bovine spermatozoa in yolk–citrate diluent at 37—39° was higher when the pH was adjusted with Na_2CO_3 to 7·1—7·4 than when it was 6·5—6·8; at 4—6°, livability was higher at the lower pH. The fertility of one-day-old Na_2CO_3-activated semen was similar to that of control semen; when two days old, the fertility of activated semen was significantly higher than the control. S. C. JOLLY.

Maintenance of the corpora lutea of the bovine with lactogen. Vearl R. Smith, W. H. McShan and L. E. Casida (*J. Dairy Sci.*, 1957, **40**, 443).—Lactogen does not appear to have a leutotrophic action in the intact bovine in dosages of 4 to 8 g.-equiv. or 300 to 1800 i.u. daily by subcutaneous injection starting 3 to 17 days after the beginning of œstrus. S. C. JOLLY.

Influence of ration and rumen inoculation on the growth of dairy calves. W. A. Hardison, G. A. Miller and G. C. Graf (*J. Dairy Sci.*, 1957, **40**, 363—368).—Restricting grain intake of new-born calves to 50% of the wt. of hay consumed decreased height at withers, but had no effect on wt. gains, chest or barrel circumference, roughage consumption or efficiency of feed utilization. Rumen inoculation had no effect on growth or roughage consumption. Development of reticulo-rumen was not affected by amount of roughage in the ration or by rumen inoculation. S. C. JOLLY.

Salt for cows. M. W. Galgan and M. E. Ensminger (*Washington agric. Exp. Sta.*, 1956, Bull. 569, 24 pp.).—Water consumption of pregnant cows increased significantly with salt intake (0·1—1·1 lb. of NaCl per day). Varying the salt contents of the dams had no effect on mortality, appearance or birth wt. of calves. Rumen micro-organism counts and blood serum level were similar at all salt levels. High salt intake increased the digestibility of crude protein and ether extract. The use of salt for regulating the consumption of concentrates is discussed. A. H. CORNFIELD.

Secretion of iodine in milk of dairy cows, using daily oral doses of ^{131}I. F. W. Lengemann and E. W. Swanson (*J. Dairy Sci.*, 1957, **40**, 216—224).—Conditions of prolonged exposure to radioactivity were simulated by giving daily oral doses of ^{131}I to dairy cows. Max. ^{131}I levels in milk and blood occurred on the 7th day and in the thyroid after the 10th day; 5—10% of a daily dose appeared in the milk each day. Massive daily doses of NaI reduced the radioactivity of the milk by 50% in two days and removed 66% of the radio-isotope from the thyroid in 10 days. The total stable I content of the milk, blood and thyroid were calculated to demonstrate the usefulness of this variation of the isotope-dilution method for studying trace-mineral metabolism. S. C. JOLLY.

Effect of season on secretion of iodine in milk. F. W. Lengemann, E. W. Swanson and R. A. Monroe (*J. Dairy Sci.*, 1957, **40**, 387—393).—Using ^{131}I in single and continuous doses, the metabolism of dairy cows was significantly affected by season, a stimulus which causes increases in the blood- and milk-I levels and in mammary gland secretion of I occurring with the onset of spring. Any effects of stage of lactation and production levels were obscured by this seasonal influence. S. C. JOLLY.

Protein production in the bovine. Daily production of the specific milk proteins during the lactation period. B. L. Larson and K. A. Kendall (*J. Dairy Sci.*, 1957, **40**, 377—386).—The daily production levels of α- and β-casein, α-lactalbumin and β-lactoglobulin were closely related, becoming max. about five days after parturition, but were unrelated to those of γ-casein, immune globulins and milk-serum albumin. Max. synthesis of protein in the bovine mammary gland occurs ~5 days after parturition, in contrast to that of fat, lactose and total milk vol., which is attained ~1 month after parturition. S. C. JOLLY.

Rate of machine milking of dairy cows. I. Normal variations. W. E. Stewart, L. H. Schultz and S. P. Coker (*J. Dairy Sci.*, 1957, **40**, 258—263).—Data for total milking and machine-stripping times for three breeds are recorded. S. C. JOLLY.

Effect of silage feeding on milk quality. A. M. Frens (*Proc. European Grassland Conf. Paris*, [1954], 1956, 248—251).—Factors affecting the occurrence and persistence of off-flavours in milk due to feeding certain types of silage and other sources of "taints" are indicated, together with other effects on dairy quality. Taint defects are largely prevented by the adoption of appropriate operational practices in the cow-sheds. A. G. POLLARD.

Value of lucerne hay and lucerne silage when fed as supplements to cows on pasture. M. Cole, D. M. Seath, C. A. Lassiter and J. Rust (*J. Dairy Sci.*, 1957, **40**, 252—257).—Supplementary feeding of lucerne hay or lucerne silage did not increase the milk production, total dry-matter intake or body wt. of cows on summer pasture, although it tended to increase the production of fat-corrected milk towards the end of a 16-week period. The dry matter derived from the pasture was reduced by 34% by hay feeding and 13% by silage feeding. The apparent digestibility of the ration by cows fed hay was significantly lower than that of the unsupplemented and silage-supplemented ration. S. C. JOLLY.

Grain-equivalent of immature lucerne for milk production when fed as spoilage and as silage. C. F. Huffman, S. T. Dexter, C. W. Duncan and C. A. Lassiter (*J. Dairy Sci.*, 1957, **40**, 264—270).—Replacement of part of the hay in an all-hay ration by immature lucerne spoilage (freshly harvested lucerne) or silage increased the daily production of fat-corrected milk; replacement of all the hay by silage increased production with smaller consumption of total digestible nutrients than when the all-hay ration was used. The spoilage and silage were equal in grain-equiv. for milk production on a dry-matter basis. Feeding spoilage or silage as a grain replacement decreased milk production. S. C. JOLLY.

Maintenance rations for Merino sheep. IV. Performance of adult Merino ewes fed daily and weekly at three levels of energy intake. P. K. Briggs, M. C. Franklin and G. L. McClymont (*Aust. J. agric. Res.*, 1957, **8**, 75—82).—The ewes were fed on oat grain at levels providing 4·0, 3·0 or 2·0 lb. of starch equivalent (S.E.) per sheep per week. The mean body wt. of the animals differed highly significantly at the three levels of feeding. Body wt. varied only slightly and no losses occurred when they were fed weekly with 4·0 lb. of S.E. per head. Those fed daily at this level had significantly greater body wt. at the end of the experiment. The addition of NaCl did not improve the body wt. or wool production of ewes fed

weekly on 4·0 lb. of S.E. The mean wt. of ewes given 3·0 or 2·0 lb. of S.E. declined over the first 12 and 18 weeks, respectively, and thereafter remained relatively constant. The differences were not significant between groups fed daily or weekly in respect of body wt., wool production or survival rates. Ewes given 4·0 lb. of S.E. grew significantly more wool than did those receiving 3·0 lb. of S.E. Losses were negligible in all groups except that given 2·0 lb. of S.E., in which few deaths occurred in the first 16 weeks, but totalled 17·1% in the subsequent 10 weeks. Ewes fed 2·0 lb. of S.E. consumed their rations at a significantly slower rate than did those fed 4·0 lb. of S.E. R. H. HURST.

Sodium chloride supplement of high-grain diets for fattening Merino sheep. G. L. McClymont, K. N. Wynne, P. K. Briggs and M. C. Franklin (*Aust. J. agric. Res.*, 1957, **8**, 83—90).—The addition of 0·25% NaCl to the diet resulted in increased food consumption and improved efficiency of food utilization, with significant increases of 19—58% in body-wt. gains. The unsupplemented diet contained 0·009—0·062% of Na and 0·05—0·42% of Cl. Lack of Na was the limiting factor in the diets, and the Na requirement of the sheep was >0·06% of the diet, or 0·88 g. per day. Dietary Na intake did not affect serum-Na levels, except when sheep were fed with a 50 : 50 mixture of oats and lucerne chaff, when they were significantly higher. Serum-K levels were higher in sheep receiving the low-Na diets. The two groups which had received the 75 : 25 mixture of oat grain and wheaten chaff were fed on the mixture for a further 29 days, but the group which had not received NaCl was given 0·37% of $NaHCO_3$; the response was similar to that of the group which received NaCl. R. H. HURST.

Effect of different levels and prolonged supplementation of chlortetracycline on a roughage digestion by sheep. J. L. Evans, R. B. Grainger and C. M. Thompson (*J. Anim. Sci.*, 1957, **16**, 110—117).—Addition to a high-roughage ration for lambs of chlortetracycline (or Aurofac 2A) at all levels exceeding 1 mg. per lb. of feed, significantly lowered the apparent digestibility of the crude fibre and produced a similar trend in the case of dry matter, org. matter and N-free extract. The effect tended to diminish with increasing period of administration. Loss of appetite was apparent 40—72 hr. after the first administration. A. G. POLLARD.

Utilization of urea by growing swine. V. W. Hays, G. C. Ashton, C. H. Liu, V. C. Speer and D. V. Catron (*J. Anim. Sci.*, 1957, **16**, 44—54).—With increase in the amount of urea added to the ration (0—1·25%) the feed efficiency and % of N retained diminished. Reduction in growth rate is associated with 0·6—0·7% of urea in the duct. With 2·45% of urea growth was severely restricted. Ill-effects of urea substitution were more marked in rations of lower protein content. A. G. POLLARD.

The *iso*leucine requirement of weanling swine fed at two protein levels. D. E. Becker, A. H. Jensen, S. W. Terrill, I. S. Smith and H. W. Norton (*J. Anim. Sci.*, 1957, **16**, 26—34).—Using synthetic diets containing 13·4 and 26·7% of protein, ratio of gain in wt. and feed efficiencies were optimal when the min. *iso*leucine levels were 0·46 and 0·65% respectively of the ration, i.e., 3·4 and 2·4% of the dietary protein. A. G. POLLARD.

Influence of changing the kind of fat in the diet at various weight intervals on carcass fat characteristics of swine. T. N. Blumer, E. R. Barrick, W. L. Brown, F. H. Smith and W. W. G. Smart, jun. (*J. Anim. Sci.*, 1957, **16**, 68—73).—High-fat rations (10% soya-bean oil) normally producing soft fat carcasses were fed to pigs up to varying stages of growth at which a hardening fat (coconut oil) replaced the soya-bean oil. Satisfactory hardening of carcass fat occurred when the change of dietary fat was made 30 days before the end of the fattening period, i.e., from approx. 150—250 lb. live-wt. During the fat-hardening period the progressive decrease in the I val. of the body fat was associated with diminishing proportions of linoleic, linolenic and arachidonic acid contents. A. G. POLLARD.

Relation of plasma-lipin levels to carcass-quality and rate of gain in swine. J. P. Bowland and R. Hironaka (*J. Anim. Sci.*, 1957, **16**, 62—67).—Plasma-lipin contents were significantly correlated with shoulder fat, back and loin fat and with the combined values and also with loin muscle area in 100-lb. pigs fasted for 16—18 hr. before bleeding. In pigs not so fasted the correlation was limited to back-fat thickness. Plasma-lipins afford useful supplementary information in predicting the proportion of fat and lean in carcasses of pigs at market wt. A. G. POLLARD.

Calcium and zinc in parakeratosis of swine. R. W. Luecke, J. A. Hoeffer, W. S. Brammell and D. A. Schmidt (*J. Anim. Sci.*, 1957, **16**, 3—11).—Supplementary feeding of Zn (50 p.p.m. of ration) as $ZnCO_3$ to pigs, improved growth rates and feed efficiency and completely prevented parakeratosis. High incidence of the disorder is associated with high Ca contents in low-Zn rations. Zn supplements probably increase alkaline-phosphatase activity. A. G. POLLARD.

Effects of orally administered diethylstilbœstrol and a fermentation product on growing-finishing swine. R. F. Sewell, E. P. Warren and C. C. O'Mary (*J. Anim. Sci.*, 1957, **16**, 20—25).—Addition of the stilbœstrol to a pig ration containing an antibiotic (a prep. of chlortetracycline) had no consistent effect on growth rates. The antibiotic, added to the basal ration increased growth rates, as also did additions of 6% of fermentation solubles. A. G. POLLARD.

Influence of chlortetracycline on the requirement of young pigs for dietary pantothenic acid. J. I. McKigney, H. D. Wallace and T. J. Cunha (*J. Anim. Sci.*, 1957, **16**, 35—43).—With a basal ration of ground maize, soya-bean oil-meal, minerals and vitamins [except pantothenic acid (**I**)], five-week weanling pigs showed symptoms of **I** deficiency. This was corrected by supplementary feeding of **I** or chlortetracycline. The **I** status of the animal was reflected more closely by the **I** concn. in the liver than by that in the brain, heart or kidney. Chlortetracycline (10 mg. per lb. of ration) had an apparent sparing effect on the dietary requirement of **I** for young pigs. A. G. POLLARD.

Influence of chlortetracycline supplementation of the ration on the distribution, quality and quantity of fat deposited in swine. I. Metabolic effects in relation to carcass composition. R. F. Kelly, R. W. Bray and P. H. Phillips (*J. Anim. Sci.*, 1957, **16**, 74—84).—Addition of chlortetracycline to a pig ration (15% protein) during varying periods from weaning increased the average daily gain in wt. of barrows but not of gilts. Absorptive blood-fat levels of treated pigs were significantly higher at 165 and 180 lb. that at 85 lb. live-wt., but differences in values between treated and control animals were not significant. Treated barrows showed greater thickness of back fat but lower **I**-values for back and leaf fat. A. G. POLLARD.

Seasonal fluctuations in the motility of cock semen. H. Schindler, R. Volcani and S. Weinstein (*Poultry Sci.*, 1957, **36**, 194—196).—Motility of cock semen was high during Jan.—May and low during Aug.—Dec. Motility was closely related to stage of moult. A. H. CORNFIELD.

Energy level of diet for laying hens. L. R. Berg, G. E. Bearse, R. S. Hansen, L. S. Jensen and J. McGinnis (*Washington agric. Exp. Sta.*, 1957, Tech. Bull. 22, 26 pp.).—Rate of lay was not affected by varying the metabolizable energy of the diet from 1100 to 1367 kg.-cal. per lb. of feed. The body wt. of birds was higher at the higher energy levels, although feed consumption was less. Efficiency of egg production with respect to feed consumption increased with the energy level of the diet. A. H. CORNFIELD.

Protein-bound iodine levels of the chick. H. L. Bumgardner and C. S. Shaffner (*Poultry Sci.*, 1957, **36**, 207—208).—The protein-bound-I content of the serum (S.I.) of four-week-old New Hampshire chicks averaged 1·06 μg. per 100 ml. There was no difference in S.I. between two lines of chicks differing in thyroid response to thiouracil. Chicks receiving 0·2% of thiouracil in their diet from four to six weeks of age showed no difference in S.I. from control chicks. Chicks receiving thiouracil and given injections of 40 μg. of thyroxine per day showed an increased S.I. Injections of 2—8 μg. of thyroxine per day had no effect on S.I. A. H. CORNFIELD.

***Cassia tora*, Linn., seed in poultry rations.** V. N. Murty and S. G. Iyer (*Poultry Sci.*, 1957, **36**, 210—211).—Inclusion of this legume seed at the 10% level (replacing fish meal) in the diet of male birds for 27 days had no adverse effect on health or metabolism of the birds. A. H. CORNFIELD.

Improvement in hatchability of turkey eggs by injection with water-soluble vitamin E. L. S. Jensen and J. McGinnis (*Poultry Sci.*, 1957, **36**, 212—213).—Injection of water-sol. vitamin E (D-α-tocopherol polyethylene glycol 1000 succinate, in amount ≡0·0005—0·001 g. of free D-α-tocopherol) into the eggs (albumin) of turkey hens receiving a vitamin E-deficient diet resulted in increased hatchability. Injection of ascorbic acid (0·005 g. per egg) had no effect on hatchability whilst methylene blue (0·001 g. per egg) killed the embryo. A. H. CORNFIELD.

Retarding thick white deterioration by holding shell eggs in sealed containers. O. W. Cotterill and F. Gardner (*Poultry Sci.*, 1957, **36**, 196—206).—Storing eggs at room temp. in an atm. of CO_2 prevented the deterioration of thick white (Haugh units) over four days. Candling scores indicated that the eggs were of no better quality than eggs stored in ordinary atm., under which thick white deteriorated over four days. Storage in a sealed container was more effective than in baskets in retaining interior quality (Haugh units). Excessive microbiological development which tended to develop on the shell surface under sealed conditions was prevented by including a desiccant (dried diatomaceous earth) in the container. A. H. CORNFIELD.

