JOURNAL

OF THE

SCIENCE OF FOOD

AND AGRICULTURE

(INCLUDING ABSTRACTS)

Published by the Society of Chemical Industry

Journal of Applied Chemistry

The following papers are appearing in the March, 1960, issue of the

Journal of Applied Chemistry

STUDIES ON STRAW AND COMPOSTS. I.—Characterising Straw, Composts and Bulky Organic Manures by Optical Extinction of Alkaline Extracts and Cation-exchange Capacity Measurements

By A. H. CORNFIELD

Both optical extinction of extracts made with 0·05N-NaOH (containing 0·5% of 'Calgon') and cation-exchange capacity measurements are suitable for characterising straw, compost prepared in various ways, farmyard manure and peat. Straw had the lowest and peat the highest optical extinction value and cation-exchange capacity, whilst the other materials had intermediate values depending on their method of preparation, composition or time of rotting. The high correlation between the two measurements for all the materials studied indicates a difference in the number but only a small difference in the nature of the chemical groups with exchange properties.

Introduction

Since Hutchinson & Richards[1] showed that straw to which nitrogenous compounds (accelerators) were added, decomposed to a material with properties similar to those of rotted farmyard manure, much work has been done on factors affecting the quality of such 'artificial farmyard manures' or 'composts'. This work has been concerned with chemical changes occurring during the composting process as affected by type of nitrogen compound added, moisture content, pH and many other factors and also with the effects of the finished materials on soil properties and crop yields. This work was reviewed by Waksman[2] and more recently in a technical bulletin[3] and by Hoyle & Mattingly.[4]

The work reported in this series of papers will be concerned with certain aspects of finished composts, prepared mainly from wheat straw, as affected by type and quantity of accelerator used during composting, and also with a comparison of the properties of composts with those of the traditional bulky organic manures such as farmyard manure and peat.

The composts used were prepared in small concrete units described elsewhere.[5] Hoyle & Mattingly[4] and the author[5] have shown that composts prepared in such small units have properties similar to those prepared in large units and offer the advantage that different types of composts may be prepared with much saving in labour and materials.

Although the chemical properties of bulky organic manures are of obvious importance, particularly insofar as they may affect the availability of nutrients when they are added to soil, their physical properties must also be considered, since the degree and type of rotting will affect the extent of absorption of water and nutrients.

The present paper describes two methods of characterising bulky organic manures based on measuring the extent of humification by determining (a) the optical extinction of an alkaline extract and (b) the cation-exchange capacity.

The extraction of humic or coloured substances from stable manure has been described by Springer,[6] who found that when the material was first extracted with HCl, hot aqueous NaOH was a good solvent for these substances. The determination of cation-exchange capacity has been used to follow the degree of rotting in composts[7, 8] and for assessing the value of rotted farmyard manure.[9]

Experimental

Materials

The samples analysed were taken from four composts, the original straw and grass from which the composts had been prepared, two sources of rotted farmyard manure, and a sample of sedge peat.

Sample 1. Compost 1, prepared from wheat straw without addition of accelerator.
Sample 2. Compost 2, prepared from straw plus sufficient Nitro-Chalk to give an initial carbon/nitrogen ratio of 40. This initial ratio had been shown[5] to be the optimum for good composting without excessive loss of nitrogen.

Sample 3.   Compost 3, prepared from straw plus extra Nitro-Chalk (compared with
    Compost 2) to give an initial carbon/nitrogen ratio of 27.
Sample 4.   Compost 4, prepared from straw plus young grass mixed in amounts to give an
    initial carbon/nitrogen ratio of 40.
Sample 5.   Original straw from which the composts had been prepared.
Sample 6.   Original grass used in preparing Compost 4 (Sample 4).
Sample 7.   A sample of farmyard manure (cow dung plus wheat straw) which had been
    allowed to rot for 3 months.
Sample 8.   As sample 7 but rotting had continued for 2 years.
Sample 9.   Sedge peat.

The composts were allowed to rot from May to October in small concrete units.[5]   Compost 1
was considered 'poor' since it had a wide final carbon/nitrogen ratio of 58 and caused con-
siderable fixation of nitrogen when incubated with soil.[10]   Composts 2, 3 and 4 were 'good'
composts and were satisfactory chemically since they had carbon/nitrogen ratios near 20 and
caused no fixation of nitrogen when incubated with soil.

All the materials were dried at 55–60° in a forced air oven and ground to pass a 50-mesh sieve.

Determination of optical extinction of alkaline extracts

The dry, ground material (0·5 g.) was shaken for 1 h. with 1 l. of 0·05N-NaOH containing
0·5% 'Calgon' (sodium hexametaphosphate) and the solution filtered through No. 50 Whatman
paper.   Optical extinction of the filtrate was measured with the Higher Biochem Absorptiometer
using the dark blue filter (approx. max. transmission at 4300 Å) and 1 cm. cell.

Determination of cation-exchange capacity

Dry, ground material (1 g.) was leached, using suction, with 0·1N-HCl to remove carbonates,
and then with N-calcium acetate, pH 7·0.   Excess calcium acetate was removed by leaching
with 90% aq. ethyl alcohol.   Adsorbed calcium was then extracted with 0·1N-HCl and deter-
mined in the filtrate as oxalate (permanganate titration).

Results and discussion

The method used for determining the optical extinction of alkaline extracts was adopted
as a result of preliminary work on the effects of varying the concentration of alkali, the solvent–
sample ratio and the shaking time.   The 'Calgon' was included to complex soluble calcium
and so prevent flocculation of the organic materials.   This was found to be as satisfactory
as giving a preliminary leaching with dilute HCl prior to extraction with alkali.   A wide material/
solvent ratio (1 : 2000) was used to reduce any possible effects due to compounds dissolved from
the materials.   Five coloured filters were tested using extracts of straw, composts and peat
in order to find the most suitable filter for the determination, and the results are shown in Fig. 1.
All of the filters were suitable for differentiating between optical extinction values of the three
materials, but the dark blue filter was the most sensitive in this respect.

Table I gives values for the optical extinctions of the alkaline extracts and the cation-
exchange capacities of the materials studied.

Both methods differentiated clearly between straw, which gave the lowest values for both
determinations, the poor compost (Sample 1) and the three good composts (Samples 2, 3 and 4).
Although the three good composts gave similar extinction values, the cation-exchange capacity
of the straw–grass compost was rather higher than that of the other two which were prepared
from Nitro-Chalk and straw.   It is of interest to note that the grass itself had a cation-exchange
capacity about three times that of straw.   This is presumably due to the higher content of
proteins and other complex organic compounds in grass which exhibit cation-exchange pro-
perties.   This difference is still present in the finished compost prepared from grass plus straw
(Sample 4), which shows how variations in the composition of the starting materials may effect
the final properties of the composts.

The compost which had been prepared with extra Nitro-Chalk (Sample 3) was little different
in cation-exchange capacity and optical extinction from that prepared using the optimum

Table I

% nitrogen, carbon/nitrogen ratio, optical extinction of alkaline extracts, and cation exchange capacity of materials studied

Sample No.	Nature of material	% N	C/N ratio	Optical extinction of alkaline extracts*	Cation-exchange capacity, mequiv. per 100 g.
1.	Compost prepared without added Nitro-Chalk	0·68	58·0	0·266	49·5
2.	Compost with initial C/N 40 (Nitro-Chalk)	1·92	19·8	0·339	77·0
3.	Compost with initial C/N 27 (extra Nitro-Chalk)	1·98	19·0	0·304	76·5
4.	Compost with initial C/N 40 (grass)	2·01	20·3	0·306	94·0
5.	Straw	0·28	143·0	0·143	23·5
6.	Grass	1·71	25·2	0·240	62·0
7.	Farmyard manure rotted 3 months	2·14	19·3	0·324	72·5
8.	Farmyard manure rotted 2 years	2·27	17·2	0·430	127·0
9.	Sedge peat	1·58	31·2	0·734	168·0

* For details of method of determination see text

quantity of Nitro-Chalk (Sample 2). It has been shown previously[5] that if excessive nitrogen is supplied during composting, the extra nitrogen is lost, probably by denitrification, so that no extra nitrogen or carbon is retained when composting is complete.

The sample of farmyard manure which had rotted for 3 months gave values comparable with those of the good composts, whilst that which had rotted for 2 years had a 40% greater value for cation-exchange capacity and a 25% greater value for optical extinction. This is due presumably to the proteinaceous nature of the dung, which increases the exchange capacity of the final material in a manner similar to that of the grass.

The highest values for both optical extinction and cation-exchange capacity were shown by the peat.

Fig. 2 shows that there is a high correlation between optical extinction of alkaline extracts and cation-exchange capacity of the materials analysed. This is rather surprising in view of the widely different sources of the materials, but indicates that the differences between them are due to the number rather than the nature of chemical groups present which exhibit exchange properties.
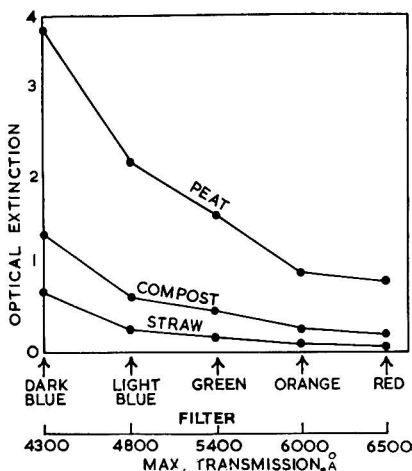

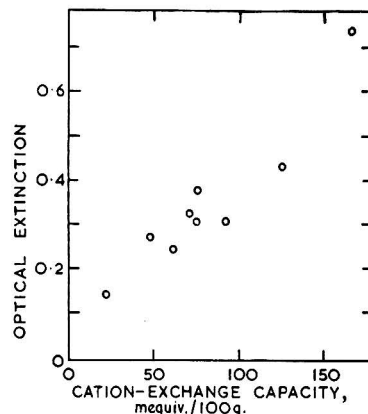FIG. 1.—*Optical extinction of alkaline extracts of peat, compost and straw using different light filters*

FIG. 2.—*Relationship between cation-exchange capacity and optical extinction of alkaline extracts*

Conclusions

The results obtained in this study indicate that both optical extinction of alkaline extracts and cation-exchange capacity are suitable for measuring the extent of humification of rotted materials ; the latter method appears to be somewhat better since it differentiates between composts prepared from different starting materials. Both methods are equally suitable for indicating differences between fresh straw, straw composts, well-rotted farmyard manure and peat.

Agricultural Chemistry Laboratory
Imperial College
London, S.W.7

References

[1] Hutchinson, H. B., & Richards, E. H., *J. Min. Agric.*, 1921–22, **28**, 398
[2] Waksman, S. A., ' Humus ', 1938, 2nd Edn. (London : Baillière, Tindall & Cox)
[3] ' Bibliography on Disposal of Organic Refuse by Composting ', *Calif. Inst. Eng. Res., Tech. Bull.*, 1950, No. 2, Series 37, 8 pp.
[4] Hoyle, D. A., & Mattingly, G. E. G., *J. Sci. Fd Agric.*, 1954, **5**, 54
[5] Cornfield, A. H., *Plant & Soil*, 1958, **10**, 183
[6] Springer, U., *Bodenk. u. PflErnähr.*, 1939, **12**, 84
[7] Miller, H. C., Smith, F. B., & Brown, P. E., *J. Amer. Soc. Agron.*, 1936, **28**, 753
[8] Broadbent, F. E., *Proc. Soil Sci. Soc. Amer.*, 1954, **18**, 165
[9] Siegel, O., *Landw. Forsch. Sonderh.*, 1953, **4**, 116
[10] Cornfield, A. H., *J. agric. Sci.*, in press

SUPPLEMENTATION OF CHICK DIETS WITH VITAMIN E TO IMPROVE MEAT QUALITY

By B. LAKSESVELA

The taste and odour of fresh chicken meat were significantly improved when the birds were fed diets containing 6 or 15% of an experimentally produced herring meal containing highly unsaturated fat (not favourable for the production of good-quality meat) or of normal herring meal, provided a supplement of 36·7 mg. of d-α-tocopheryl acetate per kg. of diet is given. Likewise such addition tended to improve the flavour of birds reared on a diet with 6% of normal herring diet or on an all-vegetable diet. High levels of d-α-tocopheryl acetate fed to chicks only in their first week of life, or only on the last 5 days before slaughter, also improved the taste of the fresh meat to some extent. The 36·7 mg. of d-α-tocopheryl acetate also apparently enhanced both growth rate and feed efficiency in normal diets ; in a diet with 36% wheat offals, feed efficiency appeared to be only very slightly improved.

Introduction

It has been known for more than a decade that vitamin E in the diet improves the quality of poultry meat, as shown chiefly by chemical determinations of the stability of depot fats in stored carcasses.[1-11] In spite of clear-cut indications from chemical data, there is still need for confirmation by organoleptic tests. Such confirmation was obtained by Mecchi *et al.*,[10] who from chemical and taste panel results for turkey and chicken meat concluded that increased chemical stability was accompanied by a significant improvement of flavour in the case of turkeys, and by a marked, though not statistically significant, tendency for improvement with chicken meat.

In the earlier experiments the vitamin E was usually administered at high and costly levels. Thus Mecchi *et al.*[10] added as much as 1000 mg. of d-α-tocopheryl acetate per kg. of feed in the experiments cited above. Others have even used much higher levels on occasions. The object of the present work was to test the effect of much smaller additions of vitamin E in improving quality, in particular when fed in combination with an experimentally produced herring meal which contained highly unsaturated fat.

This experimental type of herring meal was the subject of a long series of earlier investigations on the palatability of meat.[12] In some cases it appeared possible to distinguish between meat from chicks fed 15% of this meal as being less palatable than meat from chicks receiving all-vegetable diets, although the taste panel were unable to detect any characteristic off-taste in the least preferred samples. On the other hand, the taste panel were unable to discriminate between meat from chicks fed on an all-vegetable diet or on a diet containing 10% of the experimental meal or 15% of the normal, industrial type of herring meal.

Materials and methods

The composition of the experimental diets is presented in detail in Table I. The experimental herring meal is referred to here and throughout the paper as meal A and the commercial type as meal B. Each was fed at a level of either 6 or 15% in the different trials. Where a vitamin-E supplement was used, an additional level of 36·7 mg. of d-α-tocopheryl acetate (i.e., 50 i.u. of vitamin E) was included in each kg. of diet. New Hampshire (N.H.) chicks were used and occasionally also White Leghorns. The chicks were kept in electrically heated battery brooders, receiving their respective diets and water *ad libitum* from hatching to the time of slaughter when about 10 weeks old.

Table I

Compositions of diets used

	Diet X 15% herring meal	Diet Y 6% herring meal	Diet Z All vegetable
Maize, ground	—	15	15
Barley, ,,	36	21·5	19·8
Wheat, ,,	—	15	15
Wheat offals[1]	36	—	—
Soya-bean meal, extracted	6·7	11	13
Groundnut cake meal	—	12	14
Sunflower seed cake meal	—	12	16·2
Herring meal, A or B[3]	15	6	—
Grass meal	3	3	3
Ground oat hulls	1	1·5	—
Dicalcium phosphate	—	0·7	1·5
Mineral mix[2]	2	2	2
Vitamin mix[2] (wheat offals as carrier)	0·3	0·3	0·3

[1] The residue after 78% of the grain has been removed for human consumption.

[2] Added to contribute to each kg. the following (in mg.) : Ca 4000 ; P 2100 ; NaCl 2750 ; Mn 32 ; Fe 8 ; Cu 20 ; Co 1·6 ; I 1·5 and Zn 0·7. Choline chloride 150 ; niacin 5 ; riboflavin 1·5 ; Ca pantothenate 2 and folic acid 1. Vitamins A and D were added so as to contribute 6000 and 1200 i.u., respectively, per kg. to all diets ; and vitamin B_{12} to contribute 10 mcg. per kg. to diets Y and Z only.

[3] The herring meals were made from winter herrings. Both contained 9·2% of fat extracted by petroleum ether and about 74% of total protein. Meal A was an experimentally prepared meal containing highly unsaturated fat. Meal B was a commercial herring meal. At the time the feeding began, the extracted fat of meal A had I No. 133, and that of meal B 107. At the end of the experiments the figures had decreased to 109 and 75, respectively.

A few tentative trials of different nature as to vitamin-E supplementation were also made. Some groups received additional vitamin E only for the first week of life, others only for the last 5 days prior to slaughter. In both cases the chicks ingested massive doses, on the average altogether 125 mg. of d-α-tocopheryl acetate per head. In this way it was hoped to shed some light on the mode of the quality-improving action of vitamin E. In both cases diet X was used as basal (Table I).

Taste test technique

At the end of each trial N.H. chicks, live weight of about 1·2 kg., were bled, scalded at 60–70° until the feathers loosened, plucked by hand, eviscerated, singed, hung in a cool room overnight and judged for taste and odour in a triangular test on the following day (i.e., two carcasses representing the same diet were compared to a third representing a different diet).

The carcasses stored for one day were smeared with margarine to prevent drying out, grilled for about 30 min. to become cooked through, and served as warm, coded samples. The birds, in groups of three, were rapidly freed from skin and browned meat on one side, to make it

possible for the judges to savour the aroma of the cooked meat, without being distracted by a ' fried ' smell. Subsequent tastings of meat were made on cuts not adjoining the abdomen and free from crisp meat. Each judge always received cuts from the same part or parts of the bird to eliminate the effect of possible differences in flavour of different parts of the same bird. The same three birds were served to all judges. Between the examinations of different birds the judges refreshed their palates with unsweetened biscuits and soda water.

The judging was undertaken by a taste panel of six, or sometimes seven, members, chosen from the staff of the Institute after being tested for their ability to discriminate in triangular tests. The selected persons improved their ability considerably with practice before the tests commenced. Each judge had to allot points to each sample, 5 denoting highest and 1 lowest, and were asked to make comments on the individual samples to give further information.

Results

Tasting tests

It will be seen from Table II that the addition of 36·7 mg. of *d*-α-tocopheryl acetate per kg. of diet from hatching to the time of slaughter exerted a definite, favourable influence upon the palatability of the chicken meat. There was a significant improvement with the vitamin-E supplement in all five of the trials where the diets contained 6 or 15% of meal A.

A significant, positive effect was also found where the diet contained 15% of meal B. Similarly, there was a strong indication (though not statistically significant) of a similar effect in a comparison with the diet containing 6% of meal B. Likewise the result from a single test indicated that an all-vegetable diet (Z) produced better meat when fortified with vitamin E. Further, diet X with 15% of meal A supplemented with vitamin E, and the all-vegetable diet Z,

Table II

Effect of continuous vitamin E administration on palatability of chicken meat (triangular tests)
(36·7 mg. of d-α-tocopheryl acetate per kg. diet from hatching to slaughter)

Comparison	Correct couplings of parallel samples	Opinion of judges coupling correctly or of all in case of no correct couplings	Points for each of the 3 birds[1] (highest = best)	
			Without vitamin E	With vitamin E
Meal A with and without vitamin E				
Fed at 15% level				
Trial 1	6 out of 6***	Improved by vitamin E	4·02	4·37, 4·36
,, 2	5 ,, 6**	,, ,, ,,	4·06	4·38, 4·33
Fed at 6% level				
Trial 1	5 ,, 6**	,, ,, ,,	3·84	4·60, 4·48
,, 2	5 ,, 6**	,, ,, ,,	3·58	4·50, 4·36
,, 3	4 ,, 6*	,, ,, ,,	4·12, 3·89	4·43
Meal B with and without vitamin E				
Fed at 15% level	4 ,, 6*	,, ,, ,,	4·12	4·30, 4·35
,, ,, 6 ,, ,,	3 ,, 6	,, ,, ,,	4·09, 4·06	4·51
All-vegetable diet with and without vitamin E	2 ,, 6	,, ,, ,,	4·11, 4·17	4·63
			Experimental diet plus vitamin E	All-vegetable diet alone
15% meal A plus vitamin E *vs.* all-vegetable diet without vitamin E	0 ,, 6	Both alike	4·24	4·18, 4·25
			Experimental diet plus vitamin E	All-vegetable diet plus vitamin E
6% meal A plus vitamin E *vs.* all-vegetable diet plus vitamin E	0 ,, 6	,, ,,	4·15	4·18, 4·02

*** Significant at the 0·1% level.   ** Significant at the 1% level.   * Significant at the 5% level

[1] Averages for all judges. Figures from one trial should not be strictly compared with those from another. They are principally meant to differentiate between the 3 samples, only secondarily to indicate a certain level of quality.

were judged to give equally good birds. The same happened with diet Y containing 6% of meal A and the all-vegetable diet Z when both were supplemented with vitamin E.

The results of a short period of supplementation with vitamin E are presented in Table III. It may be noteworthy that both the early and late addition exerted detectable effect on the taste of the meat. In each case there was a significant effect in one of two trials, whilst the other trials showed a tendency only. The lower level of supplementation that was maintained throughout the entire period tended to be more effective than either method of giving large doses for a short time. This would be expected because the absorption of vitamin E would presumably be much higher when it is ingested every day at a moderate level.

When sorting different samples, the taste panel did not object to any one in particular. They ' just preferred ' those representing vitamin-E additions, finding it difficult to characterise the difference in words.

Weight gain and feed conversion

Table IV lists weight gain and efficiency of feed conversion in various groups, fed on diets with or without addition of vitamin E. In diet X with 36% of wheat offals (and 15% of herring meal A), the growth rate was about the same, but the efficiency of feed conversion was slightly better, when the diet was fortified with vitamin E for the whole time. In diet Y containing no wheat offals (6% of herring meal B) additional vitamin E for the whole time seemed to improve growth rate as well as efficiency of feed conversion. The same applies to an all-vegetable diet with no wheat offals incorporated (diet Z).

Giving a large dose of vitamin E during the first week of life apparently enhanced the growth rate in the early stages, but this was not the case later. By the age of 6 weeks, when the last weighing was made, groups given supplemental vitamin E in the beginning only had lower weight and consumed more feed per unit of weight gain than control birds with no supplemental vitamin E. No breed differences were noted, and losses were small in every case.

Table III

Effect of vitamin E on palatability of chicken meat; large doses administered either the first week after hatching or the 5 last days before slaughter

Diets with 15% meal A. Triangular tests

Comparison	Correct couplings of parallel samples	Opinion of judges coupling correctly, or of all in case no correct couplings	Points for each of the 3 birds[2] (highest = best)	
Vitamin E first week *vs.* no addition			Without vitamin	With vitamin E
Trial 1	1 out of 6	Slightly better with vitamin E	4·13, 4·33	4·36
,, 2	5 ,, 7**	Better with vitamin E	3·90	4·44, 4·54
Vitamin E first week *vs.* vitamin E whole time			Whole time	First week
Trial 1	1 ,, 6	Better with vitamin E whole time	4·09	4·21, 4·08
,, 2	2 ,, 7	,, ,, ,,	4·44	4·17, 4·23
,, 3[1]	2 ,, 5	,, ,, ,,	—	— —
Vitamin E during last 5 days *vs.* no addition			Without vitamin	With vitamin E
Trial 1	3 ,, 6	Better with vitamin E	4·12	4·32, 4·37
,, 2	5 ,, 7**	,, ,, ,,	3·96	4·48, 4·48
Vitamin E during last 5 days *vs.* vitamin E whole time			Whole time	Last 5 days
Trial 1	0 ,, 6	Both alike	4·06	4·06, 4·14
,, 2	2 ,, 7	Better with vitamin E whole time	4·52	4·23, 4·32

** Significant at the 1% level

[1] Test carried out by Statens Forsøksvirksomhet i Husstell, Stabekk.