Powder dusting to control the sheep ked. R. E. Pfadt and G. R. DeFoliart (*J. econ. Ent.*, 1957, **50**, 190—194).—A dieldrin (1·5%)

dust was the most effective material tested. Shorn sheep treated once in the spring with this insecticide were completely free from *Melophagus ovinus*. Chlordane, toxaphene, heptachlor, lindane and rotenone were all less effective against this parasite.
A. A. MARSDEN.

Spirocyclic esters. J. R. Geigy A.-G. (B.P. 754,968, 20.5.54. Switz., 22.5.53).—Compounds useful as pesticides (miticides) comprise diesters of H_2SO_3 with spirocyclic alcohols and chloroalkanols of 2—3 C. As an example of prep., a solution of 2-chloroethyl sulphite in ether is added to a mixture of 8-tert.-*butyl*-1 : 4-*dioxa*-spiro-[4 : 5]-*decyl*-(2)-*methanol* (**I**), C_5H_5N and ether at 0—5°, then after 5 hr. at this temp., the product is diluted with water, dissolved in ether and the washed extract is distilled to give 2-*chloroethyl* 1 : 4-*dioxa*-8-tert.-*butyl*spiro-[4 : 5]-*decyl*-(2)-*methyl sulphite*, b.p. 161—163°/0·2 mm. When this (1—5) is compounded with talc (99—95 wt.%), there is obtained a dusting agent highly effective against the imagines and larvæ of red spider mites, e.g., *Paratetranychus pilosus* and *Tetranychus urticæ*, and also useful for controlling ticks. To prepare **I**, b.p. 155—159°/14 mm., technical glycerol, is heated with toluene until anhydrous, then 4-*tert.*-butyl-*cyclo*hexanone is added at the boil during 2 hr., simultaneously with conc. aq. HCl. The mixture is kept at the boil until most of the water has been removed, solvent is removed at 60° *in vacuo*, then a solution of the residue in ether is washed with aq. NaOH and distilled at 155—159°/14 mm. (yield 80%.) F. R. BASFORD.

2.—FOODS

Modern methods of analysis applicable to cereal problems. J. Hawthorn (*Cereal Sci.*, 1957, **2**, 57—64).—A review of the literature relating to the application of the following techniques in cereal analysis : vapour-phase chromatography, counter-current separation, spectrophotometry, polarography, electrophoresis, ultracentrifuging and radioactive tracers. (94 references.) J. S. C.

X-Ray studies of wheat protein complex. W. Traub, J. B. Hutchinson and D. G. H. Daniels (*Nature, Lond.*, 1957, **179**, 769—770).—Sections of the endosperm of wheat, rye, maize, groats, rice and barley, photographed on a low-angle focusing camera, all showed a spacing at ~90—100 A. which was replaced by a more intense and diffuse region of scattering at 95—115 A. when the specimens were wetted. Dry and wet specimens of wheat starch, flour and dough showed the same spacings but gluten did not, which indicates that they are associated with the starch fraction. The spacing (90—100 A.) was also observed in lipins extracted from flour with light petroleum but not in dry starch from the extracted flour and appears therefore to be largely due to a lipin component of the starch fraction. Wheat grain also showed a spacing at 47 A., not observed in any of the other cereals, appearing very early in the immature grain, diminishing in intensity on milling to flour and disappearing on wetting but reappearing weakly in dry bread. High-angle observation of protein fractions is also described. (12 references.) J. S. C.

Gluten oxidation of fatty substances. H. L. Bungenberg de Jong (*Rev. Ferment. Industr. aliment.*, 1956, **11**, 261—270).—The rôle of the fat and lecithin contents of gluten in regulating the oxidation of the protein system and the resulting effects on the strength of flours are reviewed. J. S. C.

Chromatographic investigation of composition of wheat "crude fibres." A. Horovic and A. Jevtović (*Bull. Soc. chim., Belgrade*, 1956, **21**, 277—282).—"Crude fibres" of three varieties of wheat were prepared according to Kürschner and Scharrer and the carbohydrates determined by chromatography. Results show major chemical composition differences. Hydrolysate chromatograms of all three varieties disclose the presence of glucose, indicating cellulose in all the fibres investigated. But while the crude fibre of one variety consisted mainly of cellulose, that of the second contained mainly araban, and of the third predominantly xylan. Xylan was present in the crude fibres of all three varieties of wheat, araban in two of them, and mannan in the crude fibre of one variety only. Results indicated that without a chemical composition estimation, the quant. determination alone is unsatisfactory.
A. GROCHOWSKI.

Effect of ultrasonic irradiation on extraction of vitamin B_1 from flours. C. Köpke (*Ernährungsforschung*, 1956, **1**, 667—678).—Ultrasonic irradiation has no effect on vitamin B_1, and greatly facilitates its liberation from wheat and rye flour or meal. After irradiation at 5 kv. during 50 min., followed by chemical extraction during 10 min., yields are increased by 30—40% in comparison with yields obtained by ordinary chemical extraction. Irradiation cannot be used in conjunction with the thiochrome test because it liberates substances other than vitamin B_1 which cause fluorescence in this test, but in conjunction with microbiological assay consistent results are obtained. (8 references.)

Oatmeal. N. L. Kent (*Cereal Sci.*, 1957, **2**, 83—91).—A review of the literature dealing with oatmeal, including raw material requirements, milling, presence and inactivation of lipase, measurement of lipase activity, isolation of lipase, effect of steaming on the milling of groats, kilning and flavour; nutritive value and oil, N, protein, carbohydrates, vitamin B_1, niacin, riboflavin and P contents, purity of products, cooking of porridge, keeping quality of oatmeal, and the use of antioxidants. (86 references.) J. S. C.

Optimum temperatures for enzymic reactions. M. Rothe (*Ernährungsforschung*, 1956, **1**, 619—624).—Optimum temp. for lipolytic activity in rye meal containing 20, 15 and 6% of moisture are 60, 70 and 75—90°, respectively. Satisfactory conclusions as to enzymic activity *in vivo* cannot be drawn from results of experiments made *in vitro*. (13 references.) P. S. ARUP.

Gluten proteins in rye grain. N. P. Koz'mina, V. N. Il'ina and L. A. Butman (*Dokl. Akad. Nauk SSSR*, 1956, **110**, 610—612).—The data of Cunningham, Geddes and Anderson (*Cereal Chem.*, 1955, **32**, 91) concerning the extraction of proteins by weak org. acid from rye and the conditions for the formation of rye gluten are investigated. The results confirm the ability of rye proteins to form a gluten complex and consequently their approximation to wheat proteins. The experimental data also prove the hypothesis proposed by Fellenberg (*Mitt. Lebensm. Hyg., Bern*, 1920, **10**) that the main obstacle to the formation of elastic gluten in rye dough is the presence of significant quantity of mucilaginous materials in the rye flour. P. COLLINS.

Development of starch granules in maize endosperm. R. L. Whistler and W. L. Thornburg (*J. agric. Fd Chem.*, 1957, **5**, 203—207).—Electron microscopic studies showed that starch granules are present in maize endosperm as early as four days after pollination. Granules apparently originate in amyloplasts, which often rupture as granules mature, and are largest when approx. 15 cells from the aleurone, the size decreasing towards the centre and periphery. Central cavities rarely occur in undried granules and lamellae are present in <15% of the granules. (25 references.) S. C. JOLLY.

Determination of mineral matter and admixed calcium carbonate in flour. Y. Pomeranz (*Chem. Anal.*, 1957, **46**, 2—3).—An aliquot of an aq. extract of the ashed flour is passed through a cation-exchange column, which is then eluted with water and the acidity of the eluate is determined with aq. NaOH. The % of mineral matter is calculated from a linear calibration curve of ash *vs.* acidity released on the resin. The column is finally eluted with 5N-HNO_3, the eluate and washings are adjusted to pH 12, and the Ca is titrated with 0·018M-EDTA (Na_2 salt) and murexide indicator. PO_4^{3-} does not interfere. W. J. BAKER.

Determination of chemical nature of shell of a swollen starch grain. M. Ulmann (*Kolloidzschr.*, 1957, **150**, 128—134).—Separation of the components of starch chromatographically on an alumina column was studied. Swelling agents such as aq. ammonium thiocyanate give a separation of the amylopectin and amylose but are not as good as aq. sodium salicylate. Compression of the amylopectin structure of the native grain during the swelling process leads to the formation of a grain shell. Acids do not destroy the hypothetical shell of the grain, but the amylopectin and amylose dissolve; simultaneously, by partition of higher amylopectin aggregates, the total structure is loosened so that the grain becomes more soluble. Similarly, increase in temp. does not cause the destruction of this shell but leads to damage of the amylopectin framework. R. J. MAGEE.

The volume of bread. E. Maes (*Industr. agric. aliment.*, 1957, **74**, 33—36).—Bread volume can be measured by the Jorgensen method (sum of the perimeters) or the Fomet method (displacement of rape or rice seed). The vol. of the dough can be computed from height measurements. During the first min. of fermentation, dough vol. does not change appreciably. At later stages, it increases more or less rapidly according to fermentation power and elasticity. During baking, the dough vol. increases rapidly during the first 5 min., after which it remains unchanged for a period and finally decreases slightly. On cooling, the bread vol. increases during the first 5 hr., after which it remains unchanged or may decrease slightly. J. S. C.

Aërating properties of egg and mass-production of cakes. E. A. Farrand (*Chem. & Ind.*, 1957, 500—505).—Methods of measuring the amount of air incorporated into cake mixes are described and method of mathematical interpretation of the results are suggested. Data are given on the properties of aërated mixes of egg and sugar and of egg, sugar and flour. Optimum characteristics, relative to the process used and type of cake required, for an egg–

sugar–flour sandwich, without chemical aëration, are recommended as follows: (i) average bubble size ~45 μ., (ii) geometric standard deviation of bubble size <1·75, (iii) 25 × 10^6 bubbles per g. of mix (approx.), (iv) % overrun ~175. J. S. C.

Use of a molybdenum disulphide lubricant in bakery ovens. R. A. Knight and J. B. M. Coppock (*Chem. & Ind.*, 1957, 521—523).—The use of MoS_2, in the form of a 1—2% suspension in water, oil or grease, as an oven-chain lubricant in baking ovens was investigated. Although traces of Mo accumulated on the baking sheets, contamination of the baked product was insignificant. J. S. C.

Separation of glucofructosans and fructosans by two-dimensional chromatography. Comparison of natural fructoside extract of Jerusalem artichoke tuber and dilute-acid hydrolysate of inulin. M. Quillet (*C. R. Acad. Sci., Paris*, 1957, **244,** 2177—2180). J. S. C.

Phosphoric esters and sugars in sugar-beet. E. Bougy (*Industr. agric. aliment.*, 1957, **74,** 27—32).—A study of the org. P and mineral P contents of various parts of the beet plant and of various beets of different sugar content suggests the theory that P acts as the conveyor of diose in the plant, mainly in vascular region of the stem during the first year of growth. (13 references.) J. S. C.

Separation and study of the constituents of sugar beet during growth. P. Devillers, J. Dubourg and R. Saunier (*Industr. agric. aliment.*, 1956, **73,** 431—435).—Detailed analyses of the non-sugars of beet juice in various districts of France for the 1955 campaign are tabulated and correlated with the levels of N and K fertilization. J. S. C.

Specifications in ordering a vacuum pan. J. Hamill (*Sugar, N.Y.*, 1957, **52,** No. 3, 28—29).—The factors involved in selecting a design of vacuum pan for sugar boiling are defined and their practical application is discussed. The basic operating information required is listed and the criteria given are discussed in relation to various types of vacuum pan. J. S. C.

New efficiency in a continuous diffuser: continuous diffusion at Raffinerie Tuilemontoise. A. Smet (*Industr. agric. aliment.*, 1956, **73,** 877—883; *Sugar, N.Y.*, 1957, **52,** No. 3, 30—31).—A description is given of the development of a continuous diffuser for sugar beets in which retention time of the raw juice in the diffuser is reduced by 50% without increasing the draw-off rate. Two intermeshing continuous spirals replace the single continuous spiral partition, so that each partition has a spread equal to the width of two compartments. The two spirals delimit two parallel channels in which the juice circulates at double the speed as compared with that of earlier designs. J. S. C.

Scientific [sugar] crystallization process. G. H. de Vries (*Sugar, N.Y.*, 1957, **52,** No. 4, 27—30).—Thick juice is concentrated at high temp. without crystallization (to a refractometric dry matter value of ~85°) and passes to a crystallizer where controlled stepwise decreases of pressure are applied. The concn. is preferably carried out at a temp. corresponding to the saturation point, i.e., ~105°. Seed crystals are added to the conc. juice prior to cooling. Laboratory investigations and the design of a plant for the process are described. J. S. C.

Paper chromatography in fermentation chemistry [molasses]. J. Dyr and V. Krumphanzl (*Industr. agric. aliment.*, 1957, **73,** 441—446).—Paper chromatographic methods for studying the fermentation of individual sugars, the rates of fermentation of individual yeast strains and the determination of residual sugars in the alcoholic fermentation of molasses, are described. J. S. C.

Micro-scale classification and determination of sugar using phloroglucinol reaction. N. O. Lindh (*Ark. Kem.*, 1957, **10,** 569—576).—A method for the analysis of sugars is described which is based on the dehydration of the sugars with 0·1% $FeCl_3$ solution in conc. HCl–AcOH (1 : 6) for 50 min. after which they give characteristic colours with phloroglucinol. Individual sugars have specific absorption spectra depending on the time of heating at 100°. If heating is continued for 4 min. the sugars may be classified in groups as aldohexoses, ketohexoses, pentoses, methylpentoses and uronic acids. After 40 min. each member of a group may be differentiated. C. A. Slater.

Quantitative estimation of sialic acids. I. Colorimetric method with orcinol-hydrochloric acid (Bial's) reagent. L. Svennerholm (*Ark. Kem.*, 1957, **10,** 577—596).—The optimal conditions for the quant. estimation of sialic acid with Bial's reagent has been investigated. It has been found that Cu^{++} increases the sensitivity of the reagent as much as Fe^{+++} used in the original reagent. The absorbancies of various sialic acids have been investigated and the nature of the colour formation is discussed. The data indicate that Bial's reaction is both a furfural and ketose reaction. C. A. Slater.

Chromatographic studies in kinetics of production of caramel. N. A. Ramaiah, S. K. D. Agarwal and J. K. P. Agarwal (*Proc. Indian Acad. Sci.*, 1957, **45A,** 97—104).—The kinetics of production of caramel are studied using filter paper chromatographic technique. Chromatograms of the reaction mixture (glucose heated in alkaline solutions), at different intervals during the progress of the reaction show the initial production of compounds of low mol. wt., which condense to form an intermediate compound of very high mol. wt. The latter decomposes unimolecularly to give the products composing caramel. I. Jones.

Analytical and chromatographic studies of the Maillard reaction. II. Reaction between reducing saccharides and ammonia. III. Reaction between reducing saccharides and amino-acids. IV. Reaction between reducing saccharides and amino-acids. K. Täufel, H. Iwainsky and H. Berger (*Ernährungsforschung*, 1956, **1,** 704—713, 714—718, 719—726).—II. The unsuitability of ammoniacal solvents for sugar-chromatography is confirmed. In addition to the spots due to the sugars, other spots and irregular trails point to the rapid formation (in solvents containing aq. NH_3 and/or certain alcohols and AcOH) of NH_3-aldo-hexoses or pentoses, followed by the formation of identifiable mono- and diglycosylamines. Mixed diglycosylamines can also be formed. The chromatograms are also complicated by epimeric transformations (e.g. mannose to deriv. of glucose and fructose). Most of the (synthetically prepared) glycosylamines are hydrolysed rapidly in acid, and slowly in neutral or basic solvents. Fructose forms no deriv. of the glycosylamine type, but yields the (more stable) glucosamine. (17 references.)

III. Identifiable N-glycosides (analogous to the primary addition products formed with NH_3 (see previous abstract) are formed in the combined chromatographic development of reducing mono- and disaccharides with aromatic and heterocyclic primary amines. Spots corresponding with those formed by the synthetic reference-substances are formed after heating the chromatograms at 80—90° during 8—48 min. or after suspension in the solvent-vapour during 8—48 hr. Ketoses react more slowly than aldoses. In reactions with *p*-nitroaniline, double spots appear, indicating the formation of pyranose and furanose structures. The tendency for hydrolysis of the N-glycosides increases with decreasing pH of the solvent. The anthranilic acid-N-glycosides of hexoses and pentoses are readily formed and can easily be separated by chromatographic analysis with the use of a feebly alkaline solvent containing C_5H_5N. The (widely separated) spots can be located by their fluorescence in u.v. light. (11 references.)

IV. Experiments similar to those described in the previous abstract, made with sugars and α-mono- and di-amino-acids, reveal that all the synthetic reference-N-glycosides, with the exception of the ornithine- and lysine-glycosides, are readily hydrolysed in acid, neutral or basic solvents. The last-mentioned glycosides are readily formed in combined chromatograms, and remain stable. The compounds formed in the chromatograms from the sugars and the other amino-acids by forced treatment (by heating or after prolonged suspension in the solvent-vapour) appear to be of the 1-NH_2-1-deoxy-2-ketose type. The mechanism of the reactions described in this and the two previous abstracts, and their significance with respect to the Maillard reaction are discussed. (11 references.) P. S. Arup.

Detection and separation of sugar alcohols in expressed plant juices. M. Steiner and E. Maas (*Naturwissenschaften*, 1957, **44,** 90—91).—Methods for detection and separation of sugar alcohols, involving paper chromatography and electrophoresis, are described briefly. The methods have been used for examination of 270 plant specimens, but only general results are reported. C. A. Finch.

Progress report on a regional approach to the problem of flavour evaluation of fruits and vegetables as influenced by pesticides. L. P. Ditman and A. Kramer (*J. econ. Ent.*, 1957, **50,** 213—214).—The multiple comparison or variables method was suitable for the evaluation of product flavours influenced by pesticides. The co-operation of food technologists and entomologists in evaluating these flavours is emphasized. Variation in non-pesticidal factors that affect plant vigour may influence quality and flavour of a product. A. A. Marsden.

Infra-red determination of *p*-chlorobenzyl *p*-chlorophenyl sulphide and its oxidation to its sulphone on pears. F. A. Gunther, R. C. Blinn and M. M. Barnes (*J. agric. Fd Chem.*, 1957, **5,** 198—201).—An i.r. method for the determination of *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside) and its sulphone is described. The half-life period of chlorbenside on pears was 11 days and that of the corresponding sulphone formed *in situ* was seven days. S. C. Jolly.

Determination of ethylene dibromide in fumigated fruit. B. H. Kennett and F. E. Huelin (*J. agric. Fd Chem.*, 1957, **5,** 201—203).—A method involving steam distillation and benzene extraction is

described for the determination of ethylene dibromide residues on fumigated fruit. Recoveries of 99—101% were obtained when 0·5—15 mg. of ethylene dibromide were added to 100- to 150-g. samples of a wide range of fruits. S. C. JOLLY.

Pectin conversions in peaches during cold storage. I. de Haan (*S. Afr. industr. Chem.*, 1957, **11**, 26—34).—Experimental studies of the ratio between sol. and insol. pectin (**I**) in juicy and woolly peaches of the Boland, Peregrine and Elberta varieties, and of pectin conversion during the normal ripening process, show that **I** in woolly peaches is lower than in juicy ones and that pH of the fruit-pulp is mostly higher in woolly than in juicy peaches. The significance of the data in relation to ripening and preservation procedures for the fruit is discussed. (13 references.) J. S. C.

Changes in chlorophyll during sterilization in tinplate cans. K. Heintze (*Z. Lebensmitt Untersuch.*, 1957, **105**, 379—387).—The pH of common fresh vegetables and the effect of pH on chlorophyll is discussed. The loss of colour of chlorophyll-containing goods during sterilization in the customary weak acid pH range is activated by the cleavage at the central Mg atom. The resulting phæophytin colour-fading is further changed by the presence of other metallic ions derived from solution of the preserving-can material. Tests indicated that these ions, e.g. Sn or Fe, can replace the Mg giving chlorophyll-Sn (grey) or chlorophyll-Fe (brown), distinctly different from phæophytin. The addition of a small quantity of $Ca(OH)_2$ to the sterilization water lessens the phæophytin colour change and inhibits the influence of such ions as Sn and Fe. E. M. J.

Changes in vitamin C content in raw and boiled potatoes during long-term storage. A. Scheunert and E. Thiele (*Ernährungsforschung*, 1956, **1**, 657—666).—Decreases (at first large and subsequently smaller) in the vitamin C content of the raw and boiled potatoes (eight varieties) occur during the period Oct.—April, May or June, after which (generally during May—July) sudden increases are observed. Decreases during the second half of the year are irregular and do not reach the min. values observed during spring and early summer. The summer increases are probably connected with germination phenomena. (8 references.) P. S. ARUP.

Chromatographic detection of thermal damage to potato starch. M. Ulmann and F. Schierbaum (*Ernährungsforschung*, 1956, **1**, 684—692).—Thermal damage, undetectable by inspection, caused by i.r. irradiation is revealed by Al_2O_3-chromatography of cold-water extracts of the starch. Treatment of the column with dil. aq. I + KI produces no coloration after the passage of extracts of undamaged starch, but colour-bands (brown-violet in the acid section and shades of violet or blue in the basic section) appear after the passage of extracts of irradiated starch. The width and variety of the bands increase with the intensity or duration of irradiation. Similar, but less definite results are obtained on chromatography of gelatinized starch solutions. (8 references.) P. S. ARUP.

Conversion of sugars in potato tubers. A. N. Petrova (*Dokl. Akad. Nauk SSSR*, 1956, **109**, 1005—1008).—Tubers at different stages of growth and stored under different conditions have different contents of starch and reducing substances. When the latter were determined differentially it could be seen that the differences in question were due to differences in free sugar content, and not in reducing phosphorus esters. Potato (Lorch variety) taken from three repeat croppings was tested (*a*) during flowering, (*b*) after harvesting, and (*c*) after four months' storing, part of the latter being in a shed (temp. 4°) and part in a room (18°). Tuber cuttings were washed and incubated with a solution of glucose in a strongly saline medium. The results indicated that glucose absorbed by tuber tissue is transformed into polysaccharide, and that this process is not in any way connected with hexokinase reaction, but takes some other course. Z. N. PREEV.

Concentrated apple juice. R. S. Potter (*Food Manuf.*, 1957, **32**, 158—160).—The manufacture and uses of conc. apple juice are described. J. S. C.

Critical studies of micro-determination of citric acid by the pentabromoacetone method. K. Täufel and H. Ruttloff (*Ernährungsforschung*, 1956, **1**, 693—703).—Results obtained by the colorimetric method of Pucher *et al.* are affected (due to colour-fading) by $\gtrsim 1\%$, provided that the determination is carried out in diffuse daylight at 20°, and (especially) that spectrophotometric measurements are made with a delay of $\gtrsim 15$ min. The keeping of the coloured solutions in darkness prior to spectrophotometric measurement is recommended. As a colour-stabilizer, 50% glycerol (freshly distilled) is more effective than HCN or ethylene glycol. (18 references.) P. S. ARUP.

Methanol in fruit juices, fermented drinks, alcohols and spirits. P. Françot and P. Geoffroy (*Rev. Ferment. Industr. aliment.*, 1956, **11**, 279—286).—The occurrence of varying contents of methanol in a wide variety of natural fruit juices, wines, alcohols, etc. is reviewed. J. S. C.

Beverage filtration equipment and its management. I. G. B. Beattie (*Food Manuf.*, 1957, **32**, 152—157).—A review of techniques, media and plant used in the filtration of syrups, rinse waters, wines, spirits and ciders. (32 references.) J. S. C.

Analysis of aërated waters. S. N. Mitra and R. K. Chatterji (*J. Indian chem. Soc., Industr. Edn*, 1956, **19**, 159—164).—Standardized methods of analysis of aërated waters are described, for the estimation of free CO_2, total acidity, total sugar, detection of tartaric and citric acids, free mineral acid, saccharin and dulcin, lead, synthetic colouring matter and caffeine. (11 references.) I. JONES.

Riboflavin content of wines. S. Lafourcade and E. Peynaud (*Rev. Ferment. Industr. aliment.*, 1957, **12**, 9—14).—The presence of riboflavin in wines is discussed, covering (*a*) formation in process of alcoholic fermentation of grape must; (*b*) concentration in 34 white wines of Bordeaux (35—219, mean 98 μg./l.) and in 51 red wines (50—362, mean 180 μg/l.); and (*c*) the effect of various treatments of the wines, e.g., with C or bentonite, of reducing sharply the riboflavin content, especially in red wines. (15 references.) E. M. J.

Fundamental components of wines from Rioja. I. Nareca Cortés and C. Díez de Bethencourt (*Rev. Cienc. apl.*, 1957, **11**, 23—51).—A selection of red and white wines from five successive harvests in series was studied. Analytical methods are described. Glycerol concn. ranges between 54 and 80 mmoles per l. in white wines and between 64 and 104 in red, with irregular variations of $\gtrsim 30\%$ between different years within each series. Glycerol values include 2 : 3-butylene glycol. Lactic acid concn. in both white and red wines lies between 10 and 35 mequiv. per l. Age produces an increase in lactic acid content in some cases only. Acetic acid concn. shows a very slow, gradual increase with age, in a range of 7 to 20 mequiv. per l. Total acidity: The pH of the wines is $\sim 3{\cdot}5 \pm 0{\cdot}5$, with small changes by age. That of red wines is somewhat higher than that of white. Total free acid content is in the range 50—115 mequiv. per l., with max. variations of ~ 40 mequiv. per l. from one year to another, and a slight decreasing tendency with age. The fraction of acids partially neutralized to salts has been determined by acidimetry until pH = 2·5. The concn. of these acid salts has been found varying from 2 to 20 mequiv. per l. in white wines, and from 0 to 50 in red ones. There is a slight decrease with age in both cases. H. FRIEDMANN.

Micro-estimation of boron in wines of the Aeolian Islands (Sicily). G. Bionda and E. Bruno (*Z. anal. Chem.*, 1957, **155**, 183—186).—In wine μg. quantities of B are estimated photometrically with quinalizarin reagent (20 mg. dissolved in 750 ml. of conc. H_2SO_4 and 250 ml. of glacial acetic acid added). J. H. WATON.

Formation of ethyl acetate by wine yeasts. E. Peynaud (*Industr. agric. aliment.*, 1956, **73**, 253—257).—The formation of Et acetate by the action of pure cultures of various yeasts on grape must is studied quantitatively both in aërobic and anaërobic conditions. The various yeast species are classified in groups according to their behaviour in this respect. (10 references.) J. S. C.

Enhancement of biological activity of sodium dodecyl sulphate by inorganic cations. W. McD. Armstrong (*Nature, Lond.*, 1957, **179**, 780—781).—Evidence is presented and discussed which indicates that, with certain strains of yeast, inhibition of metabolism by anionic detergents will occur only when the latter are present in the system as micellar aggregates. J. S. C.

Spectrophotometric semimicrodetermination of ergosterol in yeast. O. N. Breivik and J. L. Owades (*J. agric. Fd Chem.*, 1957, **5**, 360—363).—The method described is applicable to samples containing 5 to 100 mg. of yeast solids and 0·05 to 2·0 mg. of ergosterols. The yeast is digested with alcoholic KOH and ergosterol is extracted with a measured vol. of *n*-heptane. A portion (1 ml.) of the heptane solution is diluted with abs. ethanol (10 ml.) and absorbances are determined at 281·5 and 230 mμ. The amount of "ergosterols" is calculated from the determination at 281·5 mμ. and that of 24(28)-dehydroergosterol from the determination at 230 mμ. The difference between these two findings gives the % of ergosterol. (17 references.) E. M. J.

Brewing, malting and allied processes, 1956. R. B. Gilliland, G. A. F. Harrison and E. C. Knight (*Inst. Brewing*, 30 pp.).—A literature survey. (460 references.) J. S. C.

Applications of the sclerometer in the [brewing and malting] industry. H. Beck (*Brasserie*, 1957, **12**, 45—51).—The use of the sclerometer (cf. J.S.F.A. Abstr., 1956, ii, 145) in the control of malting, to determine the optimum conditions for obtaining barley of the highest degree of disaggregation, is further reviewed. J. S. C.

Measurement of enzymic amylolytic activity. Group A. IV. Methods depending on iodine-starch reaction. (The following of the course of starch decomposition by changes in the iodine reaction.) iii. H. Wildner and G. Wildner (*Brauwissenschaft*, 1957, **10**, 71—74: cf. J.S.F.A. Abstr., 1957, ii, 69).—A descriptive review giving examples of the application of the colorimetric method to the determination of the diastatic activity of honey, the distinction between different kinds of starch by the colour of their α-amylolytic products, and the determination of the α + β and the α-amylolytic activity of malt extract and other enzymic prep. (17 references.) P. S. ARUP.

Interpretation of malt analyses. J. Vermeylen (*Fermentatio*, 1957, No. 1, 5—29).—The various tests used in the evaluation of malt are described and discussed and a diagrammatic scheme of interpretation, based on farinosity, moisture content, the Kolbach index and Hartong's dissolution no. is developed. J. S. C.

Variations of the maltose content of roasted malts. P.-A. Durieux (*Industr. agric. aliment.*, 1956, **73**, 259—262).—The method previously described (J.S.F.A. Abstr., 1955, ii, 118) was applied to a study of the variation of maltose content in relation to the time of germination. No precise correlation between the two was found. J. S. C.

Fermentation of pale beers. K. Kärnbach (*Mschr. Brauerei, wissen. Beil.*, 1957, **10**, 31—34).—A review covering past and present statistical data for the final and racking attenuation of different types of beer, a discussion regarding the regulation of their relationship, causes for apparent yeast failure and transitions from the flocculating to the film-forming type, and technical expedients for overcoming such difficulties. (27 references.) P. S. ARUP.

Hydrocarbons of essential oil of hops. G. A. Howard and C. A. Slater (*Chem. & Ind.*, 1957, 495—496).—Gas chromatograms of the steam-volatile hydrocarbons from hops show the presence of some 20 compounds. These include myrcene, farnesene, caryophyllene, humulene, α-pinene, ocimene and limonene and a no. of unidentified monoterpenes. J. S. C.

"Purity" of micro-organisms-pure cultures. H. Hecht (*Brauwelt*, 1957, **97**, 611—617).—The relevant literature including theories and view-points is examined and discussed. In practice in laboratory or brewery the question of purity from the standpoint of genetics is considered; the difficulties encountered are dealt with. Even in unicellular cultures the occurrence of spontaneous mutations and their promotion by selection makes it difficult to maintain the characteristics of a pure culture. The conditions of the appearance of deviating constituents from those of a hereditary cell are discussed. (42 references.) E. M. J.

Nutritional evaluation of coffee including niacin bioassay. L. J. Teply and R. F. Prier (*J. agric. Fd Chem.*, 1957, **5**, 375—377).—In tests on ordinary coffee on the market, ~10 mg. of niacin per 100 g. were found by microbiological and rat assays. The niacin content increases during the roasting process (e.g., up to 43 mg. of niacin per 100 g. of coffee) possibly derived from trigonelline (*N*-methylbetaine of nicotinic acid). Values for eight B vitamins, other than niacin, are given. All except thiamine survive the roasting well and are present at low levels in the extract. Moderate levels of Ca and Fe and low levels of Na and F are present in the roasted coffee. (24 references.) E. M. J.

Application of gas-liquid chromatography to the study of volatile flavour compounds. W. G. Jennings (*J. Dairy Sci.*, 1957, **40**, 271—279).—Examination of volatile compounds in a commercial starter distillate is described. Ethyl alcohol, diacetyl, acetic acid and methyl acetate were isolated. Limitations of the method are discussed. S. C. JOLLY.

Effect of certain salts on precipitation of casein by calcium chloride and heat. C. A. Zittle, E. S. Della Monica and J. H. Custer (*J. Dairy Sci.*, 1957, **40**, 280—288).—Re-solution of Ca caseinate pptd. by $CaCl_2$ and heat occurs in the presence of NaCl and Na citrate, but not in the presence of phosphate. Pptn. of casein by $CaCl_2$ and heat was reduced by NaCl, and prevented by excess of citrate or phosphate, both of which acted by binding the Ca, a reaction which in the case of phosphate results in the formation of insol. Ca phosphate; the action of Na phosphate is more effective at pH 6·6 than at pH 6·1 because more Ca phosphate is precipitated at the higher pH. S. J. C. JOLLY.

Effect of heat and storage on the stability of aureomycin in milk, buffer and water. K. M. Shahani (*J. Dairy Sci.*, 1957, **40**, 289—296).—Complete thermal inactivation of aureomycin in milk (≯1 μg. per ml.) was effected at 160°, 185°, 200° and 210°F. in 280, 90, 50 and 30 min. respectively. Inactivation was more rapid in phosphate buffer (pH 4·7) than in milk and even more rapid in water; loss in potency was directly related to heat treatment. At 250°F. all activity was completely destroyed within 5 min. in all three media. Activity was also lost during storage at 34—38°F., but the rate was slower in heated than in unheated samples; in samples heated at 143°F. for 30 min., storage loss was least in buffer and greatest in water; in samples heated at 160°F., the loss was least in milk. Neither of these heat treatments, with or without prolonged storage, nor storage in raw milk, buffer or water completely inactivated aureomycin. S. C. JOLLY.