[2] Averages for all judges. Figures from one trial should not be strictly compared with those from another. They are principally meant to differentiate between the three samples, only secondarily to indicate a certain level of quality.

Table IV

Effect of vitamin E on chick gain in weight and efficiency of feed conversion

Diet type	Vitamin E during whole period vs. no addition				Large dose of vitamin E first week only vs. no addition					
	Gain, g. at 6 weeks		g. of feed/g. gain at 6 weeks		Gain, g.				g. of feed/g. gain at 6 weeks	
					3 weeks		6 weeks			
	Without vitamin	With vitamin E	Without vitamin	With vitamin E	Without vitamin	With vitamin E	Without vitamin	With vitamin E	Without vitamin	With vitamin E
Diet X (with 36% wheat offals)										
Series 1,										
trial 1 $n = 28$	480	449	2·95	2·95						
,, 2 ,, 28	431	431	2·97	2·79						
,, 3 ,, 28	452	447	3·17	2·98						
Series 2,										
trial 1 $n = 20$	422	432	3·20	3·13	131	151	422	392	3·20	3·35
,, 2 ,, 20	415	409	3·30	3·28	133	142	415	374	3·30	3·71
Series 3,										
trial 1 $n = 18$	474	501	2·93	2·85	139	154	474	493	2·93	2·89
Average	447	445	3·09	2·99	134	149	437	420	3·14	3·32
Survivors	134/142	131/142			57/58	55/58	56/58	55/58		
Diet Y (with no wheat offals)										
Series 1										
trial 1 $n = 20$	552	577	2·82	2·47						
,, 2 ,, 20	542	543	2·79	2·48						
,, 3 ,, 20	565	587	2·47	2·57						
Series 2,										
trial 1 $n = 20$	487	508	2·38	2·30						
Average	536	554	2·60	2·45						
Survivors	74/80	76/80								
Diet Z (all vegetable diet, no wheat offals)										
$n = 20$	512	541	2·64	2·27						
Survivors	20/30	19/20								

Discussion

The present experiments show that organoleptic tests may well be used as a means to detect a favourable influence of comparatively small doses of vitamin E on the quality of chicken meat, even in the fresh state. Not only could a significant improvement due to vitamin E be found in carcasses stored for 1 day representing a type of diet that earlier had been deemed unsafe for good-quality products, but also diet types judged satisfactory. Even for the carcasses stored for one day representing diets used as good controls, some judges found a difference in favour of vitamin E.

The experiments also show that a comparatively small dose of vitamin E ensures good flavour in chicken meat, even where levels of herring meal with highly unsaturated fat, normally considered excessive and undesirable, are used. Further, they indicate the possibility of improving the quality of meat from poultry reared on a low-level 'herring meal' diet or on an all-vegetable diet. Apparently the vitamin-E supplement also improves the efficiency of feed conversion.

In addition, the experiments may be of some interest for the understanding of the mode of the action of vitamin E in improving quality. Considering only results of the type reported above, one could assume that the effect is fully explained as an inhibition of rancidification *in vivo* of unsaturated feed fatty acids. The detection of peroxides in intact tissue of chicks deficient in vitamin E serves as grounds for such an assumption.[1] However, the relatively good effect of addition of vitamin E as late as 5 days before slaughter suggests that another explanation must be sought.

Rancidification *post mortem* may of course have taken place, but it seems unlikely that this could have developed so far in the course of a single day and it cannot be readily adopted as the main reason for a significant reduction of palatability. Even the combination of *in vivo*

and *post mortem* rancidification appears insufficient as an explanation in the present case, and a fuller understanding can only be obtained by further research.

Acknowledgments

Herring Oil and Meal Industry Research Institute (S.S.F.)
Straumsgrend
Norway

References

[1] Dam, H., & Granados, H., *Acta physiol. scand.*, 1945, **10**, 162

[2] Criddle, J. E., & Morgan, A. F., *Fed. Proc.*, 1947, **6**, 247

[3] Kummerow, F. A., Vail, G. E., Conrad, R. M., & Awery, T. B., *Poultry Sci.*, 1948, **27**, 635

[4] Hood, M. P., Wheeler, R. S., & McGlamery, J. B., *Poultry Sci.*, 1950, **29**, 824

[5] Phillips, H. J., & Williams, I. L., *Poultry Sci.*, 1950, **29**, 776

[6] Dam, H., Prange, I., & Söndergaard, E., *Experientia*, 1951, **7**, 184

[7] Criddle, J. E., & Morgan, A. F., *Proc. Soc. exp. Biol. Med.*, 1951, **78**, 41

[8] Phillips, H. J., & Williams, I. L., *Food Tech. Champaign*, 1952, **6**, 74

[9] Mecchi, E. P., Pool, M. F., & Klose, A. A., *Poultry Sci.*, 1953, **32**, 915

[10] Mecchi, E. P., Pool, M. F., Behman, G. A., Hamachi, M., & Klose, A. A., *Poultry Sci.*, 1956, **35**, 1238

[11] Mecchi, E. P., Pool, M. F., Nonaka, M., Klose, A. A., Marsden, S. J., & Lillie, R. J., *Poultry Sci.* 1956, **35**, 1246

[12] Laksesvela, B., Internal Rep., 1958, No. 58 (S.S.F., Norway)

A STUDY ON THE EFFECT OF COLLOIDAL SILICA IN PEPTISING IRON OXIDE WITH REFERENCE TO RED BROWN SOIL FORMATION ON LIMESTONE

By D. H. KHAN*

Colloidal silica will peptise Fe_2O_3 in alkaline media containing Na ions, but Ca ions cause flocculation of the silica and no peptisation of Fe_2O_2 occurs. It is concluded that the theory of Reifenberg on the formation of *terra rossa* on limestone is untenable.

Introduction

Reifenberg[1] showed that a colloidal silica soil (prepared from water-glass) is able to peptise ignited iron oxide, and from the results obtained he postulated the mechanism of red soil formation on limestone, which has been accepted in principle by many pedologists. Reifenberg's experiment was done by boiling a silica sol with ignited iron oxide in a medium containing varying amounts of sodium ions, and it appears that he attributed the peptisation of iron oxide to the ' exchange of latent Na ions in the colloidal micelle '. The Na content of the sol arises from (i) the addition of caustic soda in raising the pH, and (ii) the incomplete removal of Na in dialysis.

The basic point that, if there is any production of colloidal silica during the weathering of limestone, this should take place in a medium saturated with calcium and magnesium and not with sodium, has been ignored by Reifenberg. As the alkaline earths unlike alkalis are

* Present address : Soil Science Division, Jute Research Institute, Tejgaon, Dacca, East Pakistan

strong coagulating agents, it was thought necessary to re-examine Reifenberg's experiment in both alkaline and alkaline earth media.

Kargin & Rabinovich[2] found that pure silica sols, prepared by the oxidation of SiH_4 by ozone, are inactive, uncharged and neutral in reaction, and they suggested that the high activity of silica sols observed by other workers may be related to impurities present in the system. Kargin & Rabinovich further studied the cation adsorption on silica sols of acid and alkaline reaction, prepared according to the methods of Graham[3] and Pauli & Valko.[4] The acid silica sols ranging in pH from 4·70 to 5·17 did not adsorb cations, whereas alkaline silica sols (pH raised with caustic soda) showed adsorption at pH 8·79 but none up to pH 7·9. Further, their data on cation-exchange adsorption of the silica sols up to pH 11·16 showed no equivalency in exchange adsorption.

The strong coagulating effect of the aluminium cation for silica sols—for amorphous colloid particles as well as for suspended coarser quartz particles—was shown by Russell & Rideal,[5] e.g., 1 part of $Al(OH)_3$ to 12,500 parts of SiO_2 efficiently coagulates silica. Many workers have studied the formation of adsorption compounds by interaction of colloidal silica and alkaline earth cations (e.g., [6]). Noll & McGuire[7] have shown the strong tendency for $Mg(OH)_2$ to react with silica even in the monomeric state. Addition of 300 p.p.m. of $Mg(OH)_2$ to water reduces the soluble silica content from 42 to 0·1 p.p.m.

Experimental

Silica sol was prepared by the decomposition of silicon tetrachloride with water at room temperature,[8] so avoiding any inclusion of Na ions. The initial pH of the sol obtained after prolonged dialysis (10 days) for removal of Cl^- ions, was 4·0, the low value being due possibly to the traces of Cl^- ions adsorbed on the silica micelle, as suggested by Kargin & Rabinovich[2] for Graham's silica sol even after thorough electro-dialysis. Reifenberg[1] attributed the low pH of an electro-dialysed Graham's silica sol (pH 3·0) to incomplete removal of Na ions from the system.

Both ignited and cold-precipitated forms of iron oxides (thoroughly washed to remove chlorides) were used in this experiment, the particle size of the crystals being selected in the range of 15 μ to 1 μ.

The experiment on the peptising effect of colloidal silica was done according to Reifenberg's procedure : 250 mg. of iron oxide and 100 ml. of the silica sol were boiled for 1 hour under reflux condenser, the suspension was cooled and centrifuged at about 2500 ± 100 r.p.m. for 15 min. to leave only particles below 0·5 μ in suspension. (Particles between 1 μ to 0·5 μ were removed to exclude any possible marginal effect.) The supernatant liquid was analysed for any dispersed iron oxide thus : silica was removed by evaporation with hydrofluoric acid in a platinum basin. The residue in the basin was fused with potassium bisulphate and the material taken into solution with dilute H_2SO_4 for determination of iron by the thioglycollic acid method.[9]

The other analytical determinations were carried out as follows : Silica was determined by the classical method as described by Piper,[10] pH was determined in a Beckman pH meter. The exchangeable cations of the *terra rossa* soils were determined by double leaching with N-ammonium acetate (pH 7). Exchangeable calcium was determined by Versenate titration,[11] magnesium by a spectrographic method with $FeCl_3$ as an internal standard, and sodium and potassium on the E.E.L. photometer.

Results

Table I shows the results of the experiment on the peptising effect of silica sol on ignited and hydrated forms of iron oxide and Table II the distribution of exchangeable cations in some *terra rossa* soils from Cyprus.

The silica sol, as initially prepared at pH 4·0, gave no peptisation of ignited Fe_2O_3 in absence of alkalis or alkaline earths, while hydrated Fe_2O_3 showed 0·011% peptisation under the same conditions, and CO_2-free water gave still less peptisation. The effect of acid silica sol on hydrated Fe_2O_3 is anomalous and may be due to traces of hydrogen chloride. Reifenberg,[1] Kargin & Rabinovich[2] and others found no exchange adsorption property of acid silica sol.

Table I

Peptising effect of silica sol on ignited and hydrated iron oxide

(0·3% SiO_2 in sol)

Nature of* medium	pH of medium	Peptisation of ignited Fe_2O_3, %	Peptisation of hydrated Fe_2O_3, %
$SiO_2{}^a$	8·1	0·007	0·013
H_2O^b	8·1	0·010	0·015
$SiO_2{}^c$	8·0	nil	nil
$SiO_2{}^d$	4·0	nil	0·011
CO_2-free water	6·0	nil	0·003

*a pH raised by adding 0·02N-NaOH
 b ,,   ,,   ,,   ,,   0·01N·NaOH
 c ,,   ,,   ,,   ,,   0·01N-Ca(OH)$_2$
 d pH in distilled water

Table II

Exchangeable cations in some terra rossa *soils from Cyprus*

Soil No.	Depth in in.	% Total metallic ions			
		Ca	Mg	Na	K
C_2	0–2	87·20	6·48	1·57	4·74
C_3	12–14	85·55	7·78	1·70	5·68
C_{12}	0–3	76·32	21·94	1·09	0·67

Treatment of silica sol with powdered calcium carbonate caused flocculation, 15·52% SiO_2 being precipitated at room temperature, and 89·12% at the boiling point. The pH rose from 4·0 to 7·7 and to 8·5, respectively.

Discussion

The preliminary observation on the peptisation experiment (Table I), that the supernatant silica sol at the end of the reaction and after sedimentation has the initial greyish white colour without any tinge of iron, suggests that the word ' peptisation ' has little significance. However, determination of the micro-quantity of iron present gives figures slightly higher than the blank. Both forms of Fe_2O_3 were peptised by Na–silica sol to an extent about four times less than that observed by Reifenberg,[1] and also by distilled water of pH 8·1 (NaOH) to a lesser degree (the solution contained ionic iron), while Ca–silica sol had no peptising effect. This suggests that it is the Na ions present which effect the peptisation and the colloidal silica at pH 8 makes no contribution. It may be mentioned that Bloomfield[12] found no peptisation of ignited Fe_2O_3 by silica sol up to pH 7·5 (NaOH). This might be attributed to (i) the larger particle size of ignited Fe_2O_3 and (ii) insufficient Na-saturation of the medium at pH 7·5. The absence of peptisation by Ca–silica sol is in agreement with the fact that divalent alkaline earth ions have a strong flocculating effect on a dispersed system as found by Reifenberg.[1]

In the light of the findings (Table I) which seem to relate the peptisation of iron with the nature of ion-exchange complex of the colloid, the exchange status of some *terra rossa* soils (see Appendix) collected from Cyprus by Osmond[13] was examined. The results are presented in Table II, which shows that 94–98% of the exchangeable metallic ions are alkaline earths. This suggests that the fate of silica liberated from the weathering of limestone (ionic or colloidal) is governed by the calcium and magnesium saturation of the system.

Conclusions

(i) The peptisation of cold precipitated and ignited forms of iron oxide by alkaline silica sol is due to the presence of Na ions in the system.

(ii) No peptisation of iron oxide is shown by the silica sol in alkaline earth medium and Ca ions throw out silica from dispersed phase.

(iii) The nature of reaction at the seat of limestone weathering is solely governed by the divalent alkaline earth cations.

It is concluded that Reifenberg's hypothesis on the formation of *terra rossas* on limestone is untenable.

References

[1] Reifenberg, A., ' The Soils of Palestine ', 1938 (London : T. Murby)
[2] Kargin, V. A., & Rabinovich, A. I., *Trans. Faraday Soc.*, 1935, **31,** 284
[3] Graham, T., *Philos. Trans.*, 1861, **151,** 205.
[4] Pauli, W., & Valko, E., *Kolloidzschr.*, 1925, **36,** 325 ; 1926, **32,** 289
[5] Russell, J. L., & Rideal, E. K., *Proc. roy. Soc.*, [A] 1936, **154,** 540
[6] Taylor, H. F. W., *J. chem. Soc.*, 1950, p. 3682
[7] Noll, C. A., & McGuire, J. J., U.S.P. 2,307,366
[8] Ebler, E., & Fellner, M., *Ber. dtsch. chem. Ges.*, 1915, **44,** 1111 (cited from Eitel, W., ' The Physical Chemistry of the Silicates ', 1952 (The Univ. of Chicago Press)
[9] Sandell, E. B., ' Colorimetric Determination of Traces of Metals ', 1944 (New York : Interscience Publishers, Inc.)
[10] Piper, C. S., ' Soil and Plant Analysis ', 1951 (Adelaide Univ. Press)
[11] Cheng, K. L., Kurtz, T., & Bray, R. I., *Analyt. Chem.*, 1952, **24,** 1640
[12] Bloomfield, C., *J. Sci. Fd Agric.*, 1955, **6,** 641
[13] Osmond, D. A., ' Report on some Cyprus Soils ', 1954, Soil Survey of England & Wales (H.M.S.O.)

Appendix

The profile descriptions of the *terra rossa* soils from Cyprus are as under :

I. *Sample No. C_2 and C_3*

Site : Myrtou–Kambyli road.
Relief : flat area in wide, shallow depression
Underlying rock : limestone
Vegetation : occasional *Pinus halepensis*, polerium, thyme, asphodel, etc.
Horizons :

Depth, in.	Description
0–2	Red (2·5 YR 4/6, dry) clay ; moderate number of limestone (crust) fragments ; hard, fine granular structure when dry ; little organic matter, very few roots ; friable at surface ; plastic when moist ; slightly calcareous ; no fauna seen ; merging boundary.
2–12	Red (10 YR 4/6, dry) clay with fewer limestone fragments ; fine to medium granular structure when dry ; no organic matter, very few roots ; hard when dry, plastic when moist ; slightly calcareous ; no fauna seen ; sharp boundary.
Below 12	Hard limestone rock.

Samples taken at 0–2 in. (sample No. C_2) and 12–14 in. (sample No. C_3).

II. *Sample No. C_{12}*

Locality : Karst area
Genetic type ; *terra rossa*
Underlying rock : St. Hilarian limestone (Jurassic)

Horizons :

Depth, in.	Description
0–3	Red (2·5 YR 4/6) clay, looks sandy cracked in box ; slightly hard, coarse to medium granular ; plant roots many ; little shrinkage.
Below 3	Limestone rock.

Sample No. C_{12} represents the surface soil horizon.

MINERAL COMPOSITION OF HERBAGE IN RELATION TO THE DEVELOPMENT OF HYPOMAGNESAEMIA IN GRAZING CATTLE

By J. A. F. ROOK and MARIAN WOOD

In studies of the effect of fertiliser treatment on the incidence and severity of hypomagnesaemia in grazing cows, determinations of inorganic constituents were made of herbage samples from the swards grazed. From the values obtained, some of the mineral indices of Brouwer[3a, b] and t'Hart & Kemp[2] were calculated for the individual experimental plots and their relationship to the observed incidence of hypomagnesaemia examined. For a given sward in a given season, the severity of hypomagnesaemia in cows grazing plots given different fertiliser treatments, generally increased as the alkaline earth alkalinity (Ca + Mg − P, expressed as mequiv./100 g. silica-free herbage dry matter) of the herbage decreased. None of the other mineral indices considered showed a consistent relationship with the severity of hypomagnesaemia.

Although the mineral composition of herbage may influence the development of hypomagnesaemia in grazing cattle, the effects of the palatability of herbage on dry matter (and hence magnesium) intake and of food factors other than minerals on the availability of herbage magnesium, preclude the use of mineral composition of herbage to assess the likelihood of the occurrence of hypomagnesaemia in grazing cattle.

Introduction

Dutch workers have frequently claimed that pastures in Holland which produce a high incidence of hypomagnesaemia and tetany in grazing cows show a characteristic mineral composition (see Sjollema,[1] t'Hart & Kemp[2] and Brouwer[3a, b]). Work at this Institute[4] showed that hypomagnesaemia in grazing cattle results from a combination of a low intake and a poor assimilation of magnesium from the grazed herbage, in comparison with typical winter foods. Although there is little published information on the factors that affect the assimilation of feed magnesium, the results of Stewart & Moodie[5] suggest that different salts of magnesium are absorbed to different extents and it seems reasonable that the mineral composition of herbage, and of feeds in general, should influence the absorption of magnesium from the gut.

Over the past seven years, a number of field investigations of the relationship between pasture management and the incidence and severity of hypomagnesaemia in grazing cattle have been carried out at this Institute.[6, 7] Many of the herbage samples taken during these investigations have now been analysed for mineral composition in detail and the results are reported in this paper. Using these results, an attempt has been made to relate the mineral composition of herbage to the severity of hypomagnesaemia in cattle grazing the swards.

Experimental

Details of experiments

A full account of the field investigations during which the herbage samples were collected has been given previously (Bartlett et al.[6, 7]). Relevant details are summarised in Table I.

Collection of herbage samples

Swards were sampled immediately in front of the fold wire at intervals throughout the grazing period. Herbage was cut with hand shears, at about 2 in. above soil level, from a number of areas measuring 1 ft. × 4 ft., the position of the areas being determined by a system of random pacing. Every effort was made to avoid contamination of the sample with soil; slight contamination would inevitably occur as the result of splashing during rain, but this contamination would be typical for the herbage consumed by the animal. The samples were bulked and a suitable quantity of herbage was dried to constant weight at 100° and then milled and stored in a loosely stoppered container until required.

Methods of analysis

Sub-samples of air-dry herbage were analysed as follows.

Moisture was determined gravimetrically by drying to constant weight at 100°.

Calcium, magnesium, potassium, sodium and silica were determined on duplicate 5-g. samples. The removal of organic matter was accomplished by a double-ashing procedure, which incorporated the determination of silica (Piper[8]). The ash was dissolved in dilute HCl and then made to a known volume with distilled water. Suitable dilutions of this solution were used for the determination of sodium and potassium by means of an 'EEL' flame photometer. Corrections were made for the interference of calcium and potassium in the determination of sodium. A suitable aliquot of the acid extract of the ash was evaporated to dryness and used for the determination of calcium and magnesium, according to the method of Davidson.[9]

For the determination of phosphorus and sulphur, a sub-sample of herbage was moistened with a solution of magnesium nitrate, heated to dryness and then ashed at 500°. The ash was dissolved in a slight excess of HNO_3 and diluted to a known volume. A suitable aliquot was used for the colorimetric determination of phosphorus as the vanado-molybdate complex (see Hanson[10]). A further aliquot was used for the gravimetric determination of sulphur as barium sulphate.[11]

Chloride was determined on a further sub-sample of herbage by an adaptation of the wet digestion procedure described by Davies.[12]

Results

The mean results for the mineral composition of the various swards are given in Table I, together with the means of the lowest observed blood-serum magnesium levels for the cattle grazing the swards. The occurrence of symptoms of grass tetany is also noted in the Table but the mean minimum serum-magnesium values given are considered to be the best measure of the tetany-producing capacity of the swards. The periods during which the swards were grazed and samples taken for analysis varied from 9 days in Expt. III to 21 days in Expt. I. To allow a satisfactory comparison of the mineral composition of the swards to be made and to demonstrate changes in herbage composition observed with advancing stage of growth, the results from Expt. I have been given as mean values over the first twelve and the last nine days of grazing.

Effect of sward and fertiliser treatment on mineral composition

Magnesium.—With the exception of the plots dressed with calcined magnesite, the magnesium contents of the herbage fell within a normal range of 0·09–0·16 g. per 100 g./dry matter. The magnesite-treated plot produced herbage with a magnesium content of about twice the mean level for the other plots. No systematic change in magnesium content occurred with stage of growth. The predominantly cocksfoot sward used over the period 1952–55 in Expts. I–III showed a progressive decrease in magnesium content to about two-thirds of the initial level in all but the magnesite-treated plot. In any particular season, however, the ammonium sulphate-treated plot had a significantly higher (P < 0·05) magnesium content than the control plot. This was observed also in Expt. VI with a timothy/meadow fescue sward when nitrogen was given as Nitro-chalk but not when it was given as ammonium sulphate. On only one occasion was a direct assessment of the effect of potash fertiliser application possible (Expt. II) and then a significant (P < 0·05) reduction in magnesium content of the herbage dry matter was observed.

Calcium.—With one exception, the values for calcium content of the various swards fell within the range of 0·26–0·63 g./100 g. dry matter. A high value of 0·87 g./100 g. dry matter was obtained for the sward grazed over the first 12 days in Expt. I, plot C, which is accounted for by the high proportion (about 50%) of clover in the sward. The clover growth was chemically depressed the following year and when the plot was used two years later in Expt. II C, the sward had a more typical calcium content of 0·41 g./100 g. dry matter. In general, a progressive decline in calcium content occurred throughout the period of grazing as is indicated by the results presented for Expt. I. Nitrogen, applied as ammonium sulphate, significantly (P < 0·05) decreased the calcium content (Expts. II and III) but, as would be expected, the application of Nitro-chalk on plot B in Expt. VI produced a significant (P < 0·05) increase in the calcium content of the sward.

Table I

Mineral composition of herbage samples from experimental plots, together with mean minimum blood-serum magnesium levels of animals grazing the plots

Expt. no.	Location and sward†	Fertiliser applied per acre††	Period over which samples were taken	No. of samples on which mean values are based	Silica, % of dry matter	Ca	Mg	Na	K	P	S	Cl	Means of lowest-observed blood serum magnesium levels in the individual cattle grazing the plot (no. of cattle on which the mean is based in brackets)
						←(as a % of silica-free dry matter)→							
I A	Churchlands, Church Farm, N.I.R.D., Shinfield (S.143 7 lb.; S.37 7 lb.; S.100 3 lb./acre, sown 1951)	2·5 cwt. T.S.P., 12/2/52; 25 cwt. calcined magnesite 22/2/52; 3 cwt. S/A, 24/2/52; 3 cwt. S/A, 12/3/52	17/4/52 to 29/4/52; 29/4/52 to 10/5/52	4; 3	3·42; 2·31	0·37; 0·26	0·27; 0·23	0·09; 0·10	1·77; 1·60	0·80; 0·67	0·48; 0·26	0·65; 0·54	1·63 (4)
I B	,,	2·5 cwt. T.S.P., 12/2/52; 3 cwt. S/A, 24/2/52; 3 cwt. S/A, 12/3/52	17/4/52 to 29/4/52; 29/4/52 to 10/5/52	4; 3	3·65; 2·08	0·39; 0·33	0·16; 0·15	0·14; 0·15	1·44; 1·73	1·02; 0·99	0·50; 0·51	0·38; 0·26	0·86 (8)*
I C	,,	2·5 cwt. T.S.P., 12/2/59; 4 cwt. K.S., 22/2/52	17/4/52 to 29/4/52; 29/4/52 to 10/5/52	4; 3	3·46; 2·60	0·87; 0·65	0·14; 0·14	0·08; 0·07	1 74; 1·75	0·91; 0·85	0·41; 0·40	0·52; 0·67	1·63 (6)
II A	,,	2 cwt. T.S.P., 12/3/54; 3 cwt. S/A, 3/4/54**	14/5/54 to 27/5/54	5	2·06	0·37	0·28	0·36	2·32	0·45	0·54	0·67	1·83 (4)
II B₁	,,	2 cwt. T.S.P., 12/3/54 3 cwt. S/A, 3/4/54	14/5/54 to 27/5/54	5	2·25	0·39	0·13	0·31	2·44	0·46	0·53	0·49	0·88 (4)
II B₂		2 cwt. T.S.P., 12/3/54	14/5/54 to 27/5/54	5	2·59	0·49	0·12	0·24	2·19	0·43	0·34	0·50	1·90 (3)
II C		2 cwt. T.S.P., 12/3/54; 4 cwt. K/S, 12/3/54	14/5/54 to 27/5/54	5	2·28	0·41	0·10	0·09	2·92	0·43	0·35	0·64	1·50 (3)
III B₁	,,	2½ cwt. F.37, 5/2/55; 2¼ cwt. S/A, 18/3/55; 2 cwt. S/A, 15/4/55	11/5/55 to 20/5/55	5	1·73	0·33	0·11	0·25	2·99	0·51	0·44	1·23	0·96 (4)
III B₂	,,	2½ cwt. F.37, 8/2/55	11/5/55 to 20/5/55	5	2·12	0·42	0·10	0·16	2·73	0·47	0·29	1·04	1·61 (4)
IV	Bridgett's Experimental Farm, Martyr Worthy, Hants. (S.143 4 lb.; I.R.G. 3 lb.; S.23 2 lb.; S.24, 10 lb.; S.48 4 lb.; W.W.C. 1 lb./acre; undersown 1953)	2 cwt. F.37, Dec. 1953; 2 cwt. S/A, Mar. 1954	13/4/54 to 13/5/54	5	2·88	0·49	0·09	0·18	2·34	0·31	0·50	0·64	1·48 (6)*
V	Aborfield Hall Farm, N.I.R.D., Shinfield (S.143 6 lb.; S.37 6 lb./acre, sown 1951)	4 cwt. N.C., 13/4/54	12/5/54 to 26/5/54	3	1·78	0·53	0·11	0·27	2·40	0·39	0·37	1·03	1·47 (6)
VI A	Lower Ryeish, Church Farm, N.I.R.D., Shinfield (S.215 4 lb.; S.53 4 lb.; S.51, 4 lb.; S.100 2 lb./acre, sown 1949)	2½ cwt. F.37, 8/2/55; 2½ cwt. S/A, 18/3/55; 2½ cwt. S/A, 15/4/55	27/4/55 to 6/5/55	5	2·59	0·54	0·11	0·03	2·99	0·47	0·58	0·96	0·87 (2)
VI B	,,	2½ cwt. F.37, 8/2/55; 3 cwt. N.C., 18/3/55; 3 cwt. N.C., 15/4/55	27/4/55 to 6/5/55	5	2·47	0·63	0·13	0·14	3·11	0·49	0·45	1·27	1·27(2)
VI C	,,	2½ cwt. F.37, 8/2/55	27/4/55 to 6/5/55	5	3·86	0·55	0·11	0·04	2·44	0·44	0·41	0·87	0·79 (2)

* Cases of clinical tetany observed   ** 25 cwt./acre of calcined magnesite applied in 1952 (see Expt. I A)
† S.37, S.143, strains of cocksfoot; I.R.G., Italian ryegrass; S.53, S.215, strains of meadow fescue; S.23, S.24, strains of perennial ryegrass; S.48, S.51, strains of timothy; S.100 strain of white clover; W.W.C., wild white clover.
†† F.37, Fison's 37 (16% K₂O, 14·5% sol. P, 1·5 insol. P); K.S., sulphate of potash; T.S.P., triple superphosphate; N.C., Nitro-Chalk; S/A, sulphate of ammonia.

Potassium.—Variations in the potassium content of the swards were not extreme and even on plot C, of Expts. I and II, which received annually from 1952 to 1954 4 cwt. of sulphate of potash per acre, the highest mean value obtained was 3% of the dry matter. (Equally high figures were obtained for the sward grazed in Expt. VI which received only a small application of potash in a mixed fertiliser.) Application of potash fertiliser had no effect on the potassium content of the sward in the first season, but in the third season (Expt. II) the sward on the potash-treated plot had a significantly ($P < 0.05$) higher potassium content than the swards on either the control or nitrogen-treated plots. An effect in the first season may have been masked by the high proportion of clover in the sward on the potash-treated plot.

A progressive increase in the potassium content of the herbage from all plots used in Expts. I, II and III occurred over the period 1952–55. In Expts. II, III and VI, the application of nitrogenous fertiliser, as either ammonium sulphate or Nitro-chalk, gave a small but significant increase in the potash content of the herbage. This is the reverse of the effect generally found by Stewart & Holmes.[13]

Sodium.—A tenfold variation in the sodium content of the herbage dry matter was observed from sward to sward, with a value as low as 0.03–0.04% for the sward grazed in Expt. VI. Sodium contents as low as 0.04–0.05% are not exceptional, and values as low as 0.01% have been obtained for certain swards in South Africa.[14] Application of ammonium sulphate in Expts. II and III significantly increased the sodium content of herbage but with the sward grazed in Expt. VI, in which the sodium content was low, the application of either ammonium sulphate or Nitro-chalk had no effect. Application of potash fertiliser in Expt. II produced a marked depression in sodium content.

Phosphorus.—The most marked variation in phosphorus content observed was a decrease in phosphorus content of the sward used in Expts. I, II and III over the period 1952 (Expt. I) to 1955 (Expt. III). The phosphorus content of herbage appeared to be independent of fertiliser treatment.

Sulphur.—Variations in sulphur content in general were small, but the application of ammonium sulphate to a sward consistently increased the sulphur content.

Chloride.—Variations in chloride content from 0.3 to 1.3% were observed, but no consistent variations were apparent.

Relationship between mineral composition of the sward and the incidence of hypomagnesaemia

Magnesium.—The most striking contrast in magnesium content was achieved in Expts. I and II with a cocksfoot sward, treated with 6 cwt. of ammonium sulphate/acre, in a comparison of 0 (plots B or B_1) and 25 (plot A) cwt. of calcined magnesite/acre applied to the sward shortly before the beginning of the first grazing season (1952). The magnesium content of the sward on the magnesite-treated plot was about double that of the untreated plot. In both seasons, the severity of hypomagnesaemia was markedly less on the magnesite-treated plot, but in each of the grazing seasons reported, one of four cows grazing the plot showed a fall in blood-serum magnesium to 1.0 mg./100 ml.

Potassium.—No consistent relationship between the potassium content of a sward and the degree of hypomagnesaemia in cattle grazing it, was present, even when the magnesite-treated plot was excluded. In Expt. II, however, in which a direct assessment of the effect of potash fertiliser was possible, the potash-treated sward produced a greater degree of hypomagnesaemia in grazing cattle than did the control sward. The same effect was observed[7] in the previous grazing season (1953), for which results are not reported in the present paper. The most marked difference in the mineral composition of the swards of the potash and control plots was the higher potassium and lower sodium content of the potash-treated sward.

Other minerals.—No relationship between the calcium, sodium, phosphorus, sulphur or chloride content of the herbage and the degree of hypomagnesaemia in grazing cattle was observed.

Mineral ratios.—The values given in Table I were first converted to mequiv./100 g. dry matter (for the purposes of this conversion it was assumed that phosphorus was present solely in the form of PO_4^{3-}) and then used to calculate various mineral indices (Table II) which, according to other workers,[2, 3] are related to the incidence of tetany in grazing cattle.

Table II

Characteristic indices of mineral composition of swards, in relation to the development of hypomagnesaemia
(Indices calculated from mineral contents expressed in mequiv.)

Expt. plot no.	Days from the commencement of grazing for which calc. values are representative	$\frac{K}{Mg}$	$\frac{K}{Na}$	$\frac{K}{Ca}$	$\frac{K}{Ca+Mg}$	$\frac{K}{Ca+Mg+Na}$	$\frac{K}{Na+Ca}$	$\frac{K}{K+Na+Ca+Mg}$	$Ca+Mg-P$	$K+Na-Cl-S$	$\frac{(Ca+Mg+Na+K)}{-(P+Cl+S)}$	$\frac{K\times100}{K+Ca+Mg}$	$\frac{Na\times100}{K+Na+Ca+Mg}$	Means of the lowest observed blood-serum magnesium levels in individual cattle grazing the plots mg./100 ml.
I A	12	2·06	11·28	2·49	1·13	1·02	2·04	0·51	−36·7	−9·1	−45·8	53·0	4·48	1·63
I B	12	2·79	6·02	1·89	1·13	0·95	1·44	0·49	−66·1	1·0	−65·0	53·0	8·09	0·86
I C	12	3·79	13·74	1·02	0·81	0·76	0·95	0·43	−26·9	7·8	−19·2	44·7	3·15	1·63
II A	14	2·62	3·84	3·20	1·44	1·05	1·74	0·51	−2·1	25·1	23·0	59·0	13·33	1·83
II B$_1$	14	5·79	4·68	3·20	2·06	1·43	1·90	0·59	−14·3	29·2	14·9	67·3	12·57	0·88
II B$_2$	14	5·86	5·23	2·28	1·64	1·25	1·59	0·56	−7·5	−31·6	−39·1	62·2	10·63	1·90
II C	14	8·74	18·83	3·67	2·58	2·27	3·07	0·69	−12·9	39·1	26·2	72·1	3·69	1·50
III B$_1$	9	8·45	7·13	4·64	3·00	2·11	2·81	0·68	−24·0	25·2	1·2	75·0	9·51	0·96
III B$_2$	9	8·38	9·82	3·34	2·39	1·92	2·49	0·66	−15·9	29·6	13·7	70·5	10·09	1·61
IV	17	8·59	8·57	2·63	2·01	1·63	2·01	0·62	−0·6	24·6	24·1	66·8	7·23	1·48
V	14	7·11	5·23	2·35	1·77	1·32	1·62	0·57	−2·6	21·2	18·7	63·8	10·88	1·47
VI A	10	8·10	69·42	2·82	2·09	2·03	2·71	0·67	−8·8	14·0	5·2	67·7	0·97	0·87
VI B	10	7·61	57·24	2·53	1·90	1·84	2·42	0·65	−5·7	17·2	11·6	65·5	1·13	1·27
VI C	10	6·74	40·86	2·26	1·69	1·62	2·14	0·62	−5·9	12·1	6·2	62·9	1·51	0·79

Of the various indices considered, only Ca + Mg − P showed a reasonably consistent variation with the degree of hypomagnesaemia and only then for a given sward as it varied with management in any season. In any particular experiment, Ca + Mg − P was generally more negative the higher the degree of hypomagnesaemia (see Fig. 1).
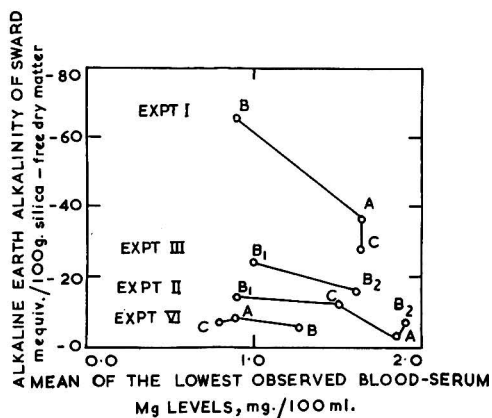
FIG. 1.—*The relationship between the severity of hypomagnesaemia in grazing cows and the alkaline earth alkalinity (Ca + Mg − P, in mequiv./100 g. silica-free dry matter) of the sward*

The ratios $\dfrac{K\times100}{K+Ca+Mg}$ and $\dfrac{Na\times100}{K+Na+Ca+Mg}$, to which t'Hart & Kemp[2] attach particular significance, showed no consistent variation with an increase in the degree of hypomagnesaemia. Such ratios are clearly dependent almost wholly on the potassium and sodium contents of a sward and are likely to be most markedly influenced by an application of potash fertiliser which, it is well known, increases considerably the potassium and decreases the sodium content of herbage. That such values are of greater use than solely the potassium or sodium contents of a sward is questionable.

Discussion

The possibility of a causal relationship between the mineral composition of pasture and the incidence of 'grass tetany' in grazing cattle was first proposed by Sjollema[1] in 1932 on the basis

of observations showing that a high potassium content in pasture was frequently associated with a high incidence of the disease during the spring grazing period. This empirical approach to the study of the factors producing hypomagnesaemia was extended by Brouwer[3] who claimed that for swards which produced a high incidence of tetany in grazing cattle, a characteristically high figure for the alkali-alkalinity (the sum of $K + Na - Cl - S$, when expressed in mequiv./ 100 g. herbage dry matter) and a characteristically low figure for the alkaline earth alkalinity (the sum of $Ca + Mg - P$, when expressed in mequiv./100 g. herbage dry matter) was obtained. Characteristically high or low values for many other mineral indices, most of which appear to have little or no physiological basis, have since been observed for pastures that have produced a high incidence of tetany in the grazing animal.[2, 3b]

The present results do not show a general relationship between the degree of hypomagnesaemia in grazing cattle and the concentration of any particular mineral constituent or the magnitude of any mineral index. That this should be so seems reasonable in view of the results of earlier work[4] in which the development of hypomagnesaemia was shown to be dependent on the magnesium intake, its assimilation and the magnesium requirements of the cow for milk production and body storage. Variations in herbage intake and in the requirements of the cow for magnesium could be expected to offset or to make more critical any effect that mineral composition might have on the assimilation of the herbage magnesium.

For a particular sward and under any given set of grazing conditions, however, an increase in the severity of hypomagnesaemia, brought about by the application of nitrogenous or potash fertilisers, generally was associated with a lowering of the alkaline earth alkalinity ($Ca + Mg - P$) of the grazed herbage. This was true also for the results of Brouwer[3] and t'Hart & Kemp.[2] That the alkaline earth base excess should influence the degree of hypomagnesaemia, presumably through an effect on magnesium absorption, seems reasonable and that the effect should not be apparent in comparisons involving different swards and different seasons is in accord with the probable importance of other factors such as palatability of the herbage, magnesium content of herbage dry matter, etc.

In Expts. I and II, the considerable increase in the magnesium content of the sward achieved by the application of a massive dressing of calcined magnesite was associated with a marked reduction in the degree of hypomagnesaemia observed, which is in line with the known value of oral supplements of magnesium for the control of hypomagnesaemia.[15, 16] Furthermore, the increased degree of hypomagnesaemia in cattle grazed on the potash-treated plot in Expt. II C, was associated with an increase in the potassium content and a decrease in the sodium content of the herbage dry matter. This effect of potash fertiliser on the occurrence of hypomagnesaemia and on herbage composition is now well known and it seems likely that any straight-forward comparison of potash versus no potash fertiliser application must give a consistent relationship between the degree of hypomagnesaemia and the herbage content of potash or sodium, or of the magnitude of any mineral indices that are affected primarily by potassium and sodium content. The massive application of potash to certain pastures in the Netherlands in the past, as a result of their system of husbandry, could well account for the relationships reported by Dutch workers between the various mineral indices which they have considered and the incidence of tetany that has been observed. It cannot be concluded, however, that such changes in the mineral make-up of herbage are necessarily responsible for the increase in the incidence of tetany.

The results presented here suggest that changes in the magnesium content, the potassium content and the alkaline earth base excess of a sward are associated with, and thus may possibly lead to a change in, the incidence of hypomagnesaemia in grazing cattle. It is, however, clear that in assessing the likelihood of the occurrence of tetany in cattle grazing a particular pasture, these effects would have to be considered together with the effects of herbage intake, herbage dry matter content and any other food factor (such as herbage nitrogen content, see Head & Rook[17]) that may influence the intake or availability of herbage magnesium. Any attempt to use a single sward characteristic as a general diagnostic test for a pasture that is likely to produce a high incidence of hypomagnesaemia and tetany in the grazing cow must inevitably fail.

References

1 Sjollema, B., *Tijdschr. Diergeneesk.*, 1932, **59**, 57, 329
2 t'Hart, M. L., & Kemp, A., E.P.A. Project 204, O.E.E.C. Conf., Utrecht, Sept. 1957, p. 193
3 Brouwer, E., (a) *Brit. vet. J.*, 1952, **108**, 123 ; (b) E.P.A. Project 204, O.E.E.C. Conf., Utrecht, Sept. 1957, p. 161
4 Rook, J. A. F., & Balch, C. C., *J. agric. Sci.*, 1958, **51**, 199
5 Stewart, J., & Moodie, E. W., *J. comp. Path.*, 1956, **66**, 10
6 Bartlett, S., Brown, B. B., Foot, A. S., Head, M. J., Line, C., Rook, J. A. F., Rowland, S. J., & Zundel, G., *J. agric. Sci.*, 1957, **49**, 291
7 Bartlett, S., Brown, B. B., Foot, A. S., Rowland, S. J., Allcroft, R., & Parr, W. H., *Brit. vet. J.*, 1954, **110**, 3

8 Piper, C. S., 'Soil and Plant Analysis', 1950, 1st Edn (Adelaide University Press.)
9 Davidson, J., *Analyst*, 1952, **77**, 263
10 Hanson, W. C., *J. Sci. Fd Agric.*, 1950, **1**, 172
11 'Methods of Analysis of Ass. off. agric. Chem.', 6th Edn, 1945 (Menasha, Wis.: George Banta Publ. Co.)
12 Davies, W. L., *Analyst*, 1932, **57**, 79
13 Stewart, A. B., & Holmes, W., *J. Sci. Fd Agric.*, 1953, **4**, 401
14 Russell, F. C., & Duncan, D. L., *Tech. Commun. Commonw. Bur. Anim. Nutr.*, 1956, No. 15
15 Allcroft, R., *Vet. Rec.*, 1954, **66**, 517
16 Line, C., Head, M. J., Rook, J. A. F., Foot, A. S., & Rowland, S. J., *J. agric. Sci.*, 1958, **51**, 353
17 Head, M. J., & Rook, J. A. F., *Proc. Nutr. Soc.*, 1956, **16**, 25

ANTIOXIDANTS IN DRY FAT SYSTEMS: INFLUENCE OF THE FATTY ACID COMPOSITION OF THE SUBSTRATE

By C. H. LEA

The activities of a number of antioxidants have been compared at 37° and 50° in purified distilled methyl esters of cottonseed, linseed and cod liver oil fatty acids, to which a small quantity of the pre-oxidised ester had been added as ' starter '. Relative activities were found to vary considerably with the fatty acid composition of the substrate and with the temperature and level of oxidation at which the measurements were made.

Introduction

While there is no doubt that the only completely reliable criterion of the usefulness or otherwise of an antioxidant is its performance in the commodity it is desired to stabilise under practical processing and storage conditions, testing in this way is too slow and laborious for the examination of any considerable number of compounds and the great majority of substances in current use have been discovered initially by the use of simple, rapid, accelerated tests. Increase in the rate of oxidation has most frequently been brought about by heating in air or oxygen at some constant temperature between 60 and 115°, commonly at or near 100°, the progress of the accelerated oxidation being followed by measurement of the volume of oxygen absorbed or by titration of the peroxides produced. Lard has most frequently been used as substrate, but other fats or distilled methyl esters have sometimes been employed.

Of the wide variety of procedures of this type used to date only one has achieved any considerable measure of adoption as a standard method : the AOM or ' active oxygen ' method, after many years' use in the U.S.A. and more recently in Europe has been adopted by the

American Oil Chemists' Society as a tentative standard method for evaluating the stability of oils, including those containing antioxidants.[1]   In this method cleaned, dry air is bubbled at a controlled rate through a number of tubes of fat maintained at 97·8° and the number of hours required for the fat to reach an arbitrarily chosen peroxide value of 125 mequiv./kg. (62·5 μmoles/g.) is determined.

An even more rapid method which has recently found some favour for use with fats or foods is the oxygen 'bomb' method[2] of the petroleum industry, in which the oxidisable material is heated at 100° under pressure in an oxygen-filled vessel and the pressure recorded on a chart until the sharp reduction which indicates the end of the induction period.

A third type of procedure which has the advantage of requiring very little specialised equipment is the oven-testing method, as exemplified by that of Everson *et al.*[3]   In this method a number of aliquots of lard, with and without antioxidant, are held in small beakers at 100° and the time to reach a peroxide value of 20 mequiv./kg. (10 μmoles/g.) (the 'induction period') is determined.

Doubts have often been expressed, however, concerning the validity of high-temperature testing as a guide to behaviour under more normal storage conditions and a limited number of investigations have been carried out at lower temperatures using more highly unsaturated fats or esters as substrate or employing acceleration by means other than heat to achieve results in a reasonable period.   Paquot & Mercien,[4] for example, compared the activities of antioxidants at 30° by using as substrate the distilled esters of linseed oil acids, determinations of the peroxide value being made at intervals.