Certain factors affecting the concentration of active sulphydryl compounds in heated cream. I. A. Gould and P. G. Keeney (*J. Dairy Sci.*, 1957, **40**, 297—308).—Heating cream (40% fat) to 190°F. for 60 sec. produced a concn. of sulphydryl compounds (**I**) nearly as high (90%) as that produced with a 5-min. heating period; the latter produced higher concn. than did heating at 180°F. for 10 min. or 170°F. for 20 min. The concn. of **I** developed in flash-heated cream was directly related to fat content and inversely related to temp. of separation of the cream. Approx. 60—70% of heat-produced **I** was retained in cream stored for 13 weeks at 5°F., but only 10—20% was retained during nine weeks at 40°F. Addition of 1 p.p.m. of Cu, but not of Mn, before or after heating increased the loss of **I** during storage at 5°F. Oxidized flavour developed in cream containing Cu when the concn. of **I** had decreased to a level equiv. to 3 mg. of cysteine HCl per l. The commercial significance of these findings is discussed. S. C. JOLLY.

Lactose crystallization in ice cream. III. Mode of action of milk powder in preventing sandiness. T. A. Nickerson (*J. Dairy Sci.*, 1957, **40**, 309—313).—Lactose crystallization proceeds at the same rate in ice cream containing milk powder as it does in seeded ice cream. Milk powder apparently prevents the development of sandiness in ice cream by providing a multitude of crystal nuclei that serve as seeds on which form minute undetectable crystals of lactose in the partially frozen ice cream, which may be supersaturated with lactose. S. C. JOLLY.

Displacement separation of some component fatty acids of milk fat. S. Kuramoto, J. J. Jezeski and R. T. Holman (*J. Dairy Sci.*, 1957, **40**, 314—322).—Nine fatty acids of milk fat, ranging from butyric to stearic acid, have been separated by carrier displacement chromatography. Losses of the lower fatty acids due to volatilization were overcome by placing the sample on the column as a soap and then acidifying before development. S. C. JOLLY.

Naturally occurring salts in milk. I. S. Verma and H. H. Sommer (*J. Dairy Sci.*, 1957, **40**, 331—335).—Based on analyses of 15 samples of commercial milk, total amounts of Ca, Mg, P and citric acid present averaged 132·1, 10·8, 95·9 and 156·6 mg. per 100 ml. of milk respectively. The average amounts of whey(rennet-prepared)-sol. constituents were 39·2, 73·2, 37·9 and 90·4% respectively of the total amounts in the milk. Molar ratios of inorg. Ca–Mg to inorg. P in rennet curd indicate a predominance of $CaHPO_4$ rather than $Ca_3(PO_4)_2$. S. C. JOLLY.

Determination of the solids in milk by a lactometric method at 102°F. Paul D. Watson (*J. Dairy Sci.*, 1957, **40**, 394—402).—Total solids % (*T.S.*) in milk can be calculated from fat % (*F*) and lactometer reading, in degrees, at 102°F. (*L*) by use of the equation: $T.S. = 1{\cdot}33F + 273L/(L + 1000) - 0{\cdot}40$; *T.S.* of skim milk can be calculated by omitting the constant (0·40). Sources of error in lactometer readings and fat determinations are discussed, and an improved lactometer for use at 102°F. is described. The average deviation and standard error of results on 200 milk samples are indicated. S. C. JOLLY.

Insoluble scum-like materials on reconstituted whole milk powders. I. I. Litman and U. S. Ashworth (*J. Dairy Sci.*, 1957, **40**, 403—409).—Much insol. scum occurred on reconstituted spray dried whole milk powder which had been stored at 85°F., but little occurred with powder stored at 45°F. The amount of scum was related to the initial free-fat content of the powder, which decreased rapidly during storage at 85°F. but changed little at 45°F., suggesting that the defect results from the formation of a complex from the free fat and protein, with possible involvement of Ca. Fat in the scum had a higher m.p. and was more saturated than the remaining free fat. S. C. JOLLY.

Specificity of milk lipase. IV. Partition of the lipase system in milk. N. P. Tarassuk and E. N. Frankel (*J. Dairy Sci.*, 1957, **40**, 418—430).—At least two lipases occur in the plasma of warm freshly drawn cow's milk. One, the membrane lipase, is irreversibly absorbed on the fat globules as the milk is cooled, and is abundant and active in milk from cows in late lactation and on dry feed. The other, the plasma lipase, is associated with the caseinate system, and can be activated to produce lipolysis in milk. Data on the partition and specificity of the two systems are presented, and their modes of action are discussed. S. C. JOLLY.

Effect of slight proteolysis of fluid milk on wettability of the resulting dried milk. J. P. Julien and B. E. Baker (*J. Dairy Sci.*, 1957,

40, 444—445).—The wettability of whole milk powder was improved by subjecting the milk to mild enzymic proteolysis prior to drying, presumably due to changes in the surface of the protein mol. S. C. JOLLY.

Spectrographic analysis of two protein fractions of the fat-globule membrane of normal cow's milk. C. T. Herald, J. R. Brunner and S. T. Bass (*J. Dairy Sci.*, 1957, **40,** 446).—Many of the trace elements reported in whole milk are concentrated on the fat-globule membrane, possibly as constituents of various enzymes and metabolic complexes. S. C. JOLLY.

Influence of temperature on the generation time of bacteria commonly found in milk. W. Yotis and R. Teodoro (*J. Dairy Sci.*, 1957, **24,** 27—32).—The generation times of *Salmonella typhosa, Shigella dysenteriæ* (both 50—26 min.), *Streptococcus hæmolyticus, Micrococcus pyogenes aureus* (both 37—23 min.), *Escherichia coli, Alicaligenes fæcalis, Bacillus subtilis* (all 41—16 min.) and *Lactobacillus acidophilus* (52—125 min.) in milk at 4—60° have been determined. At 4° none of the micro-organisms multiplied during 6 hr. The optimum growth temp. for all the micro-organisms occurred between 5° and 45°, above which temp. growth slowed until at 60° viability was apparently lost. S. C. JOLLY.

Factors affecting the freezing point of milk. I. Sato, C. L. Hankinson, I. A. Gould and T. V. Armstrong (*J. Dairy Sci.*, 1957, **40,** 410—417).—The average f.p. of 59 authentic milks from herds and individual cows was −0·546° (range −0·533° to −0·560°); the difference from the standard of −0·550° established by A.O.A.C. as the normal f.p. is equiv. to 0·7% of added water. The average f.p. of 108 milks received at dairy plants and fo 53 milks from retail outlets were −0·538° (range −0·450° to −0·550°) and −0·530° (range −0·437° to −0·549°) respectively, and equiv. to 2·1 and 3·6% of added water respectively. Processing operations when properly performed had no effect on f.p., but careless practices in the use of water raise the f.p. of processed milk. A max. f.p. of −0·530° is suggested for unadulterated milk. S. C. JOLLY.

Lactose–chloride contributions to the freezing-point depression of milk. II. Examination of partial contributions over the full lactation periods of two cows. E. R. Cole, J. B. Douglas and M. Mead (*J. Dairy Res.*, 1957, **24,** 33—42).—For Jersey milk, 80% of the total f.p. depression is due to the lactose and Cl′ contents (on a fat- and protein-free basis); for Friesian milk, the contribution of these constituents was approx. 75%. Linear relations existed between the partial f.p. depressions due to each of these constituents in both milks; the relations differed considerably but not significantly in each milk. Formulæ for calculating one of these constituents from the f.p. and determined amount of the other constituent need to be treated with caution. The f.p. of both milks remained relatively constant throughout a lactation, although slight but consistent differences existed between the milks. No seasonal changes occurred, but changes in the f.p. of one milk were accompanied by corresponding changes in that of the other. S. C. JOLLY.

Microscopical appearance of fat on the milk surface as affected by application of surface-active substances to the surface. N. King (*J. Dairy Res.*, 1957, **24,** 43—50).—When applied to the surface of whole milk, methanol and ethanol cause fat globules, clumps, lenses and patches to rise to the surface to a moderate extent; other members of the monohydric aliphatic alcohol series up to decanol are strongly active. The butanols were approx. equally active. The rising of fat under the influence of members between ethanol and pentanol is promoted by ageing the milk. Higher alcohols, beginning with propanol, bring fat to the surface more effectively than does mechanical disturbance of the milk surface. Glycerol is almost inactive, but monobutyrin has a strong raising action. In contrast, tributyrin, Spans and Tweens (sorbitan esters and polyoxyethylene sorbitan esters of higher fatty acids respectively), cetrimonium chloride and cetylpyridinium chloride sweep the milk surface clear of fat. S. C. JOLLY.

Calorimetric study of milk, cream and fat in cream. L. W. Phipps (*J. Dairy Res.*, 1957, **24,** 51—67).—The thermal behaviour, particularly sp. heat–temp. relations, of whole and separated milk, cream (15% fat) and milk fat in the temp. range 0° to 50° is reported. The melting and solidifying behaviour of milk fat was deduced from the effects of different heat treatments on the sp. heat curves of the fat. The degree of dispersion of the fat in cream was an important factor. S. C. JOLLY.

Rapid method for estimating the size distribution of fat globules in cream. R. M. Dolby (*J. Dairy Res.*, 1957, **24,** 68—76).—The proportion of fat present in cream as small globules ($\gtrless 1\ \mu$.) is estimated from the proportion of the total fat remaining in the serum when the sample, diluted to 10% of fat, is centrifuged at 3000 r.p.m. (equiv. to 2000 *g*) for 30 min. at 60°. The proportion of large globules ($\lessgtr 7$—8μ.) is estimated from the proportion of total fat which rises 1 cm. in 60 min. when the diluted sample is held at 60° in a modified Andreasen particle-size apparatus. S. C. JOLLY.

Effect of pH on the extent of splitting or clumping of fat globules caused by agitation of hot cream. R. M. Dolby (*J. Dairy Res.*, 1957, **24,** 77—84).—In hot cream agitated by Vacreator treatment, vigorous mechanical stirring or simple aëration, the splitting of fat globules was maximal and clumping minimal at pH 8. As pH was lowered towards pH 6, splitting decreased and clumping increased. Clumping during single-state homogenization also increased as pH was lowered. Practical applications of these observations are suggested. S. C. JOLLY.

Factors influencing the vitamin content of milk fat. II. Influence of botanical composition of the pasture. N. A. Worker and W. A. McGillivray. **III. Seasonal changes in vitamin A and carotenoid content of blood plasma and milk fat of cows on pasture. IV. Source of milk-fat vitamin A and carotene.** W. A. McGillivray. **V. Changes in vitamin A and carotenoid content of blood plasma of cows and heifers near parturition in relation to secretion of these substances in milk fat.** S. Y. Thompson and W. A. McGillivray (*J. Dairy Res.*, 1957, **24,** 85—94, 95—101, 102—107, 108—114).—II. The effect of clover intake on the vitamin-A potency of milk fat from Jersey cows in New Zealand is reported. Diets high in white clover (containing ~0·03% of CN′) tended to depress total potency, I val., and oleic acid and tocopherol contents; diets low in clover reversed these effects. Red clover had no such effects, which may be due to the low oleic acid and tocopherol contents and high HCN content of white clover compared with grass, or to a factor(s) associated with the stage of development of the pasture. Drenching cows with thiocyanate, the probable detoxication product of HCN in the ruminant, had no effect on levels of vitamin-A alcohol and ester, carotene and xanthophyll in the blood and milk fat.

III. The seasonal trends in vitamin A and carotene contents of N.Z. milk fat and commercial butters is a reflection of corresponding changes in the levels of these substances in the blood plasma of the cows. The decreasing levels of carotene, xanthophyll and vitamin A ester in the blood during summer is consistent with a decreased absorption or utilization of carotenoids. Throughout the year, vitamin A is present in the fat mainly as ester; the absence of increase in the alcohol form suggests that hepatic-vitamin-A reserves are not being mobilized.

IV. The level of vitamin-A ester in milk fat reflects the level in the plasma of the cows, but, irrespective of the immediate carotene and vitamin-A intake or hepatic reserves, some of the milk-fat ester is derived apparently from vitamin A of other than immediate dietary origin. Most of the plasma carotene probably contributes little to the milk-fat-carotene level, which is derived mainly from carotene of immediate dietary origin, which, during transport to storage organs, is associated with dietary fat and vitamin A-ester in the chylomicrons.

V. Despite high carotene intakes prior to calving, plasma-vitamin-A and -carotene levels decreased about calving time in cows and, to a lesser extent, in heifers; the decreases for cows were approx. the same as those reported in U.K. and U.S.A. Although the concn. of vitamin A and levels of carotenoids were higher in heifer's colostrum than in cow's, the total daily secretion of these substances by cows was much greater during the first few days of lactation. The decrease in plasma components is probably related to the extra drain of colostrum synthesis rather than to hormone changes during parturition. S. C. JOLLY.

Properties and composition of colostrum from Egyptian buffaloes and cows. A. M. El Negoumy (*J. Dairy Res.*, 1957, **24,** 115—120).—Buffaloes' colostrum (*B*) is richer in total solids, lactose, total N, globulin N and proteose–peptone N than is cows' colostrum (*C*); the fat content of *B* varies more widely than does that of *C*, and is lower than that of normal buffaloes' milk, while that of *C* is higher than normal cows' milk. During the transition period from *B* to milk, the sp. gr., acidity and Cl′ content of buffaloes' mammary secretion decrease and become normal by the 5th milking; pH increases gradually and becomes normal sooner. Total solids and N fractions are maximal at the 1st and 2nd milkings and then decrease rapidly to normal; lactose changes are slight after the 2nd milking. Buffaloes' mammary secretion is comparable in composition to normal buffaloes' milk and suitable for human consumption from 5—7 days after parturition. S. C. JOLLY.

Protein sulphur. VI. Combined forms of sulphur in milk. R. Springer and R. Woller (*Z. LebensmittUntersuch.*, 1957, **105,** 387—390).—Analyses of sulphur in six compounds obtained after hydrolysis of milk by HCl or HI are presented. The S-content of milk amounts to about 50 mg./100 ml. of which 60% of the total S or 75% of the protein-S exists as the S component of methionine. The formation of traces of H_2S during heating of milk is discussed. (13 references.) E. M. J.

Rennet and its action on milk casein. XI. Terminal amino-groups of α-casein before and after rennet curdling. H. Wissmann and H. Nitschmann (*Helv. chim. Acta*, 1957, **40**, 356—363).—In native α-casein the terminal amino-acids are found (using Sanger's DNP method) to be lysine (**I**) and arginine (**II**). After treatment with cryst. rennin, both **I** and **II** can still be detected (**I** in smaller quantities), and phenylalanine also appears. In addition to chromatography, a new method (determination of DNP-arginine optically, using the Sakaguchi colour reaction, in the mixture of DNP-amino-acids) is used to determine *N*-terminal arginine. The results suggest that the primary reaction in the rennet curdling of milk is a specific limited proteolysis, and lead to the conclusion that α-casein cannot be a homogeneous protein and that only a fraction of it is altered in this enzymic reaction. (22 references.) M. DAVIS.

Influence of cottage cheese starter organisms on strength of curd at time of cutting. B. Heinemann (*J. Dairy Sci.*, 1957, **40**, 437 438).—The starter used in the manufacture of cottage cheese significantly affects the firmness of the curd at the time of cutting. The differences are probably due to variations in the proteolytic activities of micro-organisms constituting the culture. S. C. JOLLY.

Determination of the total volatile fatty acids in cheese. A. J. G. Barnett and G. A. Tawab (*J. Dairy Res.*, 1956, **23**, 277—282).—A rapid and accurate method, based on Soxhlet extraction and micro-distillation, is described for determining the volatile fatty acids in cheese. Results agree well with those given by lengthier established methods. S. C. JOLLY.

Influence of microbiological populations on the shelf-life of creamed cottage cheese. L. G. Harmon and C. K. Smith (*Mich. agric. Exp. Sta. Quart. Bull.*, 1956, **38**, 368—384).—Microbiological data for cottage and factory cheeses are compared ; the total population was much lower in the latter class. In cottage cheeses pH <5·0 favours prolonged shelf-life ; high pH was associated with increased proteolysis, as measured by the free tryptophan content. The latter value in fresh cheese was not a good index of keeping quality. Fairly good correlation was established between the average initial coliform and lipolytic populations and keeping quality. There was little correlation between shelf-life and organoleptic quality in fresh cheeses. A. G. POLLARD.