In investigations on the antioxidant activity of the tocopherols[5] no difficulty was experienced in obtaining consistent and reproducible results at 90° in the distilled methyl esters of lard fatty acids, but some trouble was found at 50° in pure methyl linoleate and at 37° or 25° consistent results could not be obtained.

Lundberg & Chipault[6] had previously observed that methyl linoleate, when sufficiently purified, shows quite a long and irreproducible lag period before oxidation commences, even at temperatures as high as 40 or 60°, presumably owing to a lack of chain-starting free-radicals in the system.   Once a little hydroperoxide has been formed it can break down by thermal decomposition, or more rapidly under the influence of a metal or metal-containing catalyst or of light, to give free-radical fragments which can abstract hydrogen from the reactive methylene groups of the unsaturated compounds to initiate the reaction chains.

Bolland & ten Have[7] added benzoyl peroxide as an initiator in studies of the action of antioxidants in ethyl linoleate at 45° and, more recently, Bickel & Kooyman[8] compared the chain-breaking efficiencies of phenolic inhibitors in a system in which the thermal decomposition of 2,2,3,3-tetraphenylbutane in the presence of oxygen at 60° provided free radicals to initiate the chain oxidation of 9,10-dihydroanthracene.   In both of these cases the quantity of the external chain starter used was large and the activity of the antioxidant was measured by its depressing effect on the initial rate of oxidation, rather than (as is usual in edible fat systems) by its effect in increasing the duration of an induction period.   It seems doubtful whether results obtained in such artificially accelerated systems, or in the presence of added metal-containing pro-oxidants, will bear a sufficiently close relationship to results in the absence of the accelerator.

For purpose of the present work it was felt that the most satisfactory procedure for the testing of antioxidants at moderate temperatures would be to use a fatty substrate which had been freed as completely as practicable from natural antioxidants, peroxides and metallic contaminants, and then to add a known very small proportion of fat hydroperoxide prepared from the same material as 'starter'.   This would be sufficient to eliminate the erratic and irreproducible lag phase which is liable to be displayed by the purified esters in its absence, but would not otherwise alter the characteristics of the system.   The amount of fat hydroperoxide added in the experiments reported in the present paper has been 1 μmole/g., corresponding approximately to 0·03% on a weight basis.

It was felt that too little attention has been paid in the past to the possible effects of fatty acid composition of the substrate on the relative effectiveness of antioxidants and this factor has been considered in the present work.

Experimental

Preparation of the esters

Cottonseed, linseed and cod liver oils were used to prepare substrate esters of varying fatty acid composition ; the two former were freshly refined and the last, fresh ' medicinal '.

Sodium wire (4 g.) was dissolved in methanol (800 ml.) and refluxed with the oil (1000 g.) for 1 h. After removal of part of the solvent by distillation the residual esters were washed with warm water until free from alkali, dried over anhydrous Na_2SO_4 and passed in succession through two 20 cm. × 2·5 cm. columns of alumina (Merck) to remove oxidation products, antioxidants and pigments. The purified esters were distilled at a few mm. pressure with a CO_2 ' bleed ' through a short column, small first and last fractions being rejected. They were then colourless and gave no reaction for tocopherols by the 2,2'-dipyridyl method.

The main bulk of the distilled esters was then tinted yellow by the addition of 0·001% synthetic β-carotene, ampouled in 10-ml. quantities, evacuated on a manifold, sealed off, heated in a silicone oil bath at 200° for 30 min. to destroy any traces of peroxide present and stored at −20° until required.

The remaining smaller portion of the distilled esters was oxidised in a free supply of air (provided either by spreading in a layer a few mm. thick or by shaking), usually at 37°, to a peroxide value of 25–50 μmoles/g. The peroxidised oil was then ampouled *in vacuo* in 2-ml. quantities and stored at −20° until required.

When required for use, oxidised ester was added to unoxidised ester to give a calculated initial peroxide value (p.v.) of 1 μmole/g. The mixed substrate could be held over solid CO_2 at −80° for a week or more if necessary before use.

Reproducibility within a run and between runs on the same batch of substrate was good but deteriorated when the constituents of the mixture were changed. It is possible that traces of reducing substances present initially or produced by heating the esters* may have depressed the initial peroxide value slightly below the calculated figure and that for maximum reproducibility between batches of substrate the initial p.v. should have been standardised to 1·0 by the de-aeration method. A further precaution to tighten up reproducibility between batches of substrate would be to add 0·01% of citric acid in order to complex minute traces of pro-oxidant metals still present after the distillation from glass. However, neither of these precautions was adopted in the present work where the main interest was to compare the behaviour of a number of antioxidants within a run.

Testing of antioxidants

The substance to be tested was added in 0·25 ml. of methanol, to the prepared substrate ester (5 ml.) in a stoppered tube and 0·2 ml. aliquots of the mixture were pipetted into a series of small cups made from 2 in. × 0·5 in. flat-bottomed specimen tubes cut down to 0·5 in. These were stored at the required temperature in a thermostatically controlled room (37°) or oven (50° or 60°). To facilitate sampling several of the cups were usually pipetted on each of two successive days, the ester–methanol mixture meanwhile being held over solid CO_2 at −80°. Bleaching of the carotene gave a useful indication of the end of the induction period but the peroxide range over which bleaching occurred varied with the different esters, being considerably higher with the linseed than with the cottonseed or cod liver esters.

Determination of peroxide values

Determination of the peroxide value was carried out by dropping a cup into a conical flask containing 10 ml. of glacial acetic acid–chloroform (3 : 2 by volume) and 1 ml. of (freshly prepared) saturated potassium iodide solution, mixing and titrating after keeping for 3 min. in the dark. The amount of ester in a cup (e.g., 174 mg.) was determined by dry weighing 0·2 ml. aliquots of the methanolic ester solution as delivered by the pipette used : multiplication of the titration by an appropriate factor (e.g., 5·75) then converted the titration to μmoles of peroxide/g. ester.

---

* American workers[9] have demonstrated the production of reducing substances in oils heated *in vacuo* to destroy peroxides, but only in quantity sufficient to interfere with the determination of tocopherol when the initial p.v. of the oil heated was above 50 μmoles/g.

The 0·002N-sodium thiosulphate solution (prepared by dilution from 0·1N) is standardised against 0·01N-potassium iodate. A 'blank' determination is carried out on the reagents without the ester and, if this should be zero, on the reagents plus iodate in place of ester to test for the presence of iodine-absorbing impurities in the solvents.

After use, the glass cups are cleaned with solvent and/or detergent, boiled with conc. H_2SO_4, rinsed free of acid with tap water, kept for several hours in glass-distilled water, rinsed with methanol and dried.

This simple peroxide determination gives reproducible although not strictly accurate results. It is quite adequate for routine use in stability testing where the large number of determinations to be carried out would be very time-consuming with a full de-aeration method.[10]

Antioxidants used

The antioxidants used in the present series of experiments included propyl gallate (PG); lauryl (dodecyl) gallate (LG); butylated hydroxyanisole (BHA, a mixture of 2- and 3-t-butyl-4-methoxyphenol, very largely the former); butylated hydroxytoluene (BHT, 2,6-di-t-butyl-4-methylphenol), all of which are on the current U.K. 'permitted list',[11] and mono-t-butylquinol (MBQ) and 2,5-di-t-butylquinol (DBQ). In addition, bis-compounds synthesised by condensing two molecules of the phenol with a molecule of formaldehyde were prepared from MBQ[12] ['bis-MBQ', 2,2'-methylenebis-(t-butylquinol)] and from 2,6-di-t-butylphenol ['bis-BHT', 4,4'-methylenebis-(2,6-di-t-butylphenol)], the latter by Dr. T. H. Simpson of the Torry Research Station, Aberdeen.

Expression of results

'*Protection factors*'.—The commonest method of describing the activity of a given concentration of an antioxidant in a particular substrate under a given set of conditions has usually been to express the result as a 'protection factor' or 'antioxidant index' defined as the ratio of the induction periods in presence and absence of the antioxidant. An alternative, and in some ways a better definition, divides the *extension* of the induction period by the induction period of the control. The protection factor obtained in this way is reduced by one unit, an inactive substance now giving a factor of 0 instead of 1 and pro-oxidants giving negative instead of fractional values.

Both of these factors are numerically very dependent on the length of the induction period of the untreated substrate, which explains why protection factors given by different workers often vary greatly.

Use of a standard substance.—To reduce this difficulty it is sometimes of advantage to run a standard antioxidant with each series, or at least with each new batch of substrate, and to compare the performance of the other antioxidants with this. Everson *et al.*[3] used catechol as a standard and expressed their results in terms of a 'catechol index', defined as the ratio of the extension of the induction period produced by any antioxidant to that produced by an equivalent molar concentration of catechol. Catechol, however, produces strong 'off' flavours in fats and is probably toxic, and it would seem that propyl gallate, which has been approved by all countries which issue a list of permitted antioxidants, is preferable for use as a standard.

Weight or molecular basis ?—While it is scientifically more informative to relate antioxidant activity to structure on a molar concentration basis it is improbable that regulations governing the addition of antioxidants to foods will ever be drawn up on other than a weight basis and for this reason it would seem of greater practical use to compare the performances of antioxidants at equal weight percentages.

At very low concentrations of antioxidants the relationship between concentration and activity, as measured by the extension of the induction period, is usually approximately linear and results on the molar basis can, without too much error, be transferred to the weight basis and vice versa. As the concentration of the antioxidant is increased, however, the activity observed usually fails to keep pace with the increase in concentration and this departure from linearity becomes serious at much lower concentration levels with some substances than with others.

Results

The curves in Figs. 1 and 2 are the means of closely agreeing duplicate runs. They show

a wide range of lengths of induction period, rates of oxidation during the induction period and peroxide values at which the induction period ends. A p.v. of 100 μmoles/g. has been taken as a convenient point at which the induction period is virtually over in all cases, and has been used to compare the extensions of the induction period which constitute one of the most reproducible criteria of antioxidant activity.
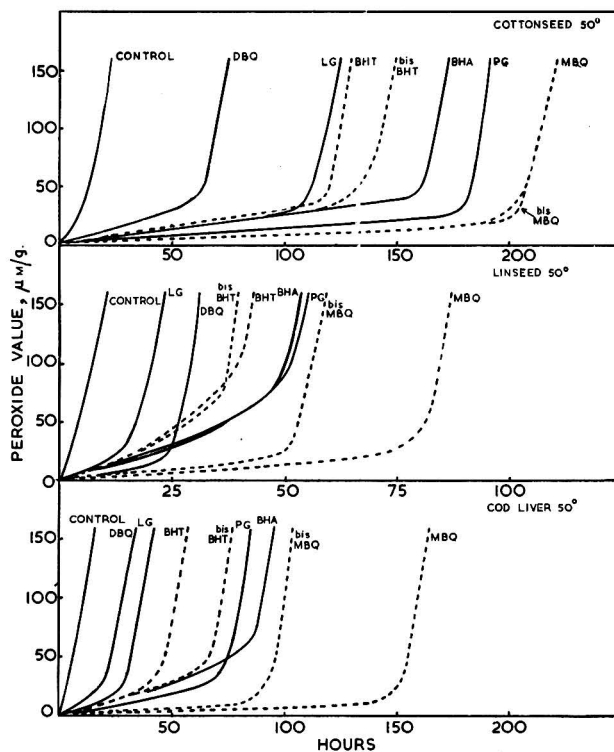

FIG. I.—*Effect of antioxidants at* 0·01% *in cottonseed, linseed and cod liver oil esters at* 50°
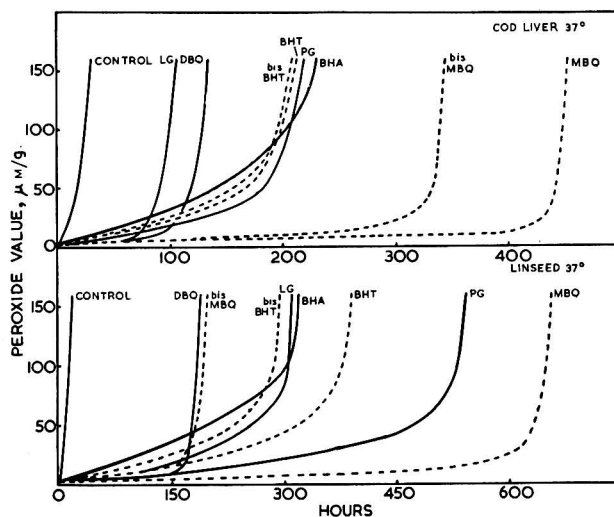

FIG. 2.—*Effect of antioxidants at* 0·01% *in cod liver and linseed oil esters at* 37°

Rates of oxidation during the induction period could not be compared so readily because the p.v./time curves, although in some cases practically linear for most of their length, in others deviated considerably from linearity. This deviation could take the form of a progressive increase in the rate of peroxide accumulation from the start or occasionally, when the induction period was long, of a plateau of almost constant p.v. which persisted for a considerable period before merging into the logarithmic phase associated with the end of the induction period. Times to reach p.v. of 10 and 25 μmoles/g. have therefore been used in Table I as an empirical measure of the rate of oxidation during the induction period. These values, particularly those at p.v. 10 are, however, subject to a greater error of determination and are likely to show poorer reproducibility than the times to p.v. 100.

Relative activities of propyl gallate, BHA and BHT

The overall average order of activity of the ' permitted ' antioxidants PG, BHA and BHT at the 0·01% level, in extending the induction period in the three ester systems was PG (1·0) > BHA (0·91) > BHT (0·74). BHA, however, was particularly effective in the cod liver oil esters (mean PG index 1·07).

Measured by their effects within the induction period (p.v. 25 and p.v. 10) BHA and BHT both averaged about two-thirds of the activity of PG, but there was a noticeable influence of temperature, BHA being rather more effective at 50° and BHT at 37°.

Propyl and lauryl gallates

On the basis of equimolecular activity lauryl gallate might be expected to show a PG index of 0·63. At the p.v. 100 level this ratio was approached in the cottonseed esters (0·60), but considerably lower factors (average 0·41) were found for the more unsaturated esters. At p.v. 25 or 10 these differences were not apparent and the average values for all three substrates were near the theoretical, although the ' scatter ' was considerable.

Bis-phenols

The widely used ' hindered phenol ' antioxidants BHA and BHT are appreciably volatile and hot foods containing BHA may have a slight phenolic odour. Moreover, both substances evaporate appreciably at high temperatures and may be lost during such processes as deodorisation, rendering, evaporation or dehydration.

From its structure ' bis-BHT ' might be expected to possess rather similar antioxidant properties to BHT, without its volatility, and in general, the two compounds were found to behave very similarly (Table I). Average PG indices for the two substances under all conditions were about the same (BHT 0·69, bis-BHT 0·70).

With MBQ and bis-MBQ the situation was rather different. In the cottonseed esters the two substances again showed virtually identical activity under all conditions (Table I), but in the cod liver esters at 50° and 37° and in the linseed esters at 50° the bis-compound was consistently only about two-thirds as active as the monomer and in the linseed esters at 37° its relative activity had fallen to one quarter.

Mono- and di-butylquinols

Substitution of alkyl groups and particularly of bulky *t*-butyl groups *ortho* to the phenolic hydroxyl in monohydric phenols, or in catechol derivatives, usually tends to increase antioxidant activity as well as fat-solubility, but in quinol derivatives antioxidant activity may be decreased. In the present experiments (Table I) the activity of DBQ ranged in cottonseed esters from 0·11 to 0·26, in linseed esters from 0·27 to 0·40 and in cod liver esters from 0·10 to 0·51 of that of MBQ, according to the temperature and level of oxidation at which the activities were compared, the overall average of all values being 0·26 : 1.

In parallel work[13] on the effect of antioxidants in inhibiting oxidation of the oil of herring meal stored at 20 or 25° a relative order of activity MBQ > BHT > DBQ has been observed, in keeping with the present results in ' model ' systems.

Effect of temperature

While the unstabilised esters showed a temperature coefficient of the order normally found

Table I

Effect of substrate, temperature and level of oxidation on the relative activity of antioxidants in fatty acid methyl esters

Protection factors* (propyl gallate index)

	Temp.	Cottonseed esters		Linseed esters		Cod liver esters	
		60°†	50°	50°	37°	50°	37°
Measured at p.v. 100							
Control (h.)		7·5	18·0	7·0	14·0	10·5	25·0
PG	3·4 (1·0)		9·3 (1·0)	6·4 (1·0)	37·9 (1·0)	6·6 (1·0)	7·2 (1·0)
LG	—		5·6 (0·60)	1·9 (0·30)	20·7 (0·55)	2·4 (0·36)	3·0 (0·42)
BHA	—		8·3 (0·89)	6·2 (0·97)	20·7 (0·55)	7·6 (1·15)	7·1 (0·99)
BHT	2·8 (0·82)		5·9 (0·64)	4·6 (0·72)	26·0 (0·69)	3·9 (0·59)	6·9 (0·96)
bis-BHT	3·0 (0·88)		7·0 (0·75)	4·3 (0·67)	19·1 (0·50)	5·8 (0·88)	6·8 (0·94)
MBQ	3·9 (1·15)		10·8 (1·16)	11·0 (1·72)	45·4 (1·20)	14·1 (2·14)	16·9 (2·35)
bis-MBQ	4·0 (1·18)		10·8 (1·16)	7·0 (1·09)	12·7 (0·34)	8·4 (1·27)	12·5 (1·74)
DBQ	—		2·8 (0·30)	3·0 (0·47)	12·2 (0·32)	1·6 (0·24)	4·1 (0·57)
Measured at p.v. 25							
Control (h.)			9·0	2·5	5·0	3·5	10·0
PG			18·1 (1·0)	7·1 (1·0)	63·7 (1·0)	16·7 (1·0)	12·0 (1·0)
LG			9·2 (0·51)	4·3 (0·61)	36·2 (0·57)	6·9 (0·41)	7·1 (0·59)
BHA			10·0 (0·55)	7·8 (1·10)	19·9 (0·31)	12·0 (0·72)	7·0 (0·58)
BHT			8·0 (0·44)	5·9 (0·83)	42·2 (0·66)	9·7 (0·58)	10·0 (0·83)
bis-BHT			9·6 (0·53)	6·0 (0·84)	27·6 (0·43)	11·1 (0·67)	9·0 (0·75)
MBQ			20·9 (1·16)	27·9 (3·93)	120 (1·88)	41·8 (2·50)	42·0 (3·50)
bis-MBQ			21·5 (1·19)	18·7 (2·63)	32·6 (0·51)	24·7 (1·48)	30·0 (2·50)
DBQ			4·1 (0·23)	8·8 (1·24)	33·4 (0·52)	4·1 (0·25)	10·2 (0·85)
Measured at p.v. 10							
Control (h.)			4·0	1·2	3·0	1·5	4·5
PG			12·7 (1·0)	6·0 (1·0)	52·0 (1·0)	16·0 (1·0)	11·2 (1·0)
LG			8·2 (0·65)	4·7 (0·78)	29·0 (0·56)	9·0 (0·56)	14·6 (1·30)
BHA			8·4 (0·66)	6·0 (1·00)	11·5 (0·22)	12·7 (0·79)	5·7 (0·51)
BHT			6·8 (0·54)	5·8 (0·97)	28·0 (0·54)	11·3 (0·71)	8·3 (0·74)
bis-BHT			8·4 (0·66)	6·0 (1·00)	19·2 (0·37)	11·3 (0·71)	7·9 (0·71)
MBQ			28·4 (2·24)	30·2 (5·03)	147 (2·83)	91·0 (5·69)	79·0 (7·05)
bis-MBQ			29·0 (2·28)	21·4 (3·57)	38·8 (0·75)	51·7 (3·23)	48·5 (4·33)
DBQ			3·2 (0·25)	12·2 (2·03)	50·2 (0·96)	4·7 (0·29)	19·9 (1·78)

* Ratio of times to reach indicated p.v.—1

† Data obtained by an earlier technique on the distilled C18 fraction of cottonseed methyl esters, without heating to destroy peroxide and without the addition of peroxide 'starter'.

for fat autoxidation, the effect of temperature on the length of the induction period was appreciably greater for several of the antioxidant-stabilised cod liver esters and much greater for most of the stabilised linseed esters (Table II). Obviously there was a tendency, more marked with the linseed than with the cod liver esters, for the antioxidant to be more effective at the lower storage temperature, but there seemed little regularity in the way in which this tendency operated. The stability of the linolenate hydroperoxides at the relevant temperatures is probably a factor.

Table II

Effect of temperature on the induction period of the stabilised esters

Antioxidant (0·01%)	Hours to p.v. 100					
	Linseed esters			Cod liver esters		
	37°	50°	Ratio	37°	50°	Ratio
None	14	7·0	2·0	25	10·5	2·4
PG	530	51·6	10·3	205	80·0	2·6
LG	304	20·4	14·9	99	36·0	2·7
BHA	304	50·4	6·0	203	90·0	2·3
BHT	378	39·4	9·6	198	51·5	3·8
bis-BHT	282	37·4	7·5	196	71·5	2·7
MBQ	650	89·3	7·3	448	159	2·8
bis-MBQ	193	56·0	3·4	338	99·0	3·4
DBQ	185	28·1	6·6	128	27·5	4·6

Discussion

The present attempt at measuring the protective effects of antioxidants in fatty substrates at temperatures nearer to normal than those generally used has given results of improved consistency by a comparatively simple technique, but marked effects of the fatty acid composition of the substrate and of the temperature of oxidation have been disclosed.

In cottonseed esters the unsaturated material primarily involved in the autoxidation will be linoleate, which is present at a concentration of about half of the total or two-thirds of the unsaturated esters. No more highly unsaturated material is present and the oleate present is much less readily oxidisable.

In the linseed esters methyl linolenate will usually be present to the extent of about one-half, or slightly more of the mixed esters, with linoleate present at only about one-third of this level. Since linolenate autoxidises at about twice the rate of linoleate it is likely to be the constituent mainly involved in the autoxidation of linseed esters.

Cod liver oil has a lower average unsaturation than linseed oil but contains a considerable proportion of very readily oxidisable polyunsaturated fatty acids with up to six double bonds which will undoubtedly play a major part in the early stages of the autoxidation of cod liver oil esters.

While some features, such as the high activity of MBQ, have tended to be common to all the conditions investigated, the considerable effect of the fatty acid composition of the substrate, and in some cases even of the slight change in temperature from 37 to 50°, on the relative activities of the inhibitors tested has been remarkable. The variability of these results emphasises the empirical nature of antioxidant testing and stresses the desirability of keeping as close as practicable in such tests to the conditions under which protection against autoxidation is required. There does not seem to be much prospect at present that any close correlation will be found between antioxidant activity on the one hand and such fundamental properties of the inhibitor molecule as its oxidation–reduction potential or free-radical stability, except as some complicated function also of substrate composition and temperature. Light, ionising radiation or metal-containing pro-oxidants would be likely also to provide disturbing influences, if present in the system.

The method described has been used successfully to compare the antioxidant activities of the several tocopherols at 60° and at 37°.[14]

Acknowledgment

References

[1] Report of the Fat Stability Sub-Commee, *J. Amer. Oil Chem. Soc.*, 1957, **34**, 394

[2] Stuckey, B. N., Sherwin, E. R., & Hannah, F. D., *J. Amer. Oil Chem. Soc.*, 1958, **35**, 581

[3] Everson, C. W., Miller, G. J., & Quackenbush, F. W., *J. Amer. Oil Chem. Soc.*, 1957, **34**, 81

[4] Pacquot, C., & Mercien, J., *Oleagineux*, 1958, **13**, 243

[5] Lea, C. H., & Ward, R. J., *J. Sci. Fd Agric.*, 1959, **10**, 537

[6] Lundberg, W. O., & Chipault, J. R., *J. Amer. chem. Soc.*, 1947, **69**, 833

[7] Bolland, J. L., & ten Have, P., *Trans. Faraday Soc.*, 1947, **43**, 201

[8] Bickel, A. F., & Kooyman, E. C., *J. chem. Soc.*, 1956, p. 2215

[9] Frankel, E. N., Cooney, P. M., Evans, C. D., & Cowan, J. C., *J. Amer. Oil Chem. Soc.*, 1958, **35**, 600

[10] Lea, C. H., *J. Soc. chem. Ind., Lond.*, 1946, **65**, 286 ; *J. Sci. Fd Agric.*, 1952, **3**, 586

[11] The Antioxidants in Food Regulations, 1958 (H.M.S.O.)

[12] Young, D. S., & McCulley, H. C., U.S.P. 2,763,672

[13] Lea, C. H., Parr, L. J., & Carpenter, K. J., *Brit. J. Nutr.*, 1958, **12**, 297 ; and in the press

[14] Lea, C. H., *J. Sci. Fd Agric.*, in the press

THE NITROGEN CONTENT OF GRASS LIGNIN

By D. L. WHITEHEAD* and G. V. QUICKE

Lignin from veld grass appears to contain nitrogen—partly in the form of -NCH₃ groups—which is not wholly removable by repeated purification with dioxan.

Introduction

The nitrogen present in the lignin, isolated by methods employing strong acid treatment, has been attributed, by nearly all workers in this field, to proteinaceous material bound to the lignin polymer.[1] The estimation of ' true ' lignin involves application of an appropriate correction—' ash-free ' lignin minus (N × 6·25)—to allow for the contamination.[2] Some investigators have claimed that the lignin molecule itself may contain atoms of nitrogen,[3] but the evidence is inconclusive.[4] ' Apparent ' (crude) lignin has never been prepared entirely free of nitrogen, but the fraction (called ' dioxan ' lignin) extracted from wood lignin, with a dioxan solution containing less than 1% of HCl,[5] does not contain nitrogen.[6]

Lignin prepared from immature, non-woody plant material contains nitrogen to a greater extent than does wood lignin.[2] The lignin isolated from finely milled veld grass hay (obtained from a bale of mixed-veld grass consisting largely of *Hyperrhenia*, *Tristachia* and *Paspalum* species) by the method of Armitage *et al.*[7] was found when corrected for ash (10·37%) to contain C 62·38, H 6·00, OCH₃ (Zeisel) 9·08 and N 1·57%, and uniquely NCH₃ 1·55% as estimated by the Zeisel method. This method proved the most satisfactory of six tested by us with regard to reproducibility, yield and purity.[8] The ' dioxan ' lignin obtained from this grass lignin fraction still appeared to contain both -N and -NCH₃,[8] [C 49·5, H 6·44, OCH₃ (Zeisel) 10·27, N 0·37 and NCH₃ (Zeisel) ±0·8%], which fact encouraged the present investigation.

Experimental

Extraction A

Dioxan (20 ml.) containing 0·7% HCl was added to 1·0 g. of finely ground grass lignin (prepared by strong H₂SO₄ or HCl digestion and consisting of the pooled samples obtained by the six methods[4, 7, 9]). After extraction for 1 h. at room temperature, the solution was filtered through sintered glass (porosity 2), concentrated to about 4 ml. and diluted with an excess of glass-distilled water. The precipitate of ' dioxan ' lignin obtained was filtered off, thoroughly washed and then dried at 105°. The residual lignin left after extraction was also washed and dried and both it and the parent lignin were analysed for -OCH₃, -NCH₃ and N (to check the effect of the extraction). The ' dioxan ' lignin was purified further by four repetitions of the extraction and precipitation procedure described, using 5-ml. volumes of the dioxan solution. This purified ' dioxan ' lignin and the original ' dioxan ' lignin were analysed for N content.

Extraction B

The ' residual ' lignin (from extraction A) was subjected to a more vigorous extraction, with 40 ml. of the dioxan solution to remove as much soluble material as possible. The mixture was kept at 60° for 24 h. with occasional shaking before the ' dioxan ' lignin (B) was precipitated with water, washed and dried as before. The process of purification was repeated five times. The product, purified ' dioxan ' lignin, was analysed for N ; the residue and ' dioxan ' lignin were analysed for their -OCH₃, -NCH₃ and -N contents.

Results and discussion

The results are presented in Table I.

The data in respect of nitrogen content may be interpreted in one of two ways : (1) they could mean that the dioxan solution is not an ideal solvent, because it removes a nitrogen-containing fraction, as well as part of the lignin, from the crude grass lignin ; or (2) they could mean that nitrogen forms a constituent part of the lignin molecule in the grass hay under investigation.

The latter conclusion is based on the observed increase in the percentage nitrogen in the

* Present address : Biochemistry Dept., The University, Oxford

Table I

Analysis of parent, ' residual ', ' dioxan ' and purified ' dioxan ' lignin

Constituent	Parent lignin	' Residual ' lignin		' Dioxan ' lignin		Purified ' dioxan ' lignin	
		A	B	A	B	A	B
% N[a]	2·20	2·89	1·55	0·95	0·52	2·19	1·35
% -OCH$_3$[a, b]	7·71	7·83	7·56	—	7·18	—	—
% -NCH$_3$[a, b]	0·37	0·35	0·38	—	0·14	—	—
% Ash	19·25	19·7	19·9	0	0·76	0	0

[a] Corrected for ash and moisture content
[b] Estimated by the Vjebök & Brecher[10] volumetric type of method (as opposed to the Zeisel method)

' dioxan ' lignin after repeated purification (compare ' dioxan ' lignins A and B with purified ' dioxan ' lignins A and B, respectively).

In contrast the markedly lower nitrogen content of the ' dioxan ' lignin fraction A and B, as compared with the parent lignin and residual lignin A respectively, suggests that the parent lignin could contain at least two nitrogen fractions, one associated with ' dioxan ' lignin and the other not.

The observed presence of -NCH$_3$ groups in the lignin, though in very small amount, is of considerable interest as this has not been reported previously.   It is not unlikely that the -NCH$_3$-containing substance is partly an impurity because the greater part of it seems to be left in the residue after extraction.   However, if this fraction is not wholly removable after repeated fractionation, it is conceivable that some nitrogen is therefore bound in the lignin molecule ; and, judging by the amount in ' dioxan ' lignin A (0·95%), there would be one atom of nitrogen for every two building units of mol. wt. 840.   Every third or fourth of these nitrogen atoms might be methylated (i.e., one -NCH$_3$ radical per six or seven building units).   This constitutes slight evidence that the nitrogen in lignin is not of proteinaceous origin, especially as the methods used to derive the lignin included pre-treatments of acid or enzymic hydrolyses.

This grass ' dioxan ' lignin not only differs from common wood lignins by containing nitrogen, but it also appears to contain about three -OCH$_3$ radicals as opposed to four to five per building unit (of mol. wt. 840) in spruce wood and bagasse native lignins.[11]   However, these lignin polymers are very similar judging from their infra-red spectra.[8]

Conclusion

While it is realised that the data presented in this communication are inconclusive, it is hoped that they may stimulate a fresh appraisal of the status of nitrogen associated with lignin fractions in non-woody and/or immature plants.

Acknowledgments

Dept. of Biochemistry, Faculty of Agriculture
University of Natal
Pietermaritzburg, South Africa

References

[1] Phillips, M., *J. Ass. off. agric. Chem. Wash.*, 1940, **23,** 109

[2] Paloheimo, L., *Biochem. Z.*, 1925, **165,** 463

[3] Bondi, A. H., & Meyer, H.. *Biochem. J.*, 1948, **43,** 248

[4] Thomas, B., & Armstrong, D. G., *J. agric. Sci.*, 1949, **39,** 335

[5] Junker, E., *Kolloid Zschr*, 1941, **95,** 213

[6] Nord, F. F., Schubert, W. J., & de Stevens, G., personal communication, Vienna, 1958

[7] Armitage, E. R., de B. Ashworth, R., & Ferguson, W. S., *J. Soc. chem. Ind., Lond.*, 1948, **67,** 241

[8] Whitehead, D. L., ' Studies on the analysis of lignin in grasses ', M.Sc. Agric. Thesis, University of Natal, 1958

[9] Moon, F. E., & Abou-Kaya, A. K., *J. Sci. Fd Agric.*, 1952, **3,** 399 ; Thacker, E. J., *J. Anim. Sci.*, 1954, **13,** 501 ; Goss, M. J., & Phillips, M., *J. Ass. off. agric. Chem., Wash.*, 1936, **19,** 341 ; Macdougall, D., & Delong, W. A., *Canad. J. Res.*, 1948, **26B,** 464, 468

[10] Vjebök, F., & Brecher, C., *Ber. dtsch. chem. ges.*, 1930, **63,** 2818, 3207

[11] Brauns, F. E., ' The chemistry of lignin ', 1952, Chapter 8 (New York : Academic Press Inc.)

THE PHENOLIC SUBSTANCES OF MANUFACTURED TEA.
VII.*—The Preparation of Individual Flavanols

By E. A. H. ROBERTS and (MRS.) M. MYERS

Methods are described for the preparation from dried green tea-leaf of (−)-epigallo-catechin, (+)-gallocatechin, (−)-epigallocatechin gallate and (−)-epicatechin gallate. The isolation of (+)-gallocatechin confirms earlier predictions that this isomer, and not the racemate, would be found in unprocessed tea-leaf.

Introduction

Studies of enzymic oxidations of individual flavanols and mixed substrate systems, reported in Parts IV and VIII of this series,[1, 2] have added much to our understanding of the mechanism of tea fermentation. The methods described by Bradfield and his co-workers[3, 4] for the preparation of individual flavanols are not suitable for large-scale work, and this paper describes alternative methods which employ Craig counter-current distributions and column chromatography on Magnesol–Celite and silica gel.

Experimental

Material

Shoots consisting of two leaves and the terminal apex were plucked from the clonal source 14/5/18 under cultivation at Tocklai, Assam. The plucked shoots were dried in a blast of hot air in a firing machine used for the drying of black tea.

Identifications by paper chromatography

With the solvent combination butanol–acetic acid–water (4 : 1 : 2·2) followed by 2% acetic acid, each of the six flavanols occurring in tea-leaf has a well-defined position on a paper chromatogram.[5, 6] This position, especially if related to that of gallic acid, has proved a reliable means of identifying the flavanols under consideration. Two-way paper chromatography has also proved useful in assessing the degree of purification attained by the methods to be described below. Identifications of the individual flavanols have also been confirmed by the use of specific spot tests. While all reducing polyphenols give a deep blue colour with ferric chloride and potassium ferricyanide, the reactions with vanillin and tetrazotised benzidine are more specific and distinguish the flavanols from gallic acid and substances yielding gallic acid and non-polyphenolic material on hydrolysis. The fluorescence in ultra-violet light, and colour reactions with ferric salts, potassium cyanide and ethylenediamine are also diagnostic.[6] Colours with 0·5N-NaOH are quite distinctive (Table I).

Table I

Colour sequences observed on spraying flavanols with 0·5N-NaOH

(+)-Gallocatechin and (−)-Epigallocatechin	Yellow-brown, slowly fading until almost colourless
(+)-Catechin and (−)-Epicatechin	Orange-brown, slowly intensifying
(−)-Epigallocatechin gallate	Pinkish-brown, slowly fading, but some residual colour
(−)-Epicatechin gallate	Pinkish-brown, deepening, finally orange-brown

Determination of phenolic nuclei

Pyrocatechol and pyrogallol groups were determined by the rather approximate method of Kursanov & Zaprometov as modified by King & White.[7] The phloroglucinol group was estimated by the method described by Swain & Hillis.[8]

Löwenthal titrations

For a Löwenthal titration of flavanols a convenient quantity to use was 20–40 mg. If necessary one-tenth of these quantities could be used, and the titration carried out with 0·02N-permanganate from a 10-ml. burette. On the larger scale 0·04N-permanganate was used for the titration with indigocarmine as an internal indicator, as described by Barua & Roberts.[9] No blank was carried out for non-tans as the non-tan fraction in tea-leaf has been shown to

consist of flavanols not precipitated by gelatin.[10]   When pyrogallol and gallic acid were titrated sharp end-points were obtained with titres of 6·1 equivalents, agreeing well with values obtained by Williams.[11]   Substances containing pyrogallol groups gave equally sharp end-points, but with pyrocatechol derivatives the end-points were much less sharp and the titration values recorded were distinctly higher than those found by Williams.

Results

Preliminary separation of flavanols

The preliminary extraction of dried green leaf with methanol and the subsequent precipitation by chloroform has already been described.[6, 12]   The chloroform precipitate was dissolved in water and extracted at least six times with equal volumes of ethyl acetate.   The united ethyl acetate extracts were evaporated to dryness under reduced pressure.   The yield of mixed flavanols was 10 g. from 150 g. of dried green leaf.   Paper chromatograms showed the product to contain the six flavanols expected, together with smaller amounts of the monoglucosides of kaempferol, quercetin and myricetin,[13] and traces of leucoanthocyanins,[14] chlorogenic acids,[15] and p-coumarylquinic acids.[16]

This mixture was fractionated in a 50-tube Craig distribution train, each tube having a lower-phase capacity of 60 ml.   The mixture was dissolved in a mixture of ethyl acetate (60 ml.) and water (60 ml.) and added to tube 0.   Tubes 1–49 each contained 60 ml. of water, saturated with ethyl acetate.   Fifty fundamental transfers were carried out, 60 ml. of ethyl acetate, saturated with water, being added to tube 0 after each transfer.   After the fiftieth transfer the upper phase of tube 49 was collected as Fraction 1.   Twenty further transfers were carried out, fresh ethyl acetate being added to tube 0 and the upper phase withdrawn from tube 49 after each transfer.   Transfers were then continued without addition of fresh ethyl acetate to tube 0, until, in all, 70 ethyl acetate layers (Fractions 1–70) had been collected.   The 50 aqueous layers left in the distribution chain constituted Fractions W 0–W 49.

When emulsions proved troublesome the contents of the leading tube were discarded, so long as there had already been at least ten fundamental transfers.   It was sometimes necessary to discard the leading fraction more than once.   The leading fractions were always very deeply coloured, so that their rejection involved no loss of eventual yield.   At the end of the distribution, colour was most apparent in Fractions 1–5 and W 0–W 4, but none of the fractions was completely free from coloured impurities.

The 120 fractions were examined by one-way paper chromatography (butanol–acetic acid–water).   Fractions of similar composition were pooled, and the combined extracts evaporated to dryness under reduced pressure.   The compositions of these pooled fractions, as revealed by two-way paper chromatography, are illustrated in Table II.

Table II

Composition of pooled fractions after Craig distribution of tea-leaf flavanols

Fraction	Yield g.	Substances detected by paper chromatography
1–5	1·45	Mainly (−)-epicatechin gallate and (−)-epigallocatechin gallate. Traces of a catechin gallate, a gallocatechin gallate and kaempferol-3-glucoside. Some orange-coloured oxidation products
6–10	1·93	Mainly (−)-epigallocatechin gallate, with traces of (−)-epicatechin gallate, (+)-catechin and kaempferol-3-glucoside
11–21	1·13	(−)-Epigallocatechin gallate, (+)-catechin, (−)-epicatechin and traces of (+)-gallo-catechin
22–33	0·24	(+)-Gallocatechin with some (−)-epicatechin and traces of (−)-epigallocatechin and *iso*quercitrin. Also an uncharacterised polyphenol of R_F values 0·45 and 0 in butanol–acetic acid–water and 2% acetic acid
34–48	0·28	(+)-Gallocatechin and (−)-epigallocatechin with some isoquercitrin and traces of leucoanthocyanins
49–70	0·48	Mainly (−)-epigallocatechin, with a little (+)-gallocatechin and traces of leuco-anthocyanins
W 40–W 49	0·08	(−)-Epigallocatechin and traces of myricetin-3-glucoside and leuco-anthocyanins
W 30–W 39	0·03	(−)-Epigallocatechin, some myricetin-3-glucoside and traces of leucoanthocyanins and chlorogenic acids
W 0–W 29	0·02	Small amounts of (−)-epigallocatechin, myricetin-3-glucoside, rutin, kaempferol-3-rhamnoglucoside, leucoanthocyanins, chlorogenic acids, p-coumarylquinic acids and theogallin

Preparation of (−)-epigallocatechin

Fractions rich in (−)-epigallocatechin (e.g., fractions 49–70 and W30– W 49 in Table II) from four separate Craig distributions were combined, and the mixture fractionated in a 50-tube Craig distribution chain in exactly the same way as described for mixed flavanols. Fractions 45–70 (yield 1·6 g.) were shown by paper chromatograms to consist almost entirely of (−)-epigallocatechin together with traces of myricetin-3-glucoside and leucoanthocyanins, and small amounts of brown oxidation products. After recrystallisation from water the product had m.p. 206–208° (decomp.) and $[\alpha]_D^{17}$ −56·3° (c = 1·243 in ethanol). Bradfield *et al.* recorded m.p. 217–218° and $[\alpha]_D^{22}$ −60°.[3] The percentages of pyrogallol and phloroglucinol found were 38·7% and 39·4%, respectively ($C_{15}H_{14}O_7$ requires 41·2% in each case). If a molecular weight of 306 be assumed, the Löwenthal titration was 6·4 equivalents per mole, corresponding with one pyrogallol group in the molecule. The product was identical in its R_F values and all spot reactions with the (−)-epigallocatechin isolated from green tea by Bradfield *et al.*[3]

Preparation of (+)-gallocatechin

Fractions rich in (+)-gallocatechin (e.g., Fractions 22–48 in Table II) from four separate Craig distributions were combined and the mixture (2·0 g.) fractionated in a 50-tube Craig distribution chain exactly as with (−)-epigallocatechin. (+)-Gallocatechin was detected in Fractions 22–45 and was the main constituent of the combined Fractions 26–39 (0·59 g.). Further purification was effected on a silica gel column following the procedure described by Bradfield *et al.*,[3] but the relatively low solubility of the crude (+)-gallocatechin proved to be a complication and only 0·13 g. of (+)-gallocatechin was obtained free from (−)-epigallocatechin. This was further purified by recrystallisation from water. The product had m.p. 180° and $[\alpha]_D^{20}$ +13·2° (c = 1·388 in 50% acetone). The (+)-gallocatechin isolated by Mayer from the bark of oak and sweet chestnut had m.p. 186–189° and $[\alpha]_D$ +14·7°.[17] Micro-analysis gave C 50·8% and H 5·5% ($C_{15}H_{14}O_7,2H_2O$ requires C 52·6%; H 5·3%). The product was identical in its R_F values and spot reactions with the (+)-gallocatechin isolated by Mayer.[17] It was also identical chromatographically with the substance of higher R_F in 2% acetic acid contained in the (±)-gallocatechin isolated by Bradfield *et al.* from green tea.[3]

Preparation of (−)-epigallocatechin gallate

Fractions 6–10 (Table II) represent a moderately pure preparation of (−)-epigallocatechin gallate. Such fractions were dissolved in the minimum quantity of ether (containing a few drops of ethyl acetate) and applied to a column of Magnesol–Celite (13 × 2 cm.) prepared as described by Pearl & Dickey.[18] The column was eluted with peroxide-free ether, saturated with water, and fractions were collected as soon as the eluate gave a positive test for polyphenols. Fractions were analysed by one-way paper chromatography ; both butanol-acetic acid–water and 2% acetic acid were used as solvents. Nearly all of the (−)-epicatechin gallate, (+)-catechin and (−)-epicatechin were found in the first 45 ml. of the eluate collected after the first break-through of the polyphenols. Subsequent fractions (255 ml.) were combined and evaporated to dryness under reduced pressure (yield 0·97 g.).

Paper chromatograms indicated very slight contamination with (−)-epicatechin and (+)-catechin ; the main constituent was identical in its R_F values and spot reactions with the (−)-epigallocatechin gallate isolated from green tea by Bradfield & Penney.[4] Its rotation $[\alpha]_D^{17}$ −151° (c = 1·234 in ethanol) was a little lower than that previously recorded (−179°).[4] The percentages of pyrogallol and phloroglucinol found were 48·3% and 28·3%, respectively ($C_{22}H_{18}O_{11}$ requires 55·0% and 27·5%). As already reported the value for $\lambda_{max.}$ at 278 mμ is approximately equal to the sum of the corresponding values for (−)-epigallocatechin and gallic acid.[19] The Löwenthal titre amounted to 12·1 equivalents per mole for a molecular weight of 458, as required for one pyrogallol and one gallic acid group. Trimethylgallic acid (m.p. and mixed m.p. 164°) was obtained by methylation with diazomethane and subsequent alkaline hydrolysis.

Preparation of (−)-epicatechin gallate

(−)-Epicatechin gallate is concentrated in Fractions 1–5 (Table II). Four such fractions were combined, and fractionated further in a 20-tube Craig distribution train, with ether and

water as the two phases. After 30 fundamental transfers, with withdrawal of the ether layers when they reached tube 19, transfers were continued without adding ether to tube 0. Eventually the material was distributed between 30 ethereal and 20 aqueous phases. Each of these fractions was analysed by one-way paper chromatography. Pooled fractions of similar composition were evaporated to dryness under reduced pressure. The composition of the pooled fractions, as determined by two-way paper chromatography, is given in Table III.

Table III

Composition of fractions obtained after Craig distribution of crude (−)-epicatechin gallate

Fraction	Yield, g.	Substances detected by paper chromatography
1–3	?	Deeply coloured oxidation products
4–9	0·29	(−)-Epicatechin gallate with small amounts of catechin gallate and gallocatechin gallate ; colour rather yellow
10–18	0·86	(−)-Epicatechin gallate with some gallocatechin gallate
19–28	0·30	(−)-Epicatechin gallate, gallocatechin gallate, and (−)-epigallocatechin gallate
29–30 +W 5–W 19	1·77	(−)-Epigallocatechin gallate

Fractions 1–9 were rejected owing to their high content of oxidation products. Fractions 29, 30 and W 5–W 19 consisted of almost pure (−)-epigallocatechin gallate. The (−)-epicatechin gallate was concentrated in Fractions 10–18. The latter were dissolved in the minimum quantity of ether, containing a few drops of ethyl acetate, and purified on a column of Magnesol–Celite in exactly the same way as described for (−)-epigallocatechin gallate. The first fractions collected, after the initial break-through of the polyphenols (total volume 135 ml.), were shown by paper chromatography to contain (−)-epicatechin gallate alone (yield 0·46 g.). Intermediate fractions (total volume 60 ml.) were shown to contain a mixture of (−)-epicatechin gallate and a gallocatechin gallate, and the final fractions (total volume 120 ml.) contained a gallocatechin gallate (40 mg.) identical chromatographically with the substance 2A described by Bradfield & Penney.[4]

The (−)-epicatechin gallate was identical in its R_F values and spot reactions with the product isolated by Bradfield & Penney.[4] Its rotation $[\alpha]_D^{17}$ −155° ($c = 1\cdot230$ in ethanol) was rather lower than that previously recorded (−190°).[4] The percentages of pyrocatechol, pyrogallol and phloroglucinol found were 17·4%, 26·6% and 24·4% respectively ($C_{22}H_{18}O_{10}$ requires 24·8%, 28·3% and 28·3% respectively). Good yields of trimethylgallic acid (m.p. and mixed m.p. 164°) were obtained by methylation with diazomethane and subsequent alkaline hydrolysis.
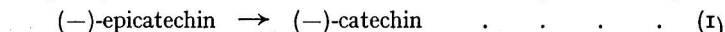
Discussion

Before this work was undertaken it was accepted that the investigations of Tsujimura,[20] Oshima,[21] and Bradfield and his collaborators[3, 4, 22] had established the presence in green tea and in unfermented tea-leaf of (−)-epicatechin, (−)-epigallocatechin and their 3-galloyl esters. The analytical data presented above are not meant to provide further evidence in favour of these views and should be taken as confirmations of the identifications made by paper chromatography

The preparations of tea oxidase substrates [(−)-epicatechin and (+)-catechin are more conveniently obtained from alternative sources] have proved entirely suitable for studies of substrate oxidation,[1, 2] but it is clear that the (−)-epigallocatechin, (−)-epigallocatechin gallate and (−)-epicatechin gallate are less pure than the substances isolated by Bradfield and his collaborators from green tea. This is considered to be due to contamination by oxidation products introduced during the drying of the tea-leaf.