General bacterial counts of meat of different kinds. H. Baumgärtner (*Ernährungsforschung*, 1956, **1**, 651—656).—Data obtained by the author's method demonstrate seasonal differences between the bacterial counts, increases after keeping during 1—2 days at room temp. in comparison with increases (or decreases) during cold storage, and decreases after boiling, ordinary roasting, or roasting by means of i.r. radiation. Roasting by the latter method gives by far the greatest decreases in the counts. P. S. ARUP.

Preservation of fowls by refrigeration. C. Paci (*Rev. int. Agric. Milano*, 1956, **1**, (8–9), 32—39).—The relative merits and defects of refrigeration and congealment as methods for preserving fowls are discussed ; in practice, congealment is shown to have the economic advantage. Fowls are best preserved by rapid congealment, followed by storage at −18 to −20° ; success mainly depends upon packing and treatment to avoid dehydration. C. A. FINCH.

Characterization of volatile nitrogen and volatile sulphur fractions of cooked chicken and their relation to flavour. E. L. Pippen and E. J. Eyring (*Food Technol.*, 1957, **11**, 53—56).—Reconstitution of the concentrate from distilled chicken broth, with distilled water or broth distillate, indicated that the latter gave detectable chicken flavour. Comparison of flavour of concentrate reconstituted with unfractionated distillate (N containing as NH_3) with that reconstituted with N-free distillate indicated significantly higher ranking of the latter. The volatile flavour is therefore associated with the neutral or acidic fractions of the distillate. Additional factors to that of the sulphide contribution to meat flavour are involved in the composite mixture of chicken flavour. (15 references.) E. M. J.

Three types of gelatin. W. M. Ames (*J. Sci. Food Agric.*, 1957, **8**, 169—173).—Gelatin from one precursor was prepared by three methods (*a*) an exhaustive alkaline treatment of collagen, (*b*) rapid conversion in the presence of a small amount of acid, and (*c*) exhaustive pretreatment with acid, this last giving a gelatin with an isoelectric point approaching pH 4·8 and similar to that obtained when exhaustive treatment with alkali was used. Variations in the N-content of collagen and gelatin result from the presence of non-nitrogenous impurity. Factors affecting the transformation of collagen to gelatin are discussed. (10 references.) E. M. J.

Effect of low temperature, sodium nitrite, sodium chloride and formaldehyde on the apyrase system of the muscular tissue. W. Partmann (*Food Res.*, 1957, **22**, 51—62).—Study of the apyrase system which hydrolyses adenosine triphosphate (ATP) revealed a close correlation between contraction and ATP splitting. The methods for measuring enzyme activity and contractility could be used to study the effects of adjuncts and freezer storage on food. With white carp muscle, $NaNO_2$ was found not to be a specific inhibitor of the apyrase system. Between pH 6 and 7 the $NaNO_2$ effect was independent of pH and primarily subject to Na-ion concn. The effect of NaCl corresponds in magnitude to that of the nitrite. Formaldehyde (0·1% concn. at pH 7) inactivated completely the muscular apyrase system. The contractility of muscle fibres declined sharply with increased concentration of the tested adjuncts, then rose slowly to zero, at the concentration which inhibited completely the apyrase activity. After storage at −3·5° a decrease of the apyrase activity in muscle brei of fresh water fish was observed. Disorganization of the fine structure of muscle fibres is correlated with the loss of contractility and decrease of apyrase activity. The loss of contractility can thus be used as a test for an inhibitive effect of food adjuncts on the apyrase system. (40 references.) E. M. J.

Recently-discovered constituents of animal fats. L. Hartman (*J. Amer. Oil Chem. Soc.*, 1957, **34**, 129—131).—The literature relating to the presence in animal fats of branched-chain fatty acids, straight-chain odd-C-numbered fatty acids, and *trans*-unsaturated acid in the fats of ruminants and non-ruminants is surveyed, and the mechanism of formation is considered. Whereas depot fats of ruminants contain substantial amounts of *trans*-unsaturated acids, non-ruminants contain little or none ; it seems probable that bacterial activity in the rumen is responsible, at least in part, for the production of the above three types of fatty acid. G. HELMS.

Animal fats. VII. Component acids of fats from mouse, porcupine and rabbit. VIII. Component acids of flamingo fat and antelope fat. IX. Relation between composition and iodine value. F. D. Gunstone and W. C. Russell (*J. Sci. Food Agric.*, 1957, **8**, 283—286, 287—290, 290—301).—VII. Continuing the work on rodent fats (*Biochem. J.*, 1955, **59**, 455) analytical data on characteristics and component acids of mouse, porcupine and rabbit fats are presented. The total content of saturated acids generally lies within the range of 30 to 40% and of unsaturated acids, 60 to 70%. Porcupine fat differs and is characterized by a high content of saturated acids (53%) and a low content of oleic acid (27%).

VIII. Analytical data are given. Flamingo fat fits closely into the general pattern of the characteristic features of bird fat composition (*Biochem. J.*, 1954, **57**, 459). Antelope fat differs from the other ruminant fats in many respects, particularly in its high I val. and low contents of palmitic and stearic acids.

IX. Consideration of the composition of animal fats (39 reported analyses from 30 types of animals, I val. 31—96) suggests an empirical relation between the I val. and the amount of each component acid. The relation is expressed mathematically. Most animal fats which contain little or no C_{20-22}-acids consist, apart from small quantities of myristic acid (1—5%) and hexadecenoic acid (2—7%), of palmitic, stearic, oleic and polyethenoid C_{18}-acids. The amount of palmitic acid is fairly constant (24—30%) and changes in I val. are reflected in the changing proportions of the C_{18}-acids. The changes in the proportion of saturated, mono- and poly-ethenoid C_{18}-acids in animal fats of I val. 90 falling to 30 are parallel to changes which occur during selective hydrogenation of mixtures of stearate, oleate and linoleate. 'Stearic-rich' depot fats are produced only by ruminants, quasi-ruminants and ruminant-feeding animals. (14 references.) E. M. J.

Isolation of *n*-heptadecanoic acid (margaric acid) and (+)-14-methylhexadecanoic acid from hydrogenated ox perinephric fat. R. P. Hansen, F. B. Shorland and N. J. Cooke (*J. Sci. Food Agric.*, 1957, **8**, 331—333).—Recent work on the fatty acid composition of natural fats is discussed. In hydrogenated ox perinephric fat it is estimated that *n*-heptadecanoic acid and (+)-14-methylhexadecanoic acid constitute ~0·4% and 0·3% respectively of the total fatty acids. (23 references.) E. M. J.

Directed interesterification of lard. C. Placek and G. W. Holman (*Industr. Engng Chem.*, 1957, **49**, 162—169).—Directed interesterification of lard improves the plastic range. The chemistry of the reaction is described. The process is illustrated by a flow sheet. Melted lard is mixed with finely-divided Na-K alloy catalyst and then rapidly cooled to induce the crystallization of trisaturated glycerides. Further interesterification takes place in the liquid phase, causing additional crystallization. The plant, operating technology control and safety are described. (34 references). O. M. WHITTON.

Rancidity of lard. II. Thiobarbituric acid test. A. Vargas Romero and R. Gutiérrez González-Quijano (*Grasas y Aceites*, 1956, **7**, 229—233).—The thiobarbituric acid test for rancidity has been applied to lard. The effect of temp. and time of stirring and heating

in carrying out the test have been examined and the colour produced is found to obey the Beer–Lambert law. Both after accelerated and normal storage the test gives results similar to those from the peroxide value and in conformity with organoleptic examination. L. A. O'NEILL.

Proposals for uniform examination and evaluation of lard with special reference to its keeping quality. K. Täufel and K. Barthel (*Ernährungsforschung*, 1956, **1**, 638—650).—The proposals include a scheme for organoleptic evaluation, and directions for carrying out the following determinations, and evaluation of the results: free fatty acids, protein-containing tissue, water, free aldehyde, and peroxide value. Descriptions are also given of the acid-indicator test (cf. *ibid.*, 142) and the filter-paper test, a slightly modified form of the Täufel–Vogel test (cf. *Anal. Abstr.*, 1954, **3**, 560). P. S. ARUP.

Serum cholesterol in populations differing in fat intake: animal fat versus olive oil. J. Brožek, R. Buzina, A. Horvat, F. Mikič and M. Zebec (*Bull Sci. Acad. Yougosl.*, 1956, **3**, 46—47).—A statistical analysis is made of the cholesterol contents of the blood of males in two areas, one of which was fed predominantly on diets rich in animal fat and the other predominantly on vegetable oil diets (olive oil). The result showed a figure at the age of 40 of 239·7 mg./100 ml. for the first area and 201·9 mg./100 ml. for the second. The investigation is part of a series of studies of the relation between diet and coronary heart disease. J. S. C.

Characteristics of vegetable fats and oils. II. C. Carola (*Olii min.*, 1957, **34**, 54—68).—The fatty acid composition and the chemical and physical characteristics of the following oils or butters are summarized: babassu kernel, safflower, wheat, tung, shinia nut, almond, niger seed, walnut, oiticica, perilla, rice, stillingia, teaseed, cacao, Japan tallow, illipé and shea. (61 references.) L. A. O'NEILL.

Determination of 2 : 6-di*tert.*-butyl-*p*-cresol in edible fats by ultraviolet spectrophotometry. M. A. Phillips and R. D. Hinkel (*J. agric. Fd Chem.*, 1957, **5**, 379—384).—A method is described for determining 20 to 200 p.p.m. (0·002—0·02%) of 2 : 6-di*tert.*-butyl-*p*-cresol (**I**) when used as an antioxidant in lard, in presence of other allowable preservatives, including butylated hydroxyanisole, nordihydroguaiaretic acid, propyl gallate, citric acid, mono*iso*propyl citrate and H_3PO_4. The sample of lard is dissolved in *cyclo*hexane and passed through a chromatographic column packed with 100-mesh silicic acid. The **I** is selectively removed with successive portions of *cyclo*hexane passed through the column; the filtrates are collected and examined by u.v. spectrophotometry at 284 mμ. Analyses of five different commercial lards gave recoveries within the range 99 ± 3%, and from other samples recoveries were consistently >93%. E. M. J.

Antioxidant action of ascorbic acid in edible fats. G. Cerutti (*Olii min.*, 1957, **34**, 41—45).—Ascorbic acid or its palmitic ester, at a concn. of ≮200 mg./kg., showed powerful antioxidant action in hydrogenated almond oil, cacao butter and cow butter, as judged by organoleptic and peroxide tests. L. A. O'NEILL.

Plasticising fats in the laboratory. A. H. Steffen and R. J. Vander Wal (*J. Amer. Oil Chem., Soc.* 1957, **34**, 159—161).—The plasticising of fats prior to evaluation for shortening quality by the pound-cake-vol. baking test can be accomplished with the use of a Hobart Kitchen Aid Mixer (Model K-4-B) immersed in a water-bath (temp. 10°). Detailed working directions are given for plasticising and subsequent tempering which give reproducible values for pound-cake vol., in good agreement with values obtained for factory-plasticised samples of the same fats. P. S. ARUP.

Identification of some marine oil constituents by chromatography. M. F. Sorrels and R. Reiser (*J. Amer. Oil Chem. Soc.*, 1957, **34**, 131—134).—The method of Dieckert and Reiser for the separation and identification of μg. quantities of lipins on glass-fibre filter paper impregnated with silicic acid has been applied to marine oils. Details of the technique are given. Tabulated data show (1) R_F values for marine oil lipins, (2) results of analysis of an artificial mixture of reference compounds and (3) results on three marine oils. The scheme of separation and identification developed is a simple method for qual. determination; irregularities in the density of the glass-fibre paper prevent accurate quant. assay. G. HELMS.

Component fatty acids and glycerides of shark (Pristis) liver oil. G. G. Kamath and N. G. Magar (*J. Indian chem. Soc., Industr. Edn*, 1956, **19**, 171—176).—Low-temp. crystallization, methyl ester fractionation and alkali-isomerization methods are used for the study of component fatty acids and glycerides of Pristis liver oil. The fatty acids consist of 26·9% saturated and 73·1% unsaturated acids. The glycerides appear to be distributed according to the random pattern as observed by the crystallization method. The results are not in agreement with those of Kartha's oxidation method (*J. Amer. Oil Chem. Soc.*, 1953, **30**, 280, 326.) I. JONES.

Component fatty acids and glycerides of shark (*Galeocerdo rayneri*) liver oil. G. G. Kamath and N. G. Magar (*J. Indian chem. Soc., Industr. Edn*, 1956, **19**, 201—205).—The component fatty acids and glycerides of *Galeocerdo rayneri* liver oil are determined by the low-temp. crystallization, methyl ester fractionation and alkali-isomerization methods. The fatty acids consist of 35·6% saturated and 64·4% unsaturated acids. The saturated acids are mainly palmitic and stearic in the proportion of 2 : 1. C_{16} (−2H) 8·53%, C_{18} (−2·8H) 30·94%, C_{20} (−3·6H) 9·35% and C_{22} (−3·8H) 11·51% constitute the unsaturated acids. The glycerides are distributed according to the even pattern and are mainly of the mixed type. Results of crystallization and oxidation methods are not in agreement. I. JONES.

Application of conversion factors for determination of vitamin A in fish liver oils. S. Balasundaram, H. R. Cama, P. R. Sundaresan and T. N. R. Varma (*J. sci. industr. Res.*, 1957, **16C**, 8—11).—It has been found that oxidation of vitamin A in fish liver oils does not alter the $E^{1\%}_{1\,cm.}$ value at 290 mμ. The vitamin-A potency of stored oil determined in this way may, therefore, be used to assess the original potency of the oil. C. A. SLATER.

Fluorescence test in paper chromatography of aliphatic acids. M. Pesez and J. Ferrero (*Bull. Soc. Chim. biol.*, 1957, **39**, 221—222).—The sol. Zn oxinate formed from solutions of a Zn salt and hydroxyquinoline, is precipitated by NH_4 salts and exhibits a yellow-green fluorescence in Wood light. This reaction has been successfully applied to the chromatographic characterization of fatty acids using an alcohol (butanol) saturated with NH_3 as solvent. E. M. J.

Structure of major component glyceride of cocoa butter, and of major oleodisaturated glyceride of lard. D. Chapman, A. Crossley and A. C. Davies (*J. chem. Soc.*, 1957, 1502—1509).—From cooling curves and *X*-ray and i.r. analyses, it is concluded that the major glyceride of cocoa butter is 2-oleopalmitostearin. Similar observations on the disaturated glycerides of lard show that the major component is 2-palmito-oleosterain. (22 references.) M. DAVIS.

Re-evaluation of biological potency of β-carotene. H. M. Barnett and H. M. Espoy (*Food Res.*, 1957, **22**, 15—24).—The biological activity of carotene, usually included as part of the vitamin-A potency in the determination of vitamin-A activity of margarine by the official U.S.P. biological assay method, was examined in terms of this method. Pure all-*trans* β-carotene has a biological activity of 2,200,000 to 2,500,000 U.S.P. units per g. in terms of the U.S.P. reference vitamin-A acetate standard. On the basis of these results and earlier data, the purity of the International Provitamin A prep., or that it is indicative of the biological activity of pure *trans* β-carotene is questioned. A re-evaluation of the accepted vitamin-A potency of β-carotene is warranted. (24 references.) E. M. J.

Vitamin values of human foods used in Hawaii. C. D. Miller, B. Brenthoover, N. Sakiguchi, H. Denning and A. Bauer (*Hawaii agric. Exp. Sta.*, 1956, Tech. Bull. 30, 94 pp.).—Carotene, vitamin A, thiamine, riboflavin, niacin and ascorbic acid contents of the foods produced in Hawaii are presented. Effects of variety upon vitamin contents of some fruits, changes in ascorbic acid of some fruits during ripening and cooking, and effect of salt-pickling and cooking upon the vitamin content of some vegetables are also recorded. A. H. CORNFIELD.

Stability of certain B vitamins exposed to ethylene oxide in the presence of choline chloride. H. Bakerman, M. Romine, J. A. Schricker, S. M. Takahashi and O. Mickelsen (*J. agric. Food Chem.*, 1956, **4**, 956—959).—Destruction of practically all the thiamine and a large proportion of the riboflavin, pyridoxine, nicotinic acid and folic acid occurred when the crystalline B vitamins, alone and in combination, dispersed in a maize starch–choline chloride mixture were exposed to ethylene oxide vapour (**I**); pantothenic acid, biotin and vitamin B_{12} were little affected, but co-carboxylase was destroyed. The increase in pH that occurred in the presence of choline chloride may be responsible in part for the destruction of thiamine. Approx. 40% of the thiamine in a stock diet was destroyed by **I**; panthothenic acid, biotin and vitamin B_{12} were unaffected. (14 references.) S. C. JOLLY.