When freshly plucked leaf is dried in the equipment used for the firing of tea some time necessarily elapses before the temperature of the leaf reaches a level at which the oxidising enzymes are inactivated. When the temperature of the leaf reaches 50° the semi-permeability of the vacuolar membrane is lost and the contents of the vacuole diffuse into the cytoplasm. Until further temperature increases destroy the enzyme there will be a period in which flavanols will undergo enzymic oxidation.[23] The oxidation products, so formed, are not completely separable from flavanols by Craig distributions and the flavanols prepared from dried green leaf are therefore less pure than those obtained from green tea.

The use of green tea as a source of flavanols introduces another complication. In green tea manufacture[24] the leaf is first steamed, after which it is subjected to relatively prolonged rolling at temperatures of up to 70°. Such conditions would favour the epimeric changes

$$(-)\text{-epicatechin} \;\longrightarrow\; (-)\text{-catechin} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

$$(-)\text{-epigallocatechin} \;\longrightarrow\; (-)\text{-gallocatechin} \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

Instead, therefore, of isolating (+)-gallocatechin from green tea, one would expect to obtain a mixture of (+)- and (−)-gallocatechin. Mayer obtained such a mixture from green tea with a rotation of +3°.[25] It is probable that Bradfield obtained a similar mixture, but as he recrystallised his product it is not surprising that the racemate was obtained. Therefore although Bradfield's characterisation as a gallocatechin is accepted,[3] it is not necessarily true that green tea contains this racemic mixture, but can contain other mixtures of the (−)- and (+)-forms as indicated by Mayer's findings.

From purely paper chromatographic evidence it was previously concluded that unprocessed or dried green tea leaf contained the (+)-isomer, and the isolation from dried green leaf of a gallocatechin with rotation +13·2° is considered to provide the necessary confirmation of this earlier deduction. It follows that if (+)-gallocatechin is required it must be prepared from unprocessed or dried leaf, and not from green tea.

Acknowledgments

Indian Tea Association Chemical Laboratory
   Butler's Wharf
      London, S.E.1

References

1 Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1959, **10**, 167

2 Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1960, **11**, 158

3 Bradfield, A. E., Penney, M., & Wright, W. B., *J. chem. Soc.*, 1947, p. 32

4 Bradfield, A. E., & Penney, M., *J. chem. Soc.*, 1948, p. 2249

5 Roberts, E. A. H., & Wood, D. J., *Biochem. J.*, 1953, **53**, 332

6 Cartwright, R. A., & Roberts, E. A. H., *J. Sci. Fd Agric.*, 1954, **5**, 593

7 King, H. G. C., & White, T., Symposium Soc. Leather Trades' Chemists (Cambridge), 1956, p. 31

8 Swain, T., & Hillis, W. E., *J. Sci. Fd Agric.*, 1959, **10**, 63

9 Barua, D. N., & Roberts, E. A. H., *Biochem. J.*, 1940, **34**, 1524

10 Roberts, E. A. H., & Wood, D. J., *Biochem. J.*, 1951, **49**, 414

11 Williams, A. H., *Annu. Rep. agric. hort. Res. Sta. Bristol*, 1952, p. 223

12 Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1958, **9**, 701

13 Roberts, E. A. H., Cartwright, R. A., & Wood, D. J., *J. Sci. Fd Agric.*, 1956, **7**, 637

14 Roberts, E. A. H., Cartwright, R. A., & Wood, D. J., *J. Sci. Fd Agric.*, 1956, **7**, 253

15 Roberts, E. A. H., *Chem. & Ind.*, 1956, p. 985

16 Cartwright, R. A., Roberts, E. A. H., Flood, A. E., & Williams, A. H., *Chem. & Ind.*, 1955, p. 1062

17 Mayer, W., Symposium Soc. Leather Trades' Chemists (Cambridge), 1956, p. 127

18 Pearl, I. A., & Dickey, E. E., *J. Amer. chem. Soc.*, 1951, **73**, 863

19 Roberts, E. A. H., & Williams, D. M., *J. Sci. Fd Agric.*, 1958, **9**, 217

20 Tsujimura, M., *Sci. Pap. Inst. phys. chem. Res., Tokyo*, 1929, **10**, 253 ; 1930, **14**, 63 ; 1931, **15**, 155 ; 1934, **24**, 149 ; 1935, **26**, 186

21 Oshima, Y., & Goma, T., *J. agric. chem. Soc., Japan*, 1933, **9**, 948 ; Oshima, Y., *ibid.*, 1936, **12**, 103

22 Bradfield, A. E., & Bate-Smith, E. C., *Biochim. biophys. Acta*, 1950, **4**, 427

23 Roberts, E. A. H., *Nature, Lond.*, 1941, **148**, 285 ; *Biochem. J.*, 1941, **35**, 1289

24 Leonard, W. H., & Roberts, R., 'Tea in Japan', Natural Resources Section, General Headquarters, Supreme Commander for the Allied Powers, Report Number 125, 1949, Washington, U.S.A.

25 Mayer, W., personal communication

THE PHENOLIC SUBSTANCES OF MANUFACTURED TEA.
VIII.*—Enzymic Oxidations of Polyphenolic Mixtures

By E. A. H. ROBERTS and (MRS.) M. MYERS

When a mixture of substrates is acted upon by the tea oxidase the substrate of lower rH is oxidised preferentially. In tea fermentation, therefore, oxidations are largely limited to those affecting the gallocatechins. When a mixture of two substrates is oxidised mixed dimers are not produced unless both have similar rH values. In tea fermentation there is only a limited coupled oxidation of gallic acid and theogallin. The trace substances Q (now confirmed to be a mixture) are produced by coupled oxidation of gallic acid ; oxidation of theogallin probably results in the formation of substances chromatographically similar to the thearubigins. The catechins function as carriers for coupled oxidations of theaflavins, bisflavanols and thearubigins. Such coupled oxidations probably form part of the fermentation process and it is possible that such oxidations of theaflavins and bisflavanols yield thearubigins.

Introduction

The enzymic oxidations of individual substrates were considered in Part IV of this series,[1] when it was established that the theaflavins and bisflavanols were oxidation products of (—)-epigallocatechin, (—)-epigallocatechin gallate or a mixture of these two substances. Apart from the formation of constituent Q from (—)-epicatechin gallate, oxidation products of other tea oxidase substrates did not appear to be present in black tea in any significant amount.

A mixture of substrates will not necessarily behave in the same way as individual substrates. There are possibilities of oxidative condensation between two different substrate molecules, as already established in the case of a mixture of (—)-epigallocatechin and its gallate.[1] Substances such as gallic acid and theogallin, which are not themselves substrates for the tea oxidase, may undergo coupled oxidations. Further, the end-products of enzymic oxidation of one substrate may be oxidised further in the presence of another substrate of higher rH (the rH scale[2] is in many ways preferable to the use of oxidation–reduction potentials). The extent to which oxidations of the above types are of importance will be discussed in this paper.

Experimental

Materials

Methods have already been described for the preparation of (—)-epigallocatechin, (—)-epigallocatechin gallate, (—)-epicatechin gallate, theogallin, theaflavins, thearubigins and washed tea oxidase.[3–7] The (+)-catechin and chlorogenic acid were purchased and the (—)-epicatechin was a gift from Dr. T. Swain. The mixture of bisflavanol A and theaflavin was one of the fractions obtained by Craig distribution of an ethyl acetate extract of black tea.[6]

Methods

Enzymic oxidations were carried out in Warburg vessels by the method already described.[1] Oxidations were allowed to continue until the rate of uptake had become very small (3–5 hours). The total uptake of oxygen was calculated from the final manometric reading. In coupled oxidations the carrier was dissolved in a suitable buffer and added from the side-bulb ; the substance to undergo coupled oxidation was dissolved in the 2 ml. of buffer added to the main compartment. A significant increase in total oxygen uptake or carbon dioxide output, compared with the values obtained with the carrier only, showed that a coupled oxidation had taken place. The extent of enzymic inactivation was measured by adding fresh substrate to the system after oxygen uptake had come to a standstill. Enzymic activity was proportional to the slope of the uptake curve, and if there was no stimulation of uptake on addition of fresh substrate the enzyme was considered to be inactivated. The initial slope of the uptake curve provided a measure of the extent of enzymic inhibition by substances added at the commencement of the reaction.

At the end of the oxidation the contents of the Warburg vessel were filtered free from the enzyme, extracted with ethyl acetate or butanol, and examined by paper chromatography.

* Part VII : preceding paper

Results

Oxidations of mixed substrates

Table I shows the total oxygen uptakes and carbon dioxide outputs recorded for various substrate mixtures.   In Experiments I and II the enzyme was still active at the end of the run, and uptakes and outputs with the mixed substrates were greater than the sums of the uptakes and outputs with the individual substrates.   In both cases, therefore, some interaction between the two substrates is indicated.   In Experiment III the enzyme became completely inactivated during the run with the mixed substrates.   The oxygen uptake figures therefore do not exclude the possibility of an interaction between the two substrates.   In this experiment the limited quantities of (−)-epicatechin gallate available made it impracticable to measure carbon dioxide outputs.

Table I

Total oxygen uptakes and carbon dioxide outputs associated with the enzymic oxidation of mixtures of tea flavanols

Experiment	Substrate	O_2 uptake, μl.	CO_2 output, μl.
I	(+)-Catechin (6 mg.)	275	15
	(−)-Epigallocatechin (6 mg.)	202	35
	(+)-Catechin + (−)-epigallocatechin	503	95
II	(+)-Catechin (6 mg.)	275	15
	(−)-Epigallocatechin gallate (9 mg.)	245	54
	(+)-Catechin + (−)-epigallocatechin gallate	594	172
III	(−)-Epicatechin gallate (9 mg.)	390	—
	(−)-Epigallocatechin gallate (9 mg.)	250	—
	(−)-Epicatechin gallate + (−)-epigallocatechin gallate	632	—

Examination by paper chromatography of the products of oxidation at various stages (Table II) showed that in all three cases the theaflavins and bisflavanols, formed by oxidation of (−)-epigallocatechin or its gallate, underwent further transformations when the substrate mixture contained (+)-catechin or (−)-epicatechin gallate, and could not be detected at the end of the period of oxidation.   In these experiments practically all the (−)-epigallocatechin or (−)-epigallocatechin gallate was oxidised before there was any sensible decrease in the amount of (+)-catechin or (−)-epicatechin gallate.   A similar experiment, also recorded in Table II, showed that with a mixture of (+)-catechin and chlorogenic acid the former substrate was oxidised preferentially.

In none of these experiments was there any indication on the chromatograms of substances produced by the combination of the two different substrates.

After 5 h. shaking most of the (−)-epicatechin gallate in Experiment III remained un-oxidised.   The oxygen uptake figures in Table I therefore establish that an interaction between the two substrates must have taken place.   The chromatogram, after 5 h. oxidation, also showed a streak similar to that given by thearubigin S I fractions.[6]

Coupled oxidations of gallic acid and theogallin

Although neither gallic acid nor theogallin is oxidised by the tea oxidase alone, coupled oxidations take place readily in the presence of suitable carriers.[8]   Typical results for such coupled oxidations are recorded in Table III.   In some cases the amounts of the substrates available made it impracticable to measure carbon dioxide outputs as well as oxygen uptakes.

The results leave no doubt that (+)-catechin, (−)-epicatechin and (−)-epicatechin gallate are efficient carriers for the coupled oxidation of gallic acid.   Theogallin also is oxidised in the presence of (+)-catechin and (−)-epicatechin gallate, and it is to be presumed that (−)-epicatechin would be an equally effective carrier.   Oxygen uptake figures show that (−)-epigallocatechin is a rather indifferent carrier for the oxidation of gallic acid.   The ability of (−)-epigallocatechin gallate to act as a carrier for the oxidation of gallic acid was not demonstrable by oxygen uptakes owing to the considerable enzymic inactivation which took place, but the

Table II

Paper chromatographic analyses at stages in the oxidation of mixed substrates

Expt. I. (+)-Catechin + (−)-epigallocatechin

Time, min.	(−)-Epigallo-catechin	(+)-Catechin	Bisflavanol C	Catechin oxidation products
0	+ + + +	+ + + +	−	−
30	(+)	+ + + +	+ +	−
60	−	+ + +	−	−
90	−	+ +	−	+ +
150	−	+	−	+ + +

Expt. II. (+)-Catechin + (−)-epigallocatechin gallate

Time, min.	(−)-Epigallo-catechin gallate	(+)-Catechin	Catechin oxidation products
0	+ + + +	+ + + +	−
38	(+)	+ + + +	−
75	−	+ + +	+
180	−	+	+ +

Spots for theaflavin gallate and bisflavanol A were no longer visible after 38 min. shaking.

Expt. III. (−)-Epicatechin gallate + (−)-epigallocatechin gallate

Time, min.	(−)-Epigallo-catechin gallate	(−)-Epicatechin gallate	Theaflavin gallate	Bisflavanol A	Thearubigins
0	+ + + +	+ + + +	−	−	−
45	+	+ + + +	+ +	+ +	−
90	−	+ + + +	+ +	+ +	−
135	−	+ + + +	+	+	(+)
300	−	+ + +	−	−	+ +

Expt. IV. (+)-Catechin + chlorogenic acid

Time, min.	(+)-Catechin	Chlorogenic acid
0	+ + + +	+ + + +
30	+ +	+ + + +
60	−	+ + + +
240	−	+

Table III

Coupled oxidations of gallic acid and theogallin

	Total O$_2$ uptake, μl.	Total CO$_2$ output, μl.
I. (+)-Catechin (5 mg.)	240	10
,, + gallic acid (3 mg.)	565	301
II. (+)-Catechin (6 mg.)	266	10
,, + theogallin (4 mg.)	406	142
III. (−)-Epicatechin (6 mg.)	300	—
,, + gallic acid (3·4 mg.)	684	—
IV. (−)-Epicatechin gallate (9 mg.)	397	—
,, ,, + gallic acid (3·4 mg.)	690	—
,, ,, + theogallin	450	—
V. (−)-Epigallocatechin (10 mg.)	268	—
,, + gallic acid (3·4 mg.)	335	—
VI. (−)-Epigallocatechin gallate (18·4 mg.)	488	92
,, ,, + gallic acid (6·8 mg.)	485	148

increase in carbon dioxide output showed that a coupled oxidation had taken place, although on a much smaller scale than with (+)-catechin as a carrier.

After oxidation of a mixture of (+)-catechin and gallic acid, paper chromatograms showed a strong yellow spot corresponding with that of substance Q. Like purpurogallincarboxylic acid it gave a yellow-orange colour when sprayed with ethanolic aluminium chloride, but differed in darkening to orange when sprayed with the vanillin reagent. When sprayed with dilute alkali the upper portion of the spot gave the colour sequence blue–green–pale yellow shown by purpurogallin, but the lower two-thirds of the spot gave a mauve colour which slowly faded. Measurement of the absorption spectrum of the lower portion of the spot gave values for λ_{max} of 282 and 395 mμ, which again distinguished it from purpurogallincarboxylic acid.[1, 9]

Oxidation of a mixture of gallic acid and (−)-epigallocatechin also produced a substance occupying the same position as substance Q. Its colour reactions suggested its identification with purpurogallincarboxylic acid. The effect of adding gallic acid to the (−)-epigallocatechin gallate–tea oxidase system was to intensify spot Q. Spray reagents indicated this spot to be due to a mixture of several substances.

Paper chromatograms of the products of coupled oxidation of theogallin showed a marked decrease in the intensity of the theogallin spot, but no spots corresponding with oxidation products were detected. It is possible that these were of zero R_F in 2% acetic acid, in which case they would be obscured by the normal oxidation products of (+)-catechin.

Coupled oxidations of theaflavins, bisflavanols and thearubigins

Theaflavins and bisflavanols are the end-products of the enzymic oxidation of (−)-epigallocatechin and its gallate and are not oxidised by the tea oxidase at an appreciable rate. As shown in Table IV, theaflavin and theaflavin gallate undergo coupled oxidations with (+)-catechin and (−)-epicatechin as carriers. The failure of (−)-epicatechin gallate to behave as a carrier is probably due to enzymic inactivation, which was complete at the end of the period of shaking. (−)-Epigallocatechin did not behave as a carrier for the oxidation of theaflavin gallate.

Table IV

Coupled oxidations of theaflavins, thearubigins and bisflavanol A

			Total O$_2$ uptake, μl.
I.	(+)-Catechin (6 mg.)		310
	,,	+ theaflavin gallate (6 mg.)	472
	,,	+ theaflavin (4·8 mg.)	392
II.	(+)-Catechin (6 mg.)		297
	,,	+ mixture of bisflavanol A and theaflavin (10 mg.)	473
	,,	+ thearubigins (S I) (6 mg.)	383
	,,	+ thearubigins (S II) (6 mg.)	353
III.	(−)-Epicatechin (6 mg.)		300
	,,	+ theaflavin gallate (6 mg.)	410
	,,	+ theaflavin (4·8 mg.)	366
IV.	(−)-Epicatechin gallate (9 mg.)		337
	,,	,, + theaflavin gallate (6 mg.)	332
	,,	,, + theaflavin (4·8 mg).	322
V.	(−)-Epigallocatechin (6 mg.)		198
	,,	+ theaflavin gallate (6 mg.)	207

Appreciable amounts of carbon dioxide were set free as a result of coupled oxidations by (+)-catechin, 89 μl. from 6 mg. of theaflavin gallate and 38 μl. from 4 mg. of theaflavin.

Theaflavin gallate had an inhibitory effect; addition of 6 mg. of this substance usually decreased the initial rate of oxygen uptake by 30–50%. The inhibitory effect of theaflavin was much smaller. The oxidation products of (−)-epicatechin gallate were also inhibitory and usually brought about complete destruction of enzymic activity. Coupled oxidations by (−)-epicatechin gallate were therefore difficult to demonstrate by manometric methods.

The increased oxygen uptakes and carbon dioxide outputs, indicative of a coupled oxidation of the theaflavins, were accompanied by a disappearance of the characteristic yellow-orange colour of the theaflavins. At the end of the coupled oxidation the reaction medium was practically colourless and the enzyme powder was stained a deep brown. Paper chromatograms of the reaction products showed no trace of theaflavins.

Bisflavanols were not available in pure form ; the best material available was a mixture of bisflavanol A with theaflavin. The increase in oxygen uptake recorded when this mixture was added to (+)-catechin was significantly greater than that obtained with the corresponding amount of theaflavin. The chromatograms of the reaction products also showed that there was a considerable decrease in the amount of bisflavanol A in addition to the complete disappearance of the theaflavin.

The increased oxygen uptakes obtained when thearubigin fractions were added to enzyme-(+)-catechin systems showed that thearubigins were also capable of undergoing further oxidation. Carbon dioxide (79 μl. from S I and 55 μl. from S II) was also produced during these coupled oxidations.

Discussion

(1) In the four mixed substrate systems studied the oxidation of one substrate went almost to completion before that of the other commenced. This is readily understandable if the two substrates in each pair have differing rH values, for if the substrate of high rH becomes oxidised it will immediately become reduced again by the substrate of low rH. So long as substrates of low rH are present, the substrates of high rH will remain unoxidised. The results obtained, therefore, show that the gallocatechins have lower rH values than the catechins, and that the catechins have lower rH values than that of chlorogenic acid. This is the same order as deduced from the ability of these substances to function as carriers in coupled oxidations.[8] The view is strengthened that oxidations in tea fermentation are largely confined to those of the gallocatechins.

(2) As there is no apparent decrease in the concentration of the substrate of higher rH while the substrate of lower rH is undergoing oxidation, there is unlikely to be any condensation between the *o*-quinone of a gallocatechin and unoxidised catechins. Paper chromatography also fails to detect dimers produced by copolymerisation of two different flavanols. As was demonstrated in the case of enzymically produced benztropolones,[10] a pyrogallol-*o*-quinone will condense preferentially with other *o*-quinones of approximately the same rH value. Mixed dimers, therefore, are only produced when two substrates have approximately the same rH values, as with a mixture of (−)-epigallocatechin and its gallate.

(3) Substance Q appears to be a mixture of three different substances.[1] One of the components, purpurogallincarboxylic acid, can obviously result from a coupled oxidation of gallic acid. A second component, the galloyl ester of substance R,[11] is formed by an oxidative condensation of (−)-epigallocatechin gallate with pyrogallol.[12] It seems probable that gallic acid could replace the pyrogallol in this reaction, in which case this second component of Q could be considered as produced by a coupled oxidation of gallic acid with (−)-epigallocatechin gallate as the carrier. The product obtained by coupled oxidation of gallic acid with (+)-catechin as carrier appears not to be identical with either of the above constituents of Q ; its reactions with vanillin, dilute alkali and aluminium chloride suggest that it may have structure (I).
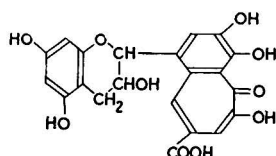
(I)

Gallic acid and (+)-catechin have rH values of the same order, so that this type of condensation is considered a probability. A similar product could be obtained with (−)-epicatechin as the carrier.

It is considered that substance Q contains all three of these substances, all of which originate from gallic acid by coupled oxidation. As the rH of gallic acid is appreciably greater than that of the gallocatechins, the amounts of these substances in black tea are unlikely to be very great.

(4) The rH of theogallin is of the same order as that of gallic acid, and its coupled oxidation during fermentation is unlikely to be a major factor. Its oxidation products may possibly be present as minor constituents of the thearubigin complex.

(5) Theaflavins and bisflavanols can undergo coupled oxidations with the catechins as carriers. It seems probable that such coupled oxidations take place during a normal tea-fermentation. There is some evidence to suggest that such coupled oxidations lead to the production of thearubigins, although it would be premature to conclude that this is the sole pathway by which thearubigins are formed.

(6) The observation that thearubigins themselves can undergo further coupled oxidations is of considerable interest as it suggests that the thearubigin fraction undergoes continual change during fermentation. The thearubigins in a tea which has received a long fermentation may be chemically quite different from those of a short-fermented tea.

Acknowledgments

References

[1] Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1959, **10**, 167

[2] Dixon, M., 'Multi-Enzyme Systems', 1949 (Cambridge University Press)

[3] Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1960, **11**, 153

[4] Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1958, **9**, 701

[5] Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1959, **10**, 176

[6] Roberts, E. A. H., Cartwright, R. A., & Oldschool, M., *J. Sci. Fd Agric.*, 1957, **8**, 72.

[7] Roberts, E. A. H., & Wood, D. J., *Biochem. J.*, 1950, **47**, 175

[8] Roberts, E. A. H., *Chem. & Ind.*, 1957, p. 1354

[9] Roberts, E. A. H., & Williams, D. M., *J. Sci. Fd Agric.*, 1958, **9**, 217

[10] Roberts, E. A. H., & Oldschool, M., *Chem. & Ind.*, 1958, p. 99

[11] Roberts, E. A. H., & Myers, M., *J. Sci. Fd Agric.*, 1959, **10**, 172

[12] Roberts, E. A. H., *Chem. & Ind.*, 1957, p. 1355

APPLICATION OF THERMOGRAVIMETRY TO THE ANALYSIS OF CARBONATES OCCURRING IN SOILS. I.—Analysis of Pure Carbonates and Naturally Occurring Limestones*

By J. R. WRIGHT, I. HOFFMAN and M. SCHNITZER

The thermogravimetric behaviour in an atmosphere of carbon dioxide of pure carbonates and naturally occurring limestones has been examined. The pyrolysis curves permitted quantitative determinations of total carbonates and the partitioning thereof into dolomite and calcite. The results have been compared with those found by chemical and X-ray diffraction methods.

Introduction

Classical methods for the determination of calcite and/or dolomite in carbonates are based on chemical analysis for calcium oxide and magnesium oxide and treatment of the sample

with acid followed by measurement of the evolved carbon dioxide. On the basis of these analyses allocations are made between calcium and magnesium forms. Other methods make use of differences in the rates of solution of calcite and dolomite in dilute hydrochloric and acetic acids. While calcite is easily soluble in these acids, dolomite shows little or no effervescence.[1] Calculations of the amounts of calcite and dolomite from chemical analyses require the assumption of an ideal dolomite formula and the absence of other calcium and magnesium minerals. Dana[2] states that, in the case of dolomite, calcium can substitute for magnesium up to a maximum Ca/Mg ratio of 1 : 5 in the magnesium positions and magnesium similarly can substitute for calcium up to a maximum Mg/Ca ratio of 1 : 20 in the calcium positions. It is obvious, therefore, that the assumption of an ideal formula for dolomite may lead to serious discrepancies.

X-ray diffraction[3] can be reasonably accurate but requires elaborate equipment and careful standardisation.

The behaviour towards heat has been the basis for a number of analytical applications. Differential thermal analysis has been used with some success.[4, 5] Tsvetkov[6] heated carbonates in a current of carbon dioxide gas and measured weight losses due to the dissociation of magnesium carbonate (700–800°) and calcium carbonate (900–950°) in dolomite on a sensitive torsion balance. He recommended this method for the analysis of carbonates with less than 5% contamination. With the introduction of the commercial recording thermobalance this approach became more practical and convenient. Recently, a number of papers describing the thermogravimetric behaviour of carbonates in air[7–10] and in an atmosphere of carbon dioxide[8] have appeared in the literature.

In the present paper the thermogravimetry in an atmosphere of carbon dioxide of carbonates, pure and in mixture, and also of a number of naturally occurring limestones was investigated in order to define optimum conditions for their analysis. The carbonates studied were those which normally occur in soils in significant amounts. Thermogravimetry in an atmosphere of carbon dioxide is especially attractive because it permits the accurate determination of total carbonates and the partition thereof into calcite and dolomite in one operation. This makes it unnecessary to determine the calcium and magnesium contents of the sample and eliminates uncertainties connected with the assumption of the ideal formula mentioned above.

Experimental

Apparatus and method

A Stanton recording thermobalance of 0·1 mg. sensitivity was used and the samples were held in platinum crucibles. The rate of heating was 300° per hour with a maximum attainable temperature of 1030°. If weight losses still occurred at 1030°, the thermobalance was held at this temperature until constant weight was obtained. This is represented in some of the graphs by a break at this temperature. For pyrolysis in an atmosphere of carbon dioxide gas a special silica sheath was placed inside the furnace and a small but steady flow of gas was maintained.

Materials

Besides dolomite (National Bureau of Standards No. 88), crystalline calcite and magnesite were used. Table I gives the description and origin of the limestone samples examined.

Results and discussion

Thermogravimetry of pure carbonate minerals

The curves in Fig. 1 show the pyrolysis in air of crystalline calcite, dolomite and magnesite slightly contaminated with dolomite. Calcite and dolomite give very similar curves, in agreement with data published by Gibaud & Geloso,[8] but it is not possible to distinguish between the two. Carbon dioxide starts to evolve from magnesite at 500°, in contrast to dolomite and calcite where decomposition starts at 620° and 670°, respectively.

Since pyrolysis in air, although quantitative for the total carbonate content, did not permit differentiation between calcite and dolomite, thermogravimetry in an atmosphere of carbon dioxide gas was investigated. Fig. 2 shows thermogravimetric curves under carbon dioxide for pure calcite, magnesite, dolomite and mixtures thereof. Carbon dioxide is evolved from pure calcite (curve 1) at about 1000°. In the case of magnesite (curve 2) decomposition starts

Table I

Key to samples examined

Sample designation	Description	Origin
A-298 to A-328	Limestones and dolomites supplied by Geol. Survey of Canada	Manitoulin Island, Ontario
5	White crystalline dolomite (Grenville series)	Portage du Fort, Quebec
6	Ordivician limestone, Pamelia and Lowville formation, 0–24 in.	Kingston, Ontario
8	Ordivician limestone, Pamelia and Lowville formation, 30–36 in.	Kingston, Ontario
9	Oxford dolomite	Gore of Lochaber, Quebec

at about 640° and is completed at about 850°. *X*-ray diffraction and chemical analysis showed that the magnesite contained a small amount of dolomite. The second break in curve 2, starting at 950°, is due to the decomposition of the calcite portion of this dolomitic impurity. Curve 3 illustrates the pyrolysis of dolomite. Carbon dioxide due to what might be considered the magnesite portion of dolomite is expelled at about 760° and evolution is completed at 850°. Carbon dioxide from the so-called calcite portion of dolomite comes off at about 980°. As expected, the losses of carbon dioxide as represented by the two steps are of equal magnitude. Curve 4 shows that the decomposition temperatures of magnesite and calcite are sufficiently different to allow for their quantitative determination. Free magnesite can be determined in the presence of dolomite (curve 5) because it loses carbon dioxide earlier than the magnesium carbonate portion of dolomite. A mixture of dolomite and calcite (curve 6) can be analysed similarly. The second step of this curve represents the sum of the weight losses resulting from the evolution of carbon dioxide from the calcium carbonate portion of dolomite and from calcite itself. Since dolomite displays a two-step break-up of equal magnitudes (curve 3), it is only necessary to subtract the weight loss due to the first step (820–870°) from that of the second step (970–1010°) to obtain a value for the calcite. It is noteworthy that calcite in mixtures loses carbon dioxide earlier (up to 50°) than when present alone. Weight losses as read from all curves shown in Fig. 1 were in quantitative agreement with theoretical values.

Thermogravimetry of limestones

Since sharp breaks were obtained for pure carbonates and their mixtures the technique was applied to a number of naturally occurring limestones, several representative curves of which are shown in Fig. 3. The evolution of carbon dioxide due to the decomposition of dolomite and of pure calcite occurred at the same temperatures as in the case of the pure compounds. The well-defined breaks permitted accurate readings for quantitative determinations. The analytical data are tabulated in Table II with results by chemical and *X*-ray methods for the same samples. The chemical and *X*-ray diffraction data were taken from a paper by Skinner *et al.*[11] The chemical method of these authors is based on differences in the rates of evolution of carbon dioxide resulting from differences in the rates of solution of calcite and dolomite in dilute HCl.

X-ray diffractometer patterns were used to confirm the presence of calcite and/or dolomite and to ensure the absence of other carbonates. The relative intensities of the main calcite and dolomite peaks at 3·04 and 2·89A respectively are included in the table for comparison.

FIG. 1.—*Thermogravimetry (in air) of carbonates*

    Curve 1 calcite (90·0 mg.)
    Curve 2 dolomite (90·1 mg.)
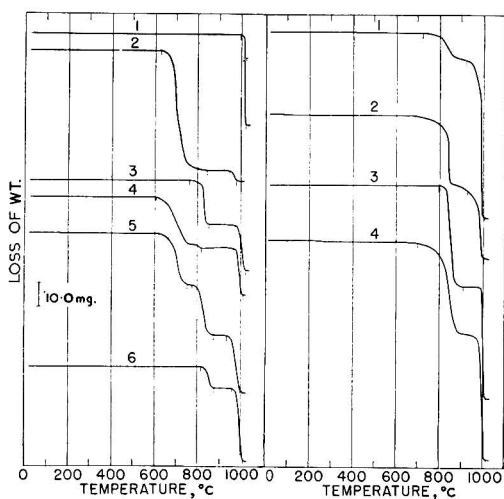   Curve 3 magnesite (87·2 mg.)
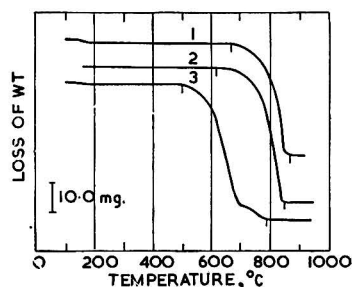
FIG. 2.—*Thermogravimetry (under CO_2)*

of carbonates

Curve 1 calcite (96·0 mg.)
Curve 2 magnesite (95·0 mg.)
Curve 3 dolomite (84·0 mg.)
Curve 4 magnesite (50·0 mg.)
 + calcite (45·0 mg.)
Curve 5 magnesite (55·1 mg.)
 + dolomite (94·4 mg.)
Curve 6 dolomite (46·4 mg.)
 + calcite (46·6 mg.)

FIG 3.—*Thermogravimetry (under CO_2)*

of limestones

Curve 1 A-302 (203·9 mg.)
Curve 2 A-298 (197·6 mg.)
Curve 3 Sample 5 (205·5 mg.)
Curve 4 A-328 (225·6 mg.)

FIG. 2   FIG. 3

Table II shows that thermogravimetric values for the total carbon dioxide content agree well with chemical data. In most cases the thermogravimetric and chemical values for dolomite are in reasonable agreement. The X-ray diffraction intensities qualitatively support these data. The agreement between thermogravimetric and chemical data for calcite is not unsatisfactory when the sensitivity of the chemical method is taken into account. In this case also, X-ray diffraction intensities qualitatively support the chemical and thermogravimetric data.

It appears that the thermogravimetric method is generally more sensitive than the chemical procedure. For example, the thermogravimetric method shows 10·7% of calcite for sample 8 which is supported by a weak X-ray intensity, whereas chemically, calcite is reported as absent. The same applies to sample A-298 where the presence of a small amount of calcite is not detected by the chemical method.

Table II also shows the percentages of dolomite and calcite as calculated from the CaO, MgO and CO_2 contents (calculated value). In this calculation it is assumed that all of the magnesium is present in the dolomite and that the Ca/Mg ratio is 1 : 1. The remaining CO_2 and corresponding calcium is considered to be present as calcite. In the case of the first six samples the agreement between the calculated and thermogravimetric values for both dolomite and

Table II

Analysis of limestones by thermogravimetric, chemical and X-ray diffraction methods

Sample	CaO %	MgO %	% total CO_2 chem.	% total CO_2 therm.	% dolomite chem.	% dolomite therm.	% dolomite calc.*	% calcite chem.	% calcite therm.	% calcite calc.†	X-ray diffraction dolomite I**	X-ray diffraction calcite I**
A-298	24·2	13·6	33·1	32·0	69·3	63·6	62·2	0	1·7	7·3	str.	v.w.
A-300	38·2	10·9	41·5	40·0	58·2	49·0	49·9	31·1	37·0	40·0	str.	str.
A-302	47·3	4·2	41·4	40·0	18·2	22·6	19·2	74·3	65·8	73·2	w.	str.
A-308	12·8	7·6	17·2	16·5	34·3	34·5	34·8	2·0	0	1·1	str.	0
A-320	33·3	13·5	39·5	38·7	61·2	63·8	61·8	23·3	17·9	22·3	str.	w.
A-328	34·0	16·0	44·2	43·0	81·4	74·3	73·2	12·1	15·1	20·7	v.str.	v.w.
5	32·7	17·5	46·7	46·0	97·8	91·8	80·1	0	4·4	14·8	v.str.	0
6	37·4	9·7	41·0	40·0	65·2	69·2	44·4	22·4	15·9	42·7	str.	m.
8	26·2	9·4	34·6	34·5	72·4	62·0	43·0	0	10·7	23·4	v.str.	w.
9	28·3	14·2	39·5	39·2	82·7	82·0	65·0	0	0	15·2	v.str.	0

* calculated from the CaO, MgO and CO_2 contents assuming that all Mg is present in dolomite in a Ca/Mg ratio of 1 : 1
† calculated from the remaining CO_2 and corresponding CaO
** relative intensities : v.str. = very strong ; str. = strong ; m. = medium ; w. = weak ; v.w. = very weak

calcite is generally closer than that between the calculated and chemical values. In the case of the remaining four samples it is obvious that the assumption of a 1 : 1 Ca/Mg ratio is not valid since calculated values do not agree with either thermogravimetric or chemical values. This is especially noticeable for calcite and points to substitution of Ca for Mg in the dolomite structure. It should be borne in mind that the thermogravimetric method is based, not on the Ca/Mg ratio, but on CO_2 evolution in a 1 : 1 ratio from what might be considered the magnesite and calcite portions of the dolomite structure. The evidence presented in Table II indicates clearly that in the case of these four samples a partitioning of total carbonate into dolomite and calcite on the basis of CaO and MgO determinations would have led to serious errors.

In the absence of generally accepted standard methods for these determinations, thermogravimetry in an atmosphere of carbon dioxide gas should find valuable applications.

Acknowledgments

Research Branch
    Canada Dept. of Agriculture
        Ottawa

References

[1] Hillebrand, W. F., Lundell G. F., Bright, H. A., & Hoffman, J. I., ' Applied Inorganic Analysis ', 1955, Part IV (New York : John Wiley & Sons, Inc.)

[2] Dana, J. D., & Dana, E. S., ' The System of Mineralogy ', 1951, Vol. II, p. 211 (New York : John Wiley & Sons, Inc.)

[3] Tennant, C. B., & Berger, R. W., *Amer. Min.*, 1957, **42**, 23

[4] Graf, D. L., *Amer. Min.*, 1952, **37**, 1

[5] Rowland, R. A., & Beck, C. W., *Amer. Min.*, 1952, **37**, 76

[6] Tsvetkov, A. I., *Dokl. Akad. Nauk SSSR*, 1951, **79** 295

[7] Guennelon, R., *Chim. anal.*, 1957, **39**, 334

[8] Gibaud, M., & Geloso, M. M., *Chim. anal.*, 1954, **36**, 153

[9] Hoffman, I., Schnitzer, M., & Wright, J. R., *Chem. & Ind.*, 1958, p. 261

[10] Schnitzer, M., Wright, J. R., & Hoffman, I., *Analyt. Chem.*, 1959, **31**, 440

[11] Skinner, S. I. M., Halstead, R. L., & Brydon, J. E., *Canad. J. Soil Sci.*, 1959, **39**, 197

APPLICATION OF THERMOGRAVIMETRY TO THE ANALYSIS OF CARBONATES OCCURRING IN SOILS. II.*—Analysis of Carbonates in Soils†

By I. HOFFMAN, M. SCHNITZER and J. R. WRIGHT

The values for total carbonates in soils as measured by thermogravimetry were in good agreement with those obtained by chemical determinations. While the pyrolysis curves of some soils allowed a partitioning of the total carbonate, difficulties were encountered in this regard with others. For most of the soils where partitioning was possible, the results for dolomite were higher, and those for calcite lower, than values obtained by a chemical method.

In order to determine the possible causes for this anomalous behaviour the interaction during pyrolysis between various inorganic salts and quartz with calcite was studied. Evidence is presented to show that the difficulty can be traced to an interaction between sodium and/or potassium and silica with calcite. Accordingly, caution should be exercised in interpreting thermogravimetric curves of soils for the purpose of partitioning the total carbonate content into dolomite and calcite.

* Part I : preceding paper
† Analytical Chemistry Research Service Contribution No. 6 ; Soil Research Institute Contribution No. 5

Introduction

This paper reports further applications of thermogravimetry to the analysis of soils. Previously it was shown[1, 2] that thermogravimetry in air is useful for the determination of 'hygroscopic moisture', organic matter and carbonates in soils and 'lattice water' in clay minerals. The successful application of thermogravimetry in an atmosphere of carbon dioxide[3] to the analysis of pure carbonates and pure limestones suggested a similar application to the analysis of carbonates in soils.

Experimental

Apparatus and method

The apparatus and experimental procedure were as described in the preceding paper.

Materials

Table I lists the horizon, soil series, great soil group, geographical origin and pH of the soil samples examined. All reagents used were of the highest purity available.

Table I

Key to samples examined and pH of soils

Sample designation	Horizon	Soil series	Great soil group	Geographical origin	pH
1	BC_a	Hatton	Brown	Sask.	8·5
2	C	Hatton	Brown	Sask.	8·7
3	C_1	Cooking Lake	Grey Wooded	Alberta	7·8
4	C_2	Cooking Lake	Grey Wooded	Alberta	7·9
5	C	Mayook	Brown Wooded	B.C.	9·3
6	B_2BC_a	Oxbow	Black	Sask.	7·9
7	BC_a	Oxbow	Black	Sask.	8·0
8	BC_a	Haverhill	Brown	Sask.	8·1
9	CC_a	Haverhill	Brown	Sask.	8·5
10	BC_a	Weyburn	Dark Brown	Sask.	8·3
11	C	Weyburn	Dark Brown	Sask.	8·5
12	14–36 in.	Champagne	Brown Wooded	Yukon	8·5
13	$CaCO_3$ concretion				
14	6–17 in.	Grenville	Brown Forest	Ontario	7·5

Results and discussion

Interpretation of thermogravimetric curves

Figs. 1 and 2 show thermogravimetric curves for a number of calcareous soils. Although this paper is primarily concerned with the determination of carbonates, it is appropriate to mention briefly additional information shown by these curves. Generally, 'hygroscopic moisture' is eliminated by approximately 200°. In our experience with a large number of soils (not shown here) breaks indicating the elimination of 'hygroscopic moisture' are usually sharper when the pyrolysis is conducted in an atmosphere of carbon dioxide than in air. This, apparently, is due to a delay in the start of the pyrolysis of the organic matter in the inert atmosphere. Organic matter starts to decompose at about 260° (as exemplified by curve 6, Fig. 1) and is completely eliminated at about 600°. The slight weight losses shown in some of the curves above 600° and lasting up to the start of the decomposition of the carbonates are due to the elimination of 'lattice water' of clay minerals.

In the case of pure carbonates the magnesite portion of dolomite starts to lose carbon dioxide at about 760° and the calcite portion at about 980°.[3] In the pyrolysis of soils it was observed that carbonates often began to decompose at about 700°. Consequently, for most of the curves in Figs. 1 and 2 the start of the weight losses indicating the decomposition of carbonates was taken at 700°. The end of the decomposition was indicated by a flattening out of the curve at approximately 1000°. Total carbon dioxide as measured in this manner agreed well with the results of chemical determinations by the method of Skinner et al.[4] (see Table II).
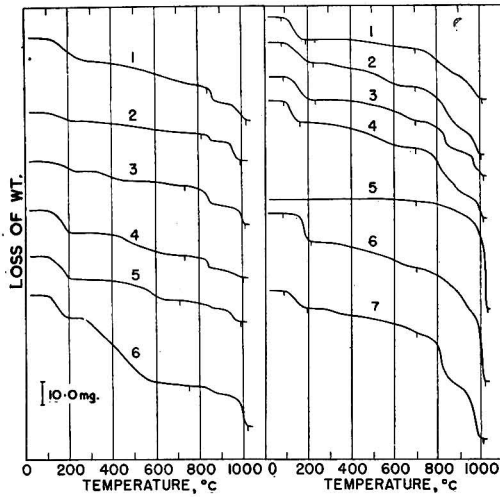
FIG. 1.—*Thermogravimetry (under CO_2) of calcareous soils*

Curve 1 Soil No. 6 (450·5 mg.)
Curve 2 Soil No. 2 (450·2 mg.)
Curve 3 Soil No. 1 (450·2 mg.)
Curve 4 Soil No. 4 (460·1 mg.)
Curve 5 Soil No. 3 (451·0 mg.)
Curve 6 Soil No. 5 (452·0 mg.)

FIG. 2.—*Thermogravimetry (under CO_2) of calcareous soils*

Curve 1 Soil No. 9 (454·6 mg.)
Curve 2 Soil No. 8 (452·8 mg.)
Curve 3 Soil No. 11 (451·9 mg.)
Curve 4 Soil No. 10 (462·5 mg.)
Curve 5 $CaCO_3$ concretion (135·0 mg.)
Curve 6 Soil No. 12 (452·0 mg.)
Curve 7 Soil No. 7 (451·1 mg.)

Partitioning of carbonates into dolomite and calcite

From the curves in Fig. 1 a partitioning of the total carbonate into dolomite and calcite appeared possible. Some difficulty, however, was experienced for some of the samples (curves 2, 4, 5, 6 of Fig. 2) because the breaks indicating the elimination of carbon dioxide from the magnesite portion and the beginning of the decomposition of the calcite portion of dolomite were poorly defined. Table II shows a comparison of thermogravimetric and chemical values for dolomite and calcite. Qualitative estimations by *X*-ray diffraction are also included in this Table. The chemical and *X*-ray diffraction data were taken from a paper by Skinner *et al.*[4] While in a few cases there is satisfactory agreement between chemical and thermogravimetric values for dolomite and calcite, wide discrepancies were found in the majority of the samples examined. In practically all cases the thermogravimetric data for dolomite were higher and

Table II

Thermogravimetry of carbonates in soils

Soil No.	% total CO_2		% dolomite			% calcite			*X*-ray diffraction	
	chem.	therm.	chem.	therm.	calc.*	chem.	therm.	calc.*	dolomite	calcite
1	3·7	3·9	2·7	8·4	5·4	5·5	0	2·5	—	—
2	2·5	2·5	3·1	3·3	5·2	2·3	2·3	0	—	—
3	2·0	2·1	2·1	3·7	—	2·3	1·0	—	—	—
4	2·2	2·2	2·1	4·5	—	2·7	0	—	d.	d.
5	3·7	3·9	4·8	3·7	—	3·2	4·8	—	d.	d.
6	2·5	3·0	4·2	5·6	—	1·1	0·8	—	d.	d.
7	10·8	10·9	8·6	22·8	12·9	15·2	0	12·7	d.	d.
8	6·5	6·6	3·8	X	7·9	10·7	X	5·9	—	—
9	5·5	5·0	5·6	10·5	—	6·4	0	—	d.	d.
10	6·7	6·7	4·8	X	—	10·0	X	—	—	—
11	5·7	5·3	5·2	11·1	—	7·3	0	—	—	—
12	9·5	11·0	0	X	—	21·6	X	—	n.d.	d.
13	33·7	35·6	1·3	X	—	75·2	X	—	trace	d.
14	2·8	3·0	5·9	6·3	—	0	0	—	d.	n.d.