Influence of addition of certain amino-acids and vitamin B_{12} to proteins in enriched milled wheat flour on growth, protein efficiency and liver fat deposition. B. Sure (*J. agric. Fd Chem.*, 1957, **5**, 373—377).—In the study of protein nutrition and amino-acid enrichment of cereal foods, the effects of increasing concn. of lysine, threonine, valine and vitamin B_{12} to the proteins in milled wheat flour fed at an 8% level, were observed in rat tests. The optimum gains in body wt. and protein efficiency were obtained by supplementation with 0·4% of L-lysine, 0·2% of DL-threonine, 0·4% of DL-methionine and vitamin B_{12} 0·1 μg. per day. Analytical data on 22 rations including % of liver fat are presented. (15 references.) E. M. J.

Comparison of chemical methods for evaluation of ascorbic acid in foodstuffs. E. B. Barrera (*An. Soc. Biol. Bogotá*, 1956, **7**, 152—168).—Titration with indophenol, colorimetric determination with indophenol and xylene, the methods of Roe (*J. biol. Chem.*, 1943, **147**, 399; 1944, **152**, 511) together with a modification of the later method of Roe, are compared. Oxalic acid is recommended for the extraction and stabilization of ascorbic acid. The Roe method, modified to allow, after osazone formation, for interfering substances, gives results very similar to those based in oxidation of the ascorbic acid by indophenol. L. G. L. UNSTEAD-JOSS.

Changes in light reflectance and ascorbic acid content of foods during frozen storage. N. B. Guerrant (*J. agric. Fd Chem.*, 1957, **5**, 207—212).—The reflectance and reduced ascorbic acid content of typical frozen fruits and vegetables stored for 12 months at 10°, 0° and −20°F. were affected by storage temp., changes being greatest at the highest temp. Changes in reflectance were paralleled by changes in ascorbic acid contents. S. C. JOLLY.

Vitamin-E deficiency. III. Determination of tissue tocopherol with phosphomolybdic acid. H. Rosenkrantz (*J. biol. Chem.*, 1957, **224**, 165—174).—A sensitive, micro-colorimetric method is described for determination of the tocopherols. It is based on the phosphomolybdic acid reagent of Nair and Magar (*Indian J. med. Res.*, 1954, **42**, 557), and is highly sp. for α-tocopherol. The reaction with the reagent is effected at 100° for 2 min. (sensitivity is improved at this high temp.) and the optical density of the resulting yellow-green colour is measured at 700 mμ. Determination of the rates of reaction distinguishes between α-, β- or γ-, δ-, and ζ-tocopherols. The method can also be used to detect the corresponding quinols on paper chromatograms. The limitations of the method are discussed; its application to blood and certain tissues is difficult. Fatty acids, glycerol and cholesterol do not interfere with the reagent or determination. (11 references.) J. N. ASHLEY.

Chemical effects of ionizing radiation on proteins. I. Effect of γ-radiation on amino-acid content of insulin. M. P. Drake, J. W. Giffee, D. A. Johnson and V. L. Koenig (*J. Amer. chem. Soc.*, 1957, **79**, 1395—1401).—Insulin (**I**) solutions (1%) of pH 8·5 and 3·0 are subjected to 0, 10, 20 and 40 million rep γ-radiation doses. Cystine, tyrosine, phenylalanine (**II**), proline and histidine are very radio-sensitive. Leucine, valine, lysine and arginine are significantly destroyed at the high irradiation-dose level. The *N*-terminal amino-acids of **I** (glycine and **II**) are deaminated. Cysteic acid is identified in the hydrolysates of irradiated **I**, for which an increase in mol. size is reported. The study was undertaken in connexion with the sterilization of food proteins by ionizing radiation. (132 references.) M. DAVIS.

Determination of glycoproteins and glucose by the diphenylamine reaction. L. A. Abreu, R. R. Abreu and G. G. Villela (*Rev. bras. Biol.*, 1956, **16**, 317—320).—A method is described for the determination of serum glycoproteins and blood glucose with diphenylamine (DPA) in acetic–HCl medium. The blue colour developed is specific for hexoses; and is measured at 635 mμ. E. M. J.

Detection of dipeptides and dipeptidase activity on paper. G. Semenza (*Experientia*, 1957, **13**, 166).—The detection of amino-acids and dipeptides, separated by paper chromatography, is achieved by spraying with a solution of Na β-naphthaquinone in aq. acetone, and heating at 100° for 3—5 min. The paper is then immersed in 2 ml. of 4N-NaOH diluted to 100 ml. with 95% alcohol, when most of the amino-acids develop a grey-green colour in 10—15 min.; dipeptides retain the colour developed by heating for a longer period, or give a different colour. The method can also be applied to detect cysteinyl-glycinase on electrophoresis paper or as a spot test. G. R. WHALLEY.

New specific reagent for methionine and its use in paper chromatography. V. Blazsek (*Naturwissenschaften*, 1957, **44**, 114).—The colour reaction between methionine and α-naphthylamine diazonium hydrochloride is used for the identification of the amino-acid. The paper chromatogram is sprayed with a freshly prepared solution of 0·1% α-naphthylamine in 10% HCl, with equal parts of a 0·5% solution of $NaNO_2$. The only other amino-acid to react is tryptophan, which gives a blue-grey colour (yellow in u.v.) in contrast to methionine, which gives an orange-yellow colour (dark red in u.v.). C. A. FINCH.

Separation of basic amino-acids by chromatoelectrophoresis on paper. S. Gerlaxhe, J. Casimir and M. Renard (*Bull. Soc. chim. belg.*, 1957, **66** 251—255).—A good separation of ornithine, lysine, histidine, arginine, glycine, threonine, β-alanine, aspartic acid and glutamic acid is obtained by paper chromatography with phenol saturated with a buffer at pH 5·6 of ionic strength 0·05, followed by electrophoresis at right-angles in the same buffer using a Pleuger "Chromatoelectrorheophor" apparatus. E. J. H. BIRCH.

Chromatographic study of phosphoric esters formed by *Penicillium griseo-fulvum* and by *P. brevi-compactum*. P. Simonart, G. Bommers and G. Parmentier (*Zbl. Bakt.*, 1957, II, **110**, 194—197).—Techniques used for the chromatographic separation and identification of the esters and acids obtained from the culture-filtrates and mycelia of the fungi are described. Glucose-6-phosphate, ribose-5-phosphate, phosphogluconic acid, glucose-1-phosphate and 3-phosphoglyceric acid are identified. Culture filtrates from *P. brevi-compactum* also contain ribulose-5-phosphate and arabinose phosphate. Similar results are obtained as regards the contents of the mycelia. The bearings of these findings are considered in relation to the metabolism of the fungi. (15 references.) P. S. ARUP.

[Analysis of] food. H. W. von Loesecke (*Analyt. Chem.*, 1957, **29**, 647—656).—A review of the literature, 1955—56, on methods of food analysis, under the following sub-headings: moisture, proteins and amino-acids, inorg. ions, fats and oils, enzymes, carbohydrates, vitamins, acids, colour and taste, insecticide residues, miscellaneous. (317 references.) J. S. C.

Glyceryl monostearate in food. S. Cressey (*Food Manuf.*, 1957, **32**, 165—168, 175).—The composition, properties and uses of commercial "glyceryl monostearate" are described and its uses in baking, ice-cream making, are reviewed. Its softening and anti-staling action in bread and the question of its toxicity are discussed in detail. (23 references.) J. S. C.

Determination of sorbic acid and its salts. W. Diemair, K. Franzen and A. Sieglitz (*Naturwissenschaften*, 1957, **44**, 180—181).—A colour reaction between sorbic acid and methylmercaptobenzthiazole-*p*-ethyltoluenesulphonate (in acetic anhydride and NaOAc at 135°) is employed. The absorption of the resulting complex gives a quant. determination by spectrophotometry of the methanolic solution at 652 mμ., for 0·1—1·2 mg. of acid. C. A. FINCH.

Does the refining of food products act to the detriment of their nutritive quality? L. de Saint-Rat (*Industr. agric. aliment.*, 1957, **74**, 7—12).—A report of the 2nd symposium on foreign matter in food organized by the *Commission Internationale des Industries Agricoles et le Bureau International Permanent de Chimie Analytique*, Amsterdam, July 6th—9th, 1956. J. S. C.

Metallic and metalloid contamination of food and drink. D. Florentin (*Industr. agric. aliment.*, 1956, **73**, 413—423).—The contamination of food or drink by As, Pb, Hg, Cu, Zn, Sb, Cd, Sn, Cr, Ni, Al, F and B is reviewed. (17 references.) J. S. C.

Colorimetric method for determination of lead in foodstuffs. J. Bonastre (*Chim. anal.*, 1957, **39**, 104—105).—A standard method for the sulpho-nitric attack of wine and extraction and determination of lead is shortened and modified. After attack the lead is extracted into chloroformic dithizone from a solution of ammonium cyanide citrate and after extraction into aq. HCl the colour is developed in CCl_4 with dithizone and compared with a standard. E. J. H. BIRCH.

Detection of coal tar dye in turmeric (*Haldi*). S. N. Mitra, S. C. Roy and R. K. Chatterji (*J. Indian chem. Soc., Industr. Edn.*, 1956, **19**, 155—158).—An extra acid wash in the usual wool-dying process removes most of the natural turmeric colour and helps in getting satisfactory spot tests for the detection of added coal-tar colour in turmeric. On a circular paper chromatogram (developed horizontally) the natural turmeric colour is completely separated from many of the common synthetic colours if a suitable solvent is used. Chromatography also helps in separating mixtures of dyes if these are used. The detection of coal-tar dye in turmeric is made easier by the use of both the modified wool-dyeing-spot test, and paper chromatography. I. JONES.

Newly-developed flavouring aromatics. A. Katz (*Perfum. essent. Oil Rec.*, 1957, **48**, 131—134).—A table is given for 44 synthetic aromatic substances listing b.p., *n*, and taste, together with some typical formulations and a general discussion of their uses for flavouring purposes. (16 references.) J. S. C.

Microscopical detection of spices and other plant elements in foods. E. Hanssen, R. Ihlenfeldt and G. Florian (*Z. Lebensmittl Untersuch.*, 1957, **105**, 361—373).—The value of microscopical-histological analysis for the detection of plant elements in foods is discussed. Descriptions are given of the necessary preliminary prep., e.g. of sausages, baked products, jams, spice or herbs, etc. Photomicrographs (29) are given showing very distinctive structure of stone cells, epidermal tissue, stomata, hairs, etc., of currants; sclerenchyma, etc., of apricots; cuticular fissures, wood fibres, etc., of paprika; and hypodermal cells and wood parenchyma of vanilla fruit wall, etc. (39 references.) E. M. J.

Fungicidal and fungistatic power of two vanillin derivatives. P. Nobécourt, P. Traynard and S. de Coligny (*ATIP Bull.*, 1956,

133—135).—5-Chlorovanillin was found to be too weak to be effective except at very high concn., whereas a vanillin deriv. named compound "9a" showed improved fungicidal properties.
K. WENDTNER.

Examination of chemical preservatives. I. Effect of sub-threshold concentrations of preservatives on reproduction of yeast. K. Raible and G. Busch (*Zbl. Bakt.*, 1957, II, **110**, 172—177).—The effects on the growth of yeast in malt-wort of increasing concn. of nine different preservatives are to prolong the preliminary induction period, to decrease activity during the log growth stage, and to reduce the final max. achieved at the static stage. Typical data are given, showing the progressive effects of Na sorbate and benzoate.
P. S. ARUP.

Method of protecting surfaces of some materials in freeze drying. J. D. Mellor (*Vacuum*, 1954 [1957], **4**, 341).—Lack of homogeneity experienced in freeze-drying materials of high sugar-content, e.g. fruit purées, is corrected by forming ice layers above and below the material in the freezing stage. J. S. C.

Ethylene oxide for cold sterilization. H. Rauscher, G. Mayr and H. Kaemmerer (*Food Manuf.*, 1957, **32**, 169—172).—Experimental work on the fumigation of foodstuffs in the cold with ethylene oxide is described and its effects on various bacterial and fungal organisms at varying concn., temp. and periods of exposure are tabulated. (27 references.) J. S. C.

The paper bag and packaging of food products. A. Mouillier (*Industr. agric. aliment.*, 1956, **73**, 237—239).—The use of a large paper bag of 20 l. capacity, holding 50 kg. of material, and fabricated from 2 to 6 layers of Kraft paper, is reviewed. J. S. C.

Plastics for food packaging. Solubility characteristics of plastics illustrated with polyvinylidene chloride of American origin. L. Robinson-Görnhardt (*Kunststoffe*, 1957, **47**, 265—267).—Analytica, procedures are described for the determination of ether-sol., edible oil-sol. (inclusive of hardened groundnut oil and molten cheese) and water-sol. contents, and volatile loss, of a polyvinylidene chloride food wrapping foil. Data on a typical specimen are reported.
J. L. PROSSER.

[Air] cleansing cereals and similar granular materials. A.-B. Hallands Frökontor (Inventor: S. Tiberg) (B.P. 755,073, 3.8.54).—Cereal is fed by gravity to the centre of a disc, raised at its centre, and flows outwards to the disc edge. The disc is surmounted by a cone, base downwards, and the entire assembly mounted in a casing which leads from a suction fan at the top, extends over the cone and disc, and is contracted below the disc. The grain falls through the air stream at the disc edge, and through it a second time at the edge of the contracted portion of the casing, into a silo. The cross-section for air passage narrows continuously from the annular inlet through to the suction fan so that dust, once entrained, is carried away. K. RIDGWAY.

Quick-cooking rice. General Foods Corp. (B.P. 755,750, 25.2.54 U.S., 29.7.53).—The rice is soaked in water to give a moisture content of 18—38%. Heating to 325—360°F. in a closed vessel and suddenly releasing the pressure, gives a product 2—3 times the vol. of the original rice. F. R. BASFORD.

Separation of flour and bran. Miag Muehlenbau u. Industrie G.m.b.H. (Asses. of Miag Vertriebs G.m.b.H.) (B.P. 754,244, 17.3.54. Ger., 18.3.53. Addn. to B.P. 717,220; J.S.F.A. Abstr., 1955, i, 271).—The method of circulating air described in the original patent is modified to prevent eddying and consequent bad separation. K. RIDGWAY.

Treatment of wheat flour. C. Brabender and C. W. Brabender' trading as Firma Brabender o.H. (B.P. 754,723, 7.1.54. Ger.' 13.1.53).—The baking qualities of wheat flour are improved by treatment in a current of moist hot air. This is effected by adjusting the moisture content of the flour to 15·5—16%, then preheating within a fraction of a sec. (in the conveying duct of a pneumatic conveyor plant operating on a closed circuit) to 45—80 (50)° by means of a current of compressed air of R.H. 60—90 (70—80)%, suddenly subjecting it to the action of live saturated steam until a temp. of 45—75 (~60)° is attained, and cooling. Apparatus is figured. F. R. BASFORD.

Coated cereals. General Foods Corp. (B.P. 754,771, 19.3.54. U.S., 24.9.53).—A hard glaze-like, humidity-stable coating is obtained on (non-porous) cereal, e.g., corn flakes, by distributing thereover an aq. syrup at 60—85 (60—70)% sol. solids (of which 1—8% is non-sucrose sugar and the remainder is sucrose), then drying to 2–3% of moisture at such a temp. during such a time (e.g., during 7—8 min. at 135–150°) that the amount of invert sugar formed during drying does not increase the level of non-sucrose sugar above 8%. The coating amounts to 10—35 wt.-% of the cereal. F. R. BASFORD.

Production of sugar from a substantially anhydrous mixture of sugar and non-sugar substances. Braunschweigische Maschinenbauanstalt A.-G. (B.P. 755,842, 29.6.53. Ger., 12.7 and 7.10.52).—Sugar is extracted from molasses by treatment with conc. acetic acid to which is added approx. three times its wt. of returned mother liquor, the acid forming at least 50% by wt. of the sugar–acid mixture. The amount of recycled mother liquor is determined by the quantity of non-sugars present. The addition of mother liquor precipitates the sugar as fine crystals which are washed with MeOH and then with MeOH containing 2% of methylene chloride. This removes the mother liquor. A 90% yield of sugar at 96% purity is obtainable. K. RIDGWAY.

Preparation of confectionery masses by evaporation of water from a starting mixture. C. Jamin N.V. (B.P. 754,601, 2.7.54. Neth., 10.5.54).—The sugar composition is flowed down a sloping gutter made of a material capable of withstanding a temp. of 200° and having high dielectric strength and low loss characteristics; suitable materials are steatite, ethoxylene resins such as Araldite, or fluoro-plastics such as Fluon or Teflon. Cu strips on the outside of the gutter subject the flowing composition to 4 kw. of high-frequency energy at 25 megacycles /sec. and 3 kv. Water is evaporated without any danger of local overheating in a time of approx. ½ min. as compared with 10 min. in the conventional boiling kettle.
K. RIDGWAY.

Honey-containing product. W. F. Straub & Co. (Inventor: W. F. Straub) (B.P. 755,593, 12.10.54).—A solidified, free-flowing, non-sticky honey product comprises a dried mixture of honey (45—65%) and gelatinized starch (natural, modified, or treated starch, or flour, e.g., wheat flour). The starch may be gelatinized prior to or after compounding with the honey.
F. R. BASFORD.

Improving the keeping qualities of plants and restoring wild plants to full freshness. R. L. Gold and P. Froeschel (B.P. 754,821—2. [A] 19.10.12 and 7.5.51. [B] 2.5.52).—A. The plants are completely submerged in water in a tank which is then evacuated so that the pores of the plant fill with water. Part of the water may be removed by subsequent centrifugation if required. The amount of vacuum applied depends on the type of material treated. Plant is described. B. Apparatus suitable for domestic use is figured.
F. R. BASFORD.

Dehydration of solutions or suspensions by freezing. Commonwealth Engng Co. of Ohio (B.P. 755,654, 8.3.54).—Fruit juice is concentrated by freezing in successive lower temp. cycles under conditions of good agitation, small temp. differential and high heat-exchange capacity. At least 1 sq. ft. of refrigerated surface is provided per 1—1·5 gal. of refrigerated juice. The freezing is carried out in vertical tubes fitted with scraper blades, the juice being passed inside the tubes and the refrigerant outside. Freezing takes place in four cycles, under a 7°F. differential. The ice formed is removed and screened by a vibrating screen. Oversize crystals are centrifuged to remove contained juice, whilst small pure ice crystals passing the screen go to waste. K. RIDGWAY.

Control of microbiological growth in beer. F. & M. Schaefer Brewing Co. (B.P. 755,370, 29.6.54. U.S., 23.7.53).—Microbiological growth in beer is controlled by addition of thiolutin (≮1), penicillin (≮0·02) and/or polymixin (≮0·5 μg. per cc.).
F. R. BASFORD.

Manufacture of [canned sterilized] butter. Unilever, Ltd. (Inventor: H. D. Schrader) (B.P. 755,727, 8.5.53).—An 80% cream obtained by centrifugation is charged, while at a temp. not lower than that at which it leaves the centrifuge (viz. ≮65°), into a can (at ≮65°) which is then sealed, and sterilized at 100—120° during ≯30 min. The can is now cooled (step-wise) to 0—20°, to effect phase inversion of the contents and give a butter product free from objectionable taste. F. R. BASFORD.

Grated high-fat cheese. Kraft Foods Co. (B.P. 755,772, 7.5.54).—Comminuted dried natural high-fat cheese (**I**) (10—15% of moisture) is admixed with finely-divided particles of spray-dried processed high-fat cheese (2—3% moisture), then the mixture is tempered at low (≯40%) R.H. above the oiling-off point of **I** (e.g., 80—200°F.) during sufficient time (e.g., 48 hr. at 98°F.) to provide a stabilized, non-agglomerating cheese product (of 4—5% moisture content).
F. R. BASFORD.

Recovery of actin-free myosin from muscle material. Armour & Co. (Inventor: A. E. Szent-Gyorgyi and A. G. Szent-Gyorgyi) (B.P. 754, 134, 22.1.54).—Muscle material, freed from adenosine triphosphate (by extraction with dil. aq. KCl), and containing myosin in intimate association with actin, is treated with ≮0·4 (0·5—0·6) M-alkali metal (Na or K) iodide or thiocyanate at <10 (<0)°, to

extract the myosin and actin, while irreversibly depolymerizing the latter. The extract is then diluted, with pptn. of actin-free myosin. F. R. BASFORD.

Sausage meat. Chemische Fabrik Budenheim A.-G. (B.P. 754,406, 10.9.54. Ger., 10.9.53 and 24.5.54).—Instead of the usual mixture of $Na_4P_2O_7$ and $Na_3H_2P_2O_7$, $Na_3HP_2O_7$ (preferably as a hydrate) gives better results when used as plasticizer in sausage meat. Additionally there may also be present other condensed alkali metal phosphate, Kurrol's salt, $Na_2H_2P_2O_7$ (to give pH <7·2), pickling agents, etc. F. R. BASFORD.

Cutting fillets from fish. A/S Atlas (B.P. 755,443, 23.2.54. Den., 7.3.53).—The continuous process described uses a machine adjustable to cut tail sections as well as body fillets as the fish passes through the machine. K. RIDGWAY.

Inhibition of oxidation of fats or fatty oils. A. W. Brickman, V. Conquest, F. J. Madden, E. T. Filbey and W. B. Oleson (Inventors: Le R. Dugan, jun. and H. R. Kraybill) (B.P. 754,388—9, 2.4.54).—A. The rancidity of glycerides due to oxidative deterioration is inhibited by addition of a minor amount of 2 : 6-di-*tert.*-butyl-*p*-cresol (**I**). Citric acid, phosphoric acid, ascorbic acid, ethyl acid phosphate, glucuronolactone and phytic acid may also be added. B. The inhibitory composition is a mixture of **I** and butylated hydroxyanisole in a mutual solvent. I. JONES.

Treating oil-containing liquors from the wet rendering of oil-containing materials. A/S Stord (Inventor: H. Onarheim) (B.P. 755,077, 20.8.54).—The oil from liquors obtained by wet rendering of oil-containing materials (fish, etc.) is separated and the liquors are desludged, each in a series of steps. One of the separation stages comprises preliminary centrifuging with a relatively low degree of oil separation and another is a refining step which is preceded by evaporation. The desludging steps are made between the separation steps. I. JONES.

Coating edible articles with edible fat-base coating. E. T. Oakes Corp. (B.P. 755,770, 30.4.54. U.S., 4.5.53).—Chocolate for feeding to the tank of an enrobing machine is passed through a tall cylindrical jacketed tank, with rotating vanes which mix in horizontal planes but allow differences in properties to exist between the top and bottom of the tank. The tank should hold 1—2 hours' supply of chocolate. The water jacket maintains the temp. at 91·5—92·5°F. for an hour so that all fats crystallizable above this temp. are crystallized. The result is that the tempered chocolate can be used for enrobing and the enrobed chocolates can be cooled in a dry air blast at 65—70°F. and <70% R.H. whilst travelling on a metal conveyor belt, the cooling being much more rapid than is applicable to conventional chocolate coatings. K. RIDGWAY.

Preparation of food. V. T. Engwall & Co., K.-B. (B.P. 754,510, 8.9.54. Sw., 24.9.53).—Food is cooked in an atm. of superheated steam at 118—300 (200—300)°/1·5—70 (~14) lb. per sq. in. in a metallic, hermetically sealed vessel maintained above the aforementioned temp. (by electric heating elements incorporated therein). After cooking thus, and releasing excess pressure, the food may be fried by means of the heat of radiation (from the oven walls). There is also claimed an oven plant comprising several oven units, each provided with means for supplying steam, for evacuation, for generation of i.r. radiation, and for generation of a high frequency a.c. field. F. R. BASFORD.

Treatment of food substances. Electronized Chemicals Corp. (B.P. 754,336, 31.12.53. U.S., 5.1.53).—In the sterilization of food by subjecting to penetrating radiation of the ionization-producing type, organoleptic changes are suppressed by previously keeping the food at >0° in a hermetically sealed container until any O_2 present is converted into stable compounds (<72 hr.) which do not yield radiation-active products on irradiation. F. R. BASFORD.

3.—SANITATION

[A] **Mechanics of a cream separator cleaned and sterilized by centrifugal force.** E. O. Herreid and E. Svereika. [B] **Sanitary aspects of the separator.** E. O. Herreid (*J. Dairy Sci.*, 1956, **39**, 1623—1628, 1629—1634).—[A] A self-cleaning centrifugal cream separator and its mechanics are described.

[B] The separator can be cleaned and sterilized centrifugally without dismantling. S. C. JOLLY.

Safe use of pesticides in food production. Food Protection Commee (*Nat. Acad. Sci., Wash.*, 1956, Publ. No. 470, 16 pp.).—The report deals with the general principles involved in discovery and development of a safe pesticide, the chemical, physical, biological and toxicological data required before it can be marketed, and the legal restrictions in force in the U.S. J. S. C.

Insecticidal performance of Strobane aërosols. J. C. McCool (*Soap, N.Y.*, 1957, **33**, No. 3, 91, 93, 95, 105, 107).—Tests are reported: results suggest that there is an optimum particle size for insecticidal aërosols which depends on the geometrical configuration of the valve employed. J. S. C.

Insect attractants and repellents. II. Attractants. V. G. Dethier (*Soap, N.Y.*, 1957, **33**, No. 3, 97, 99).—A survey. (15 references.) J. S. C.

Tentative method for determination of particle size distribution of space insecticide aërosols. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 233—235).—The aërosol sample is drawn into a wind tunnel so that the individual particles are deposited on a rotating microscope slide on which they are then counted and classified by size. A correction factor is applied to calculate the particle sizes in the original spray. J. S. C.

Aërosol test method for flying insects. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 231—232, 270—271).—The method described is based on the use of free flying flies, a standard dosage and a standing testing technique, and involves comparison with a reference insecticide. The test insect is *Musca domestica* L. and the susceptibility of the strain used is defined in relation to the reference. The fly cages, rearing and testing rooms, aërosol chamber, insecticide paper, etc., are all specified. (10 references.) J. S. C.

Peet-Grady method. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 225—226, 269—270).—The method described is a means of determining the relative efficiency of contact insecticides dissolved in fly-spray base oils suitable for household and industrial use. A standardized reference insecticide (of 100 mg. pyrethrins/100 ml. de-odorized base oil) is used. The test insect is the adult house fly (*Musca domestica* L.) and their rearing is specified, as are also fly cages, rearing room, testing room, test chamber, and test procedures. J. S. C.

Cockroach spray test method. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 223—224).—A standard procedure is laid down for testing the efficacy of a liquid insecticide sprayed on cockroaches, in comparison with a reference insecticide of 100 mg. pyrethrins/100 ml. deodorized insecticide base oil. Among the matters specified are the test insects, rearing room, testing room, spray chamber, atomizer, treatment container and recovery dishes. The rearing of test insects, their feeding, the test procedure and the evaluation of data are also defined. J. S. C.

Cockroach aërosol test method. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 227—228, 271).—The method described is intended for the determination of the relative efficiency of aërosol formulations applied as direct sprays to cockroaches and not for measurement of residual action. It is applicable to aërosols consisting of pressurized formulations of <20 wt.-% of volatile ingredients (insecticides, base oils, solvents, etc.) and >80% of liquefied propellent gases (CCl_3F, CCl_2F_2, CH_2Cl_2, etc.). The reference insecticide, dispenser, test insect, rearing and testing rooms, spray chamber, treatment container, insecticide paper and recovery dishes, and the relevant rearing, feeding and test procedures, are specified. (11 references.) J. S. C.

Aërosol insecticides storage test. Anon. (*Soap, N.Y.*, 1957 *Blue Book*, 229—230).—Two types of storage test are described. The "live" test is one in which the valves are actuated and determinations made at relatively frequent intervals with the object of simulating the conditions encountered during use of aërosol dispensers. The "dead" storage test involves an interval of 1—24 months and is intended to simulate warehouse storage conditions and provide shelf-life information. Test procedures for each type are specified. J. S. C.

Effect of acetone on toxicity in pyrethrum and allethrin space sprays. W. A. Gersdorff (*J. econ. Ent.*, 1956, **49**, 849—851).—Studies of the effect of acetone in pyrethrum–kerosene sprays against house flies showed that the ratio of toxicity of pyrethrins in the original mixed solvent to that in kerosene alone varied geometrically as the proportion of acetone varied arithmetically between 0 and 75%. The ratio corresponding to a 25% increment in acetone was 1·55. The effect of acetone in allethrin sprays was about the same. This effect was due to most of the acetone volatilizing with a consequent increase in the dosage of insecticide applied to the insects. The relative toxicities of the toxicants were not affected. A. A. MARSDEN.

Comparative effects of piperettine in pyrethrum and allethrin mixtures as house fly sprays. W. A. Gersdorff and P. G. Piquett (*J. econ. Ent.*, 1957, **50**, 164—166).—Piperettine (vinyl analogue of piperine) was an excellent synergist for pyrethrins, producing a 14-fold effect on house flies. With allethrin, however, the synergic effect of piperettine was small. Piperettine alone caused no mortality or knockdown of house flies. A. A. MARSDEN.

Relative toxicity, synergistic activity and knockdown effectiveness of mixtures of piperonyl butoxide with allethrin and its *trans*-fraction and isomers as house-fly sprays. W. A. Gersdorff, N. Mitlin and P. G. Piquett (*J. econ. Ent.*, 1957, **50**, 150—156).—Mixtures with the L-allethrolone D-*trans*-chrysanthemumic acid ester, the D-L ester, the L-L ester, the D-D ester, the DL-*trans* fraction, and allethrin were, respectively, 1·93, 0·41, 0·029, 10·34, 3·86 and 3·03 times as toxic as allethrin alone. Synergism with respect to mortality was shown by all mixtures, but there was no synergistic action with respect to knockdown in 25 min. Initial paralysis and lethal action are successive phases of one physiological action. A. A. MARSDEN.

Susceptibility to insecticides of laboratory cultures of an insect species. J. M. Holborn (*J. Sci. Food Agric.*, 1957, **8**, 182—188).—Laboratory bred adult *Calandra* were 3·5—6·5 times as susceptible to pyrethrins as was a wild strain of the same age, but the two strains were about equally susceptible to pyrethrins synergized with piperonyl butoxide. Strains of adult *Tribolium* of the same age from different laboratories differed in susceptibility to γ-BHC (up to 4 times), to pyrethrins (up to 3·5 times) and to a lesser degree, to synergized pyrethrins. Differences in susceptibility result from differences in vigour. E. M. J.

Inhibition of development in the house-fly by 3 : 4-methylenedioxyphenyl compounds. N. Mitlin (*J. econ. Ent.*, 1956, **49**, 683—684).—Nearly all the compounds tested which contained the 3 : 4-methylenedioxyphenyl-group were toxic themselves to house-fly larvæ as well as being of value as synergists. Sulphoxide and sulphone were two of the most effective materials tested. Most compounds, e.g., *iso*safrole, were effective in inhibiting larval development at very low concn. Resistant flies were as easily affected as susceptible flies.

Control of house-fly larvæ in poultry droppings. R. A. Hoffman and R. E. Monroe (*J. econ. Ent.*, 1956, **49**, 704—705).—Sprays of diazinon and Bayer L 13/59 were superior to malathion, chlorthion, Am. cyanamid 4124, diazinon, and dieldrin as larvicides under the conditions of these tests. Dieldrin caused complete mortality of first- and second-instar but not third-instar larvæ. Even with high concn. of diazinon, reinfestation occurred not later than 7—9 days. A. A. MARSDEN.

Action of radio-strontium in the house-fly and the German cockroach. N. Mitlin and F. H. Babers (*J. econ. Ent.*, 1956, **49**, 714—715).—Feeding radio-strontium to house-flies caused varying degrees of sterility and continuous feeding inhibited oviposition entirely. The absorption rate of this element was relatively slow, radioactivity increasing from 0·42 counts/min. per egg to 23·5 counts/min. per egg in 2 weeks. In the cockroach the biological half-life showed a definite difference between male and female insects, 3·5 to 0·95 days, respectively. Although none of the female roaches developed oöthecae during the experiment, there was no proof that sterility was due to ^{89}Sr feeding. A. A. MARSDEN.

Fate of radio-phosphorus ingested by house flies and German cockroaches. F. H. Babers, N. Mitlin and T. J. Shortino (*J. econ. Ent.*, 1956, **49**, 820—822).—House flies fed ^{32}P-labelled food for six days did not oviposit; two days after a return to normal diet some eggs of low viability were laid. Flies fed on ^{32}P for shorter periods showed inhibited oviposition and fertility due to immature ovaries. Larvæ reared on ^{32}P developed into normal adults. *Blattella germanica* fed ^{32}P developed oöthecæ which were very flaccid and contained no eggs. A. A. MARSDEN.