* calculated from chemical CaO, MgO and CO_2 determinations assuming all Mg is present in dolomite in a Ca/Mg ratio of 1 : 1

d. = detected ; n.d. = not detected ; — not determined ; X = could not be assigned.

those for calcite lower than those obtained by chemical methods. These discrepancies were somewhat surprising because for pure carbonates close agreement was obtained.[3]

In order to throw some light on this point, the acid-soluble calcium and magnesium were determined on four selected samples. All of the magnesium was assumed to be present in dolomite in a Ca/Mg ratio of 1 : 1. The remaining carbon dioxide and the calcium corresponding to it was considered to be present as calcite. The calculated values, shown in Table II, suggest that either the assumption of a 1 : 1 Ca/Mg ratio is not warranted for these soil samples or/and that a significant part of the acid-soluble magnesium and calcium originated from materials other than carbonates. For example, in the case of soil No. 7 thermogravimetry indicates that all of the carbonate is present as dolomite, whereas the calculated, chemical and X-ray methods show the presence of considerable amounts of calcite. This is also true for soils Nos. 4, 9 and 11. The data of Table II show that, while thermogravimetry of soils in an atmosphere of carbon dioxide is reliable for the determination of total carbonate, the partitioning of the latter into dolomite and calcite presents a number of difficulties. High values for dolomite and low values for calcite suggested strongly the possibility that evolution of carbon dioxide from both the calcite portion of dolomite and from calcite occurred at lower temperatures than in the case of pure carbonate materials. It was considered that this was probably due to some constituent(s) present in these soils. Therefore, a more detailed study of the likely source(s) of this interference was undertaken.

Sources of possible interferences

Martin[5] notes that as much as 40% of calcite and/or dolomite in soils may go undetected by differential thermal analysis because of complex reactions occurring between clay, soluble salts and the carbonates. He traces the anomalous thermal behaviour of calcite in the presence of mica clay to a reaction between the silicate and calcium. Similarly to the present experience with thermogravimetry, he found that the differential thermal analysis method gave reliable results for some calcareous soils while for others it was erratic. He attributes this anomalous thermal behaviour to differences in the reactivity of the silicate in the temperature range 800–950°. Tsvetkov[6] concluded that the thermal method should not be used for carbonate rocks with more than 5% contamination or for siliceous carbonate rocks, marls, etc.

Fig. 3 shows the thermogravimetry of a number of clays separated by conventional methods from various calcareous soils. In general most of the 'lattice water' of the illite- and chlorite-type clays is lost by 700°. In the case of the Ca-montmorillonite slight losses occur up to 900°. Curves 6 and 7 of Fig. 3 show that weight losses due to 'lattice water' do not overlap with weight losses from the decomposition of calcite since the added calcite was quantitatively recovered. If the clay content of a soil were extremely high and the carbonate content very low, a large sample weight would be needed for the analysis and some interference might result from the 'lattice water'. Curves 6 and 7 also show that in the presence of these clay minerals the decomposition of calcite starts at about 920° while pure calcite alone decomposes at about 1000°. Curve 8 shows the effect of a previously calcined (1000°) Ca-montmorillonite containing appreciable amounts of sodium, on the decomposition of calcite. In this case the evolution of carbon dioxide starts about 700°. Since clays are such complex systems, attempts were made to study the effects of pure quartz, NaCl, Na_3PO_4, KCl, $Ca_3(PO_4)_2$, $BaCl_2$, $AlCl_3$, $CaCl_2$ and potassium silicate alone and in mixtures on the decomposition of pure calcite. The effect of a mixture of quartz and NaCl on the decomposition of magnesite was also examined.

A comparison of curves 2 and 3 in Fig. 4 shows that NaCl alone has a negligible effect on the decomposition of calcite. While pure quartz has practically no effect (curve 4), a mixture of quartz plus NaCl has a marked effect on the decomposition of calcite (curve 5). Gradual losses occur as low as 700° and rapid losses at about 870°. When NaCl is replaced by Na_3PO_4 in the mixture (curve 6), the beginning of the decomposition of calcite is advanced to 650°. The effect of KCl in the presence of quartz (curve 7), is similar to that of NaCl. In contrast to Na_3PO_4, $Ca_3(PO_4)_2$ in the presence of quartz (curve 8) has practically no effect on the decomposition of calcite. Curve 9 shows that the decomposition of magnesite in contrast to that of calcite is not affected by the presence of NaCl plus quartz since magnesite alone (not shown) decomposes at the same temperature. In addition, it was found that, among others, potassium
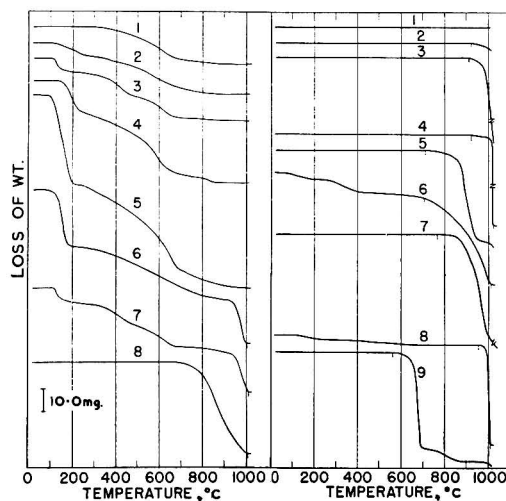
FIG. 3.—*Thermogravimetry (under CO₂) of clays with and without calcite*

Curve 1	dioctahedral chlorite (250·9 mg.)
Curve 2	trioctahedral chlorite, but mainly illite (Caribou) (273·4 mg.)
Curve 3	illite (Grenville) (254·0 mg.)
Curve 4	dioctahedral chlorite + montmorillonite (Alberni) (437·9 mg.)
Curve 5	Ca-montmorillonite (Regina) (450·4 mg.)
Curve 6	Ca-montmorillonite (250·0 mg.) + calcite (49·5 mg.)
Curve 7	illite (251·8 mg.) + calcite (44·7 mg.)
Curve 8	calcined Ca-mortmoril- lonite (213·0 mg.) + calcite (93·0 mg.)

FIG. 4.—*Thermogravimetry (under CO₂) of quartz, various salts, calcite and magnesite*

Curve 1	quartz (125·0 mg.)
Curve 2	NaCl (83·6 mg.)
Curve 3	NaCl (131·6 mg.) + cal- cite (87·5 mg.)
Curve 4	quartz (113·5 mg.) + cal- cite (94·2 mg.)
Curve 5	quartz (129·4 mg.) + cal- cite (93·0 mg.) + NaCl (75·8 mg.)
Curve 6	quartz (136·7 mg.) + cal- cite (93·9 mg.) + Na₃PO₄ (96·2 mg.)
Curve 7	quartz (120·8 mg.) + KCl (99·6 mg.) + calcite (99·1 mg.)
Curve 8	quartz (144·7 mg.) + cal- cite (98·5 mg.) + Ca₃(PO₄)₂ (103·4 mg.)
Curve 9	magnesite (95·1 mg.) + quartz (94·0 mg.) + NaCl (23·1 mg.)

silicate and barium chloride plus quartz lowered the start of the decomposition temperature of calcite to about 720° (curves not shown). $CaCl_2$ and $AlCl_3$ in the presence of quartz on the other hand had no effect.

This experimental work demonstrates that sodium, potassium and barium in the presence of quartz can have a marked effect in lowering the start of the decomposition temperature of calcite. On the other hand, calcium and aluminium have no apparent effect. Since sodium, potassium and silica are common constituents of soils, it is concluded that the anomalous results shown in Table II are due to the interaction of these materials with calcite on heating. This early decomposition of calcite results in the apparent high dolomite values shown for these samples. Attempts to circumvent the anomalous thermogravimetric behaviour by repeated washings with water until all soluble salts were removed were unsuccessful. This probably means that ions present in water-insoluble forms, possibly in the lattice of clays or other minerals, can cause these interferences. Reducing the particle size had no apparent effect on the anomalous thermogravimetric behaviour.

Fig. 5 demonstrates the effect of the addition of NaCl (approximately 1% level) to soil No. 14. Curve 1 shows that this soil behaves normally and permits the quantitative partitioning of the total carbonate (see also Table II). This soil has a negligible soluble salt content and its principal clay mineral is illite. Curve 2, Fig. 5, demonstrates that a small addition of NaCl causes carbon dioxide evolution to begin at about 650° and makes partitioning of the total carbonate impossible.
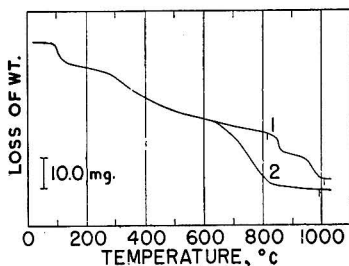
FIG. 5.—*Thermogravimetry (under CO₂) of Soil no. 14 with and without NaCl*
Curve 1   Soil no. 14 (460·0 mg.)
Curve 2   Soil no. 14 (478·3 mg.) + NaCl (6·0 mg.

Conclusion

After examination of a large number of soils of widely differing origins, it is concluded that thermogravimetry supplies valuable information with regard to a number of important soil properties including determination of total carbonate. However, great caution should be exercised in interpreting the curves for the purpose of partitioning the total carbonate into dolomite and calcite.

> Research Branch
>   Canada Dept. of Agriculture
>   Ottawa

References

[1] Hoffman, I., Schnitzer, M., & Wright, J. R., *Chem. & Ind.*, 1958, p. 261

[2] Schnitzer, M., Wright, J. R., & Hoffman, I., *Analyt. Chem.*, 1959, **31**, 440

[3] Wright, J. R., Hoffman, I., & Schnitzer, M., *J. Sci. Fd Agric.*, 1960, **11**, 163

[4] Skinner, S. I. M., Halstead, R. L., & Brydon, J. E., *Canad. J. Soil Sci.*, **39**, 197

[5] Martin, R. T., *Amer. Min.*, 1958, **43**, 649

[6] Tsvetkov, A. I., *Dokl. Akad. Nauk SSSR*, 1951, **79** 295

DETECTION AND ESTIMATION OF THE BIOLOGICALLY ACTIVE CONSTITUENTS OF PYRETHRUM

By H. J. SMITH

A method is described for the determination of Cinerin I, Pyrethrin I, Cinerin II, and Pyrethrin II in pyrethrum preparations based upon quantitative preparation and chromatographic separation of their 2,4-dinitrophenylhydrazones. The method is rapid and is suitable for routine analysis.

Introduction

The biological activity of pyrethrum is attributed to four constituents : Pyrethrin I, Cinerin I (collectively termed ' Pyrethrin I ') and Pyrethrin II, Cinerin II (' Pyrethrin II '). Pyrethrin I and Cinerin I are esters derived from chrysanthemic acid and the keto-alcohols pyrethrolone and cinerolone respectively ; Pyrethrin II and Cinerin II are esters derived from pyrethric acid and these keto-alcohols.

A method is available[1] for the estimation of these compounds in pyrethrum preparations, based on chromatographic separation of the constituents themselves on alumina.

Since the eluates are colourless and the bands invisible the course of the separation must be followed spectrophotometrically (approximately 70–90 fractions being taken and examined), which makes this method time-consuming and unsuitable for routine analysis.

The present communication is an extension of the method recently described[2] for determination of ' Pyrethrin I ' and ' Pyrethrin II ' by quantitative preparation and chromatographic separation of their 2,4-dinitrophenylhydrazones ; it has now been found that all the four constituents (as 2,4-dinitrophenylhydrazones) can be quantitatively separated on alumina columns.

This new method furnishes a very rapid means either for visually assessing the purity of any one constituent prepared by counter-current and reconstitution studies, or for quantitative analysis of pyrethrum preparations.

Experimental

Materials

The alumina used was Type ' H ' Peter Spence & Sons Ltd., 100/200 mesh, which was acidified (0·01N-HCl), washed until neutral, dried at 100° for 5 h. and then deactivated to Grade III activity on the Brockmann Scale.[3] The 2,4-dinitrophenylhydrazine (AnalaR) was twice recrystallised from benzene. Carbonyl-free methanol was prepared according to the method of Lappin & Clark.[4] The pyrethrum extract used was nominally 25% pyrethrins in odourless kerosene. Isohexane (Shell) was shaken with sulphuric acid, and then washed, dried and distilled, the fraction, b.p. 55°, being collected and used in this work.

Chromatographic step

The pyrethrins react quantitatively[2] with 2,4-dinitrophenylhydrazine (DNPH) in methanolic HCl medium to form the 2,4-dinitrophenylhydrazones which are extracted and isolated. The mixture is then dissolved in an ethyl acetate–isohexane (1 : 14) solvent mixture and introduced on to a column consisting of lengths of packed alumina (Grade III[3]), separated by spaces containing solvent and supports of tightly rolled absorbent cotton wool to correct irregular zone fronts.[5] Development with the above solvent mixture gives four distinct orange bands on the column. The small first band and large second band, comprising the DNPH derivatives of Cinerin I and Pyrethrin I, respectively, are eluted with the same solvent mixture and collected separately. The small third band and large fourth band of the DNPH derivatives of Cinerin II and Pyrethrin II, respectively, are eluted and separately collected using a stronger solvent mixture (1 : 7). Complete separation of the bands is observed.

Identification of the bands

It has been shown[2] that when ' Pyrethrin I ' and ' Pyrethrin II ' DNPH derivatives are separated on an alumina column, the bands were eluted in the order DNPH derivative of ' Pyrethrin I ' and then the derivative of ' Pyrethrin II '. Since the derivatives of the Cinerins are the minor in each of these bands it follows from *a priori* considerations that the order of the bands eluted in this work is : Cinerin I, Pyrethrin I, Cinerin II and finally Pyrethrin II.

Attempts to isolate crystalline DNPH derivatives from the fractions collected were not successful except in the case of that of Pyrethrin I ; this was isolated from the second band and had m.p. 133–134° which was not depressed on admixture with an authentic sample.[2]

The small quantities of material isolated from each of the other fractions exhibited a maximum absorption and extinction coefficient (at 377 mμ) characteristic of the DNPH derivatives of an $\alpha\beta$-unsaturated ketonic moiety[6, 7] (see Table I and Fig. 1). Data for material isolated from the bands designated Pyrethrin I and Pyrethrin II 2,4-dinitrophenylhydrazones are in reasonable agreement with literature figures for these compounds : no figures are available for the Cinerin I and II derivatives.

Cinerin II and Pyrethrin II, i.e., the esters of pyrethric acid, exhibit a hyper- and bathochromic shift in absorption over Cinerin I and Pyrethrin I respectively, i.e. the esters of chrysanthemic acid ; this is to be expected since (+)-*trans*-methyl pyrethrate itself absorbs at $\lambda_{max.}$ 236 (ε, 16,200).[8]

Furthermore, the difference in extinction coefficients of the DNPH derivatives of Cinerin I and Pyrethrin I, and Cinerin II and Pyrethrin II at the lower wavelength maxima are 19,200 and 20,700 respectively. This is in agreement with expectation since the Cinerin derivatives do not contain a pentadienyl side chain to which an average extinction coefficient of 18,700 may be attributed[9] (at 223 mμ).

Table I

Light absorption data for 2,4-dinitrophenylhydrazones of Cinerins, Pyrethrins and related compounds

Order of band elution	Identity	Observed		Literature[6, 7]	
		λ_{max}.*	ϵ	λ_{max}.	ϵ
First band	Cinerin I	222†	23,300	—	—
		377	28,100	—	—
		(377)	(27,200)	—	—
Second band	Pyrethrin I	222	42,500	222	40,900
		377	28,400	380	29,300
		(377)	(28,000)	(380)	(27,200)
Third band	Cinerin II	233	29,000	—	—
		377	26,800	—	—
		(377)	(26,000)	—	—
Fourth band	Pyrethrin II	229	49,700	229	48,000
		377	25,600	380	28,600
		(377)	(25,100)		
—	α-(±)-*trans*-Allethrin	—	—	(380)	(28,300)
—	Allethrolone ethyl ether	—	—	(380)	(27,000)
—	Pyrethrolone ethyl ether	—	—	(380)	(26,300)

* Determined in ethanol (95%) except figures in parentheses when benzene was used.
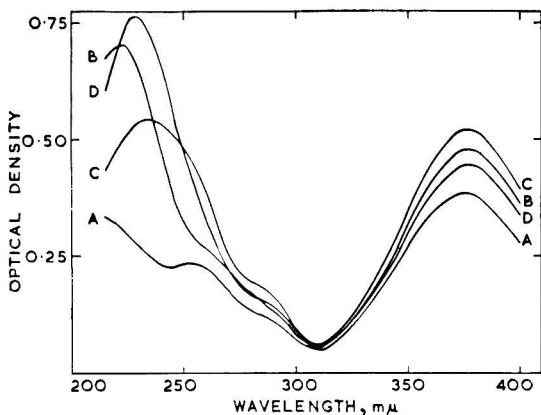† Not maxima.

Fig. 1.—*Absorption spectra (95% ethanol) of 2,4-dinitrophenylhydrazones of* (A), *Cinerin I* (0·68 mg./100 ml.), (B), *Pyrethrin I* (0·84 mg./100 ml.), (C), *Cinerin II* (1·05 mg./100 ml.), (D), *Pyrethrin II* (0·94 mg./100 ml.)

On the basis of this evidence together with that from analytical data (*vide infra*), it appears beyond reasonable doubt that the order of elution given for the constituent derivatives is correct. The extremely small scatter in the analytical figures for each constituent, about ±2% of the mean (P = 0·05), for Cinerin I, Pyrethrin I and Pyrethrin II and ±4% for Cinerin II, is in itself strong persuasive evidence for the integrity of each band.

Calculation of results

The eluted fractions are separately evaporated, made up to a fixed dilution with alcohol and the optical density measured at 377 mμ, a point of maximum absorption. The Cinerin I, Pyrethrin I, Cinerin II and Pyrethrin II contents of the preparation under examination are computed by use of a standard curve[2] for authentic Pyrethrin I 2,4-dinitrophenylhydrazone determined at 377 mμ (see Fig. 2). It has been shown previously[6, 7] and confirmed in this work that the DNPH derivatives of pyrethrins and analogues containing the cyclopentenolone skeleton have similar molecular extinction coefficients at the higher wavelength maxima (see Table I). It is thus possible from the standard curve for the derivative of Pyrethrin I to calculate the proportion of each constituent in a pyrethrum preparation as follows:

$$\% \text{ Pyrethrin I in sample} = \frac{\text{Optical density reading} \times 20 \times 1\cdot816 \times 328\cdot4 \times 100}{\text{Wt. of sample (mg.)} \times 508\cdot52}$$

(where 20 is dilution factor, 1·816 is slope of standard curve, 328·4 is mol. wt. of Pyrethrin I and

508·52 is mol. wt. of Pyrethrin I 2,4-dinitrophenylhydrazone)

$$= \frac{\text{Optical density} \times 20 \times 100 \times 1\cdot173}{\text{Wt. of sample (mg.)}}$$

Cinerin I, Cinerin II and Pyrethrin II may be similarly calculated, 1·130, 1·288 and 1·330 respectively replacing 1·173 in the final equation to account for differences in molecular weight.

Reproducibility of results

A Kenya pyrethrum extract was analysed by the new method described and replicate results are summarised in Table II together with the calculated coefficients of variation and confidence limits (P = 0·05).

Table II

Analysis of pyrethrum extract

	% Cinerin I	% Pyrethrin I	% Cinerin II	% Pyrethrin II	Total
	3·14	10·10	2·37	7·49	23·10
	3·22	10·48	2·49	7·03	23·22
	3·24	10·57	2·56	7·11	23·48
	2·94	10·38	2·66	7·65	23·63
	3·12	10·88	2·88	7·39	24·27
	3·08	10·52	2·46	6·94	23·00
	2·92	10·63	2·36	7·04	22·95
	2·94	9·90	2·36	6·94	22·14
	3·00	10·02	2·52	7·10	22·64
	3·00	10·18	2·44	7·19	22·81
	3·00	10·10	2·58	7·03	22·71
Mean	3·05	10·34	2·52	7·17	23·08
Standard deviation	0·113	0·303	0·155	0·238	0·575
Coefficient of variation	3·70	2·93	6·14	3·32	2·49
95% Confidence limits of mean	±0·076	±0·204	±0·104	±0·160	±0·386
95% Confidence limits as % of the mean	±2·50	±2·00	±4·10	±2·23	±1·70

(Results on the same extract by the method of the Ass. Off. Agric. Chemists, Washington, 8th Edn., were ' Pyrethrin I ' 11·80%, Pyrethrin II 11·35%, Total pyrethrins, 23·25%)

The 95% confidence limits were calculated from the expression, $t \times \delta/\sqrt{n}$ where t is Student's t factor, which is 2·23 for p = 0·05 with ten degrees of freedom, and δ is the standard deviation.

The previously published findings[1] for the proportions of each constituent in Kenya pyrethrum extract are as follows for duplicate analyses respectively: Cinerin I (2·95, 2·76%), Pyrethrin I (9·80, 9·25%), Cinerin II (2·75, 2·60%), and Pyrethrin II (6·50, 7·25%).

The mean values obtained in this work for the proportion of each constituent present in Kenya extract are in reasonable agreement with these findings.

Details of method adopted for analysis of pyrethrum extract

Pyrethrum extract (150–160 mg.) is dissolved in ether (2·5 ml.) and methanol (6·5 ml.) slowly added with swirling. 2,4-Dinitrophenylhydrazine (70 mg.) and methanolic HCl [1 ml. of a mixture of conc. HCl (3 ml.) and methanol (25 ml.)] are added and the mixture set aside at room temperature with occasional swirling for $3\frac{1}{2}$ h. The mixture is then transferred to a separating funnel containing water (50 ml.) with the aid of isohexane (50 ml.). The whole is mixed and the aqueous layer separated and re-extracted with isohexane until the organic liquors
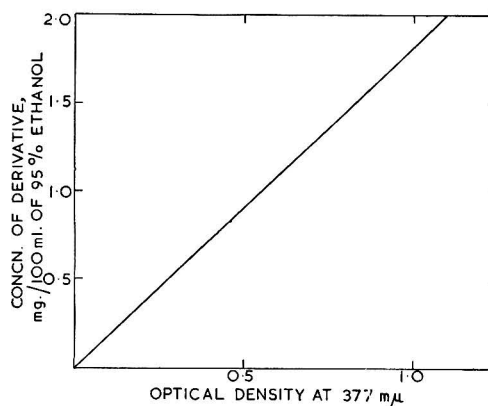

FIG. 2.—*Standard curve for Pyrethrin I 2,4-dinitrophenylhydrazone*

are colourless (5 × 20 ml.). The combined isohexane liquors are twice washed with water (2 × 30 ml.) and then filtered (cotton wool) into a flask and evaporated under reduced pressure in a bath at ∼45° (Residue A).

The chromatographic column consists of a glass tube (26 in. × 