Systemic effect of Dipterex on the bed bug and Gulf Coast tick when administered to rabbits. T. R. Adkins, jun., and F. S. Arant (*J. econ. Ent.*, 1957, **50**, 166—168).—The mortality of fifth-instar nymphs of *Cimex lectularius* ranged from 36% on rabbits fed 10 mg. of Dipterex per kg. body wt. to 98% on rabbits given 40 mg.–kg. The mortality of *Amblyomma maculatum* nymphs varied from 25% on rabbits fed 25 mg./kg. of Dipterex to 100% on those dosed at the rate of 100 mg./kg. body wt. A. A. MARSDEN.

Effectiveness of Cyclethrin with various synergists against body lice. G. S. Burden and M. M. Cole (*J. econ. Ent.*, 1956, **49**, 643—645).—When used in laboratory tests as cloth impregnants against the body louse, the α-allylpiperonyl, the α-propylpiperonyl, the 4-(3 : 4-methylene dioxyphenyl)-*sec.*-butyl, and the α-*iso*propylpiperonyl esters of chrysanthemumic acid and the α-allylpiperonyl ester of fencholic acid were the most effective synergists for Cyclethrin. Pyrethrins with sulphoxide was more effective than Cyclethrin with any synergist. In pyrophyllite dusts at 0·1% concn., Cyclethrint was rather slower in knockdown than allethrin or pyrethrins, whilst synergized Cyclethrin and allethrin were less effective than pyrethrins. A. A. MARSDEN.

Phosphorus compounds as ovicides and adulticides against body lice. M. M. Cole and G. S. Burden (*J. econ. Ent.*, 1956, **49**, 747—750).—Of 73 compounds tested in the laboratory, parathion was the most effective ovicide and sulphotep the most effective against adult lice. Malathion and chlorthion were completely effective as adulticides at 0·001% and as ovicides at 0·05 and 1%, respectively. DDT-resistant lice and eggs showed no cross-resistance to 10 P compounds. R.H. and the age of the eggs affected the efficiency of malathion and chlorthion. P insecticides are not recommended for body louse control. A. A. MARSDEN.

Habits and control of the clover mite in dwellings. L. L. English and R. Snetsinger (*J. econ. Ent.*, 1957, **50**, 135—141).—Grass-free bands (6—24 in.) around trees and buildings greatly reduced the population of *Bryobia prætiosa*. An 18-in. band was as effective as applications of Aramite, chlorbenzilate, malathion, and Ovotran. Grass-free bands supplemented with an acaricidal spray gave the best and quickest control of this pest. A. A. MARSDEN.

Determination of DDA [di-(p-chlorophenyl)acetic acid] in urine using an ion-exchange resin. C. Cueto, A. G. Barnes and A. M. Mattson (*J. agric. Food Chem.*, 1956, **4**, 943—945).—A routine method, based on adsorption on a basic ion-exchange resin, is described for extracting DDA, the metabolite excreted by animals and human beings fed DDT, quant. from urine. The DDA is then desorbed and determined by a modified Schechter–Haller method. S. C. JOLLY.

Volatile acids [determination in sewage digester sludges] by direct phosphoric acid distillation. J. E. Frook (*Sewage industr. Wastes*, 1957, **29**, 18—23).—The sample of sludge is freed from solids by settling and decanting, followed by flocculation with $Al_2(SO_4)_3$ and $Ca(OH)_2$ at pH 7·5 and filtration. The clear filtrate is placed in a Kjeldahl flask with 85% aq. H_3PO_4 and Ag_2SO_4 solution, and distilled into a graduated cylinder until all the volatile acids are in the distillate. The system is purged with water and the total condensate is titrated at ~100° with 0·1 N-NaOH using phenolphthalein as indicator. Acid recoveries of 98% of acetic, propionic, *n*-butyric, *n*-valeric and *n*-caproic acids are possible. A blank titration is made and results are expressed as p.p.m. acetic acid. J. S. C.

Dairy waste disposal by spray irrigation. F. J. McKee (*Sewage industr. Wastes*, 1957, **29**, 157—164).—The disposal of dairy plant wastes by spray irrigation has proved satisfactory. The irrigation systems normally include a collecting pump, pumping equipment, and a distribution system equipped with sprinklers. Spray heads may be attached directly to the outlet pipe or mounted on risers. Winter operation requires a buried distribution system. J. S. C.

Packing-house waste trickling filter efficiency following air flotation. K. A. Hirlinger and C. E. Gross (*Sewage industr. Wastes*, 1957, **29**, 165—169).—Investigations are described in which the object was to determine the efficiency of a trickling filter in reducing the 5-day B.O.D. of a packing-house waste pre-treated by air flotation. Average reductions in B.O.D., O_2 consumed, grease, and N_2, were computed from operating data and found to be satisfactory. J. S. C.

Whisky and industrial alcohol distillery wastes. C. J. Jackson (*J. Inst. Sewage Purif.*, 1956, 206—214).—The character and compositions of the effluents from malt, grain and industrial alcohol distilleries are reviewed and methods of treatment indicated. It is considered that, in malt distilleries, purification can be obtained satisfactorily either by percolating filters or by evaporation, the latter method being used where the output is sufficiently high. For grain distilleries, evaporation is the most economical and practicable method but pollution can be reduced by removal of insol. solids by mechanical separation or chemical pptn. For industrial alcohol distilleries, evaporation and incineration of concentrate is the only practical complete treatment. Partial purification can, however, be effected by anaërobic digestion. (14 references.) J. S. C.

California fruit and vegetable cannery waste disposal practices. W. J. O'Connell (*Sewage industr. Wastes*, 1957, **29**, 268—280).—The waste disposal problems and methods of treatment in tomato, peach and citrus canneries are described and discussed. J. S. C.

Activity of cellulose-decomposing fungi isolated from sewage-polluted water. W. B. Cooke and K. A. Busch (*Sewage industr. Wastes*, 1957, **29**, 210—217).—Fungi which are capable of utilizing cellulose as a sole source of C are present in waters polluted by sewage. Inocula of fungus mycelia are less effective in promoting cellulose removal than inocula of spore suspensions in a growth medium of raw sewage. Raw settled sewage contains organisms able to use cellulose as a C source in presence of other organisms which may remove toxic substances and/or provide growth-promoting substances. J. S. C.

High-purity oxygen in biological sewage treatment. W. E. Budd and G. F. Lambeth (*Sewage industr. Wastes*, 1957, **29**, 237—253).—

The results of pilot-plant trials of the use of pure O_2 in the treatment of sewage by activated sludge are reported and indicate the possibility of achieving significant savings in plant size. J. S. C.

B.O.D. reduction by chlorination of phenol and amino-acids. R. S. Ingols and G. M. Jacobs (*Sewage industr. Wastes*, 1957, **29**, 258—262).—The reduction of B.O.D. values for a series of amino-acids, brought about by chlorination, was determined and compared with the theoretical reduction obtainable. The values obtained are less than average reduction in B.O.D. of 2·0 mg./l. obtained in sewage plants: possible explanations of the difference are discussed. J. S. C.

Detergent builders and B.O.D. G. W. Malaney and W. D. Sheets (*Sewage industr. Wastes*, 1957, **29**, 263—267).—The effects of the following common detergent builders (0—100 p.p.m.) on a synthetic sewage were studied: org. types, viz. Versene regular, Versene Fe-3, and Na carboxymethylcellulose; inorg. types, viz. (*a*) Na hexametaphosphate, $Na_4P_2O_7$, Na_2CO_3, Na_3PO_4, Na silicate and Na_2SiO_3, and (*b*) NaCl, $NaHCO_3$ and Na tripolyphosphate. The org. types increased B.O.D. and were presumably susceptible, therefore, to metabolism of sewage organisms. Of the inorg. types, those listed under (*a*) lowered B.O.D. and are arranged in the order of increasing effect, whereas those under (*b*) were inactive in this respect. J. S. C.

Influence of sulphur dioxide from smoke fumes on vegetation in the vicinity of Bor copper works. M. Krajčinović, M. Arsenijević, J. Jovanović, B. Prohaska and M. Bravar (*Bull. Soc. chim., Belgrade*, 1956, **21**, 293—307).—Calculations were based on S contents of healthy plants as compared with S contents of the vegetation from Bor and vicinity. Taking normal healthy plants as units, following were the contamination coefficients: fruit trees 1·4—3·5, other trees 1·4—2·8, farm crops 1·6—3·5, vegetables 1·2—2·6. Degree of contamination depends not only on distance from the source of the smoke but also on the configuration of land, prevailing winds and other weather factors. A short list is given of plants with reference to their resistance: plums, acacia, wheat and paprika head their respective groups as the least resistant to SO_2 contamination. A. GROCHOWSKI.

Substances having insecticidal properties. N.V. Philips' Gloeilampenfabrieken (B.P. 755,569, 4.6.54. Neth., 9.6.53).—Compounds $NMe_2{\cdot}CO_2R$ (R is chlorophenyl of 1—3 Cl) are claimed as insecticides, especially active against house flies and plant lice. As an example of prep., a mixture of 2 : 5-dichlorophenol (1), dimethylcarbamoyl chloride (1 mol.) and pyridine is boiled during 2 hr., then cooled, and admixed with water and ether. The ethereal layer is now successively washed with 2N-NaOH, 2N-HCl, and water, then evaporated, to leave 2 : 5-*dichlorophenyl dimethylcarbamate* (64%), m.p. 53—54°. F. R. BASFORD.

4.—UNCLASSIFIED

Radio-strontium and radio-calcium measurement in biological materials to December 1956. D. V. Booker, F. J. Bryant, A. C. Chamberlain, A. Morgan and G. S. Spicer (*A.E.R.E.*, 1957, HP/R 2182, 8 pp.).—Data given in a previous report (*A.E.R.E.* HP/R 2056; cf. J.A.C. Abstr., 1957, i, 331) on the ^{90}Sr content of biological materials is extended and some data on ^{137}Cs content of milk given. Trends of activity with time show little increase in 1956 over 1955 except in samples derived from low-Ca soils. J. S. C.

Deposition of sulphur from hydrogen sulphide by bacteria and yeast. Y. B. D. Skerman, G. Dementjer and G. W. Skyring (*Nature, Lond.*, 1957, **179**, 742).—Grown in 0·1% peptone and afterwards exposed to an atm. of H_2S, *Sphærotilus natans* deposits S intracellularly. Several yeasts were similarly treated and it was found that pellicle-forming types, including *Pichia membranefaciens*, behaved similarly with quite rapid oxidation of H_2S. J. S. C.

Separation of α-glycerophosphoric acid from its β-isomer by paper chromatography. C. Urakami and Y. Kakutani (*Bull. chem. Soc. Japan*, 1957, **30**, 21—25).—The chromatographic behaviour of α- and β-glycerophosphoric acids and of their Na, Ba and NH_4 salts on Al_2O_3-impregnated paper developed with a 60 : 5 mixture of MeOH and NH_3 at 11—14° is reported; spots are revealed with bromothymol blue. A clear separation of the Na salts of the two acids can be obtained without hydrolysis or migration of the phosphoryl group. The α-acid can also be separated from a mixture of inorg. phosphates, the β-acid and the glucose 1- and 6-phosphates, whilst the β-acid can be separated from mixtures of inorg. phosphates and glucose 1- and 6-phosphates. W. J. BAKER.

Preparation of dehydracetic acid. K. Rauscher, H. W. Ardelt and P. H. Opel (*Ernährungsforschung*, 1956, **1**, 727—731).—In the prep. of the acid from Et acetoacetate by the Arndt method, the substitution of powdered Cu for $NaHCO_3$ as the catalyst results in improved yields. Tabulated data show that max. yields (70—75%) can be obtained by treatment with 1 g. of Cu per 100 ml. at 215—240° during 9 hr. (10 references.) P. S. ARUP.

Radioactive contamination of foodstuffs from fall-out as a source of error in some animal experiments. C. G. Clayton (*Nature, Lond.*, 1957, **179**, 829—830).—Measurements of the gastro-intestinal absorption of substances by fæcal measurements following oral ingestion of a test dose containing a radio-isotope were vitiated by a minute contamination in the feeding stuffs due to fall-out from nuclear weapon tests. Detailed measurements of this contamination and a discussion of its nature are presented. J. S. C.

Hydrophobization of chromatographic paper with silonite. E. Kovács (*Naturwissenschaften*, 1957, **44**, 181).—An 8% solution of silonite (ethylchlorsilane) is used for hydrophobization of chromatographic paper, which is washed with MeOH and then dried at 30—40°, in a horizontal position. C. A. FINCH.

Determination of pyruvic and α-oxoglutaric acids by paper chromatography in blood, wine and cerebrospinal fluid. B. McArdle (*Biochem. J.*, 1957, **66**, 144—148).—A simplified method is described for separation of the 2 : 4-dinitrophenylhydrazones of α-keto-acids by paper chromatography and for the determination of the separated hydrazones of pyruvic and α-oxoglutaric acids. The hydrazones are extracted from the paper with aq. Na_2CO_3–NaOH and are determined colorimetrically. The amounts of each acid are ascertained from standard graphs. J. N. ASHLEY.

Determination of serum protein-bound iodine by alkaline incineration. J. D. Acland (*Biochem J.*, 1957, **66**, 177—188).—The method, which is suitable for routine use, is described. The protein is precipitated by $Zn(OH)_2$ and after being ashed the iodide is eluted from the ash under alkaline conditions. The iodide is then determined colorimetrically at 415 mμ. by taking advantage of its catalytic effect on the reduction of ceric to cerous salts by H_3AsO_3. Analyses on trichloroacetic acid–protein ppt. do not give consistent results because of difficulties in the ashing process. There is loss of iodine if the ashing temp. is >650°. Zn partly inhibits the catalytic effect of iodide; the inhibition is greater at higher concn. of iodide. J. N. ASHLEY.

Determination of chloral hydrate and its transformation products in body fluids and tissues. A. E. Meyer and R. Per Lee-Motter (*Arzneim. Forsch.*, 1957, **7**, 194—197).—A method is described in detail for estimating chloral hydrate (**I**), trichloroacetic acid (**II**), trichloroethanol (**III**) and urochloralic acid (**IV**) in body fluids (blood, milk, urine, etc.) which is based on a Fujiwara colorimetric determination of **I** (or **I** + **II**) (at concn. 1—40 μg./c.c.) after treatment with strong aq. NaOH and pyridine (**V**); **I** and **II** give the same lines. After removing any protein and suitably diluting (concentrating in the case of urine) the fluid is divided into four fractions. **I** and **II** together are estimated in fraction A by first adding it to **V** and then adding the alkali (in that order to avoid subsequent decomposition of **I**), heating the mixture, cooling, and effecting the colorimetric determination. **II** (and hence **I** by difference) is determined in a similar manner in fraction B, but the fraction is first mixed with the alkali and set aside for 1 hr. to decompose **I** before adding **V**. Fraction C is rapidly evaporated at 100° to expel **I** and **III**, then treated with CrO_3 and conc. H_2SO_4 to oxidize **IV** to **II**, after which total **II** (initial **II** and that from **IV**) is determined after addition of **V** and alkali and proceeding as above; the figure for **IV** is calculated using the figure for initial **II** obtained with fraction B. Fraction D is similarly treated omitting the step of evaporation; thereby all compounds are present as **II** and are so estimated; the figure for **III** is calculated with use of the values for **I**, **II** and **IV** found as above. (11 references.) H. L. WHITEHEAD.

Relationship between the chemical structure and bacteriostatic action of di- and tri-phenylmethane dyestuffs. I. Basic di- and tri-phenylmethane dyes. E. Fischer (*Arzneim. Forsch.*, 1957, **7**, 192—194).—The bacteriostatic properties (towards streptococcus) of basic di- and tri-phenylmethane dyestuffs of various constitution are reported and discussed in the light of the findings of earlier workers. For high bacteriostatic activity the dyes must contain three 6-membered rings and ≤2 (substituted) amino-groups. For highest activity each amino-group must be substituted by two Et radicals, Me substituents give somewhat lower activity than Et, other alkyls appear to give a still lower activity, and Ph substituents a markedly reduced activity. The monoamino triphenylmethane derivatives and the diphenylmethane derivatives, the latter in particular, all show much lower or only slight bacteriostatic properties. (12 references.) H. L. WHITEHEAD.

Journal of Applied Chemistry

The following papers are appearing in the October, 1957, issue of the *Journal of Applied Chemistry*

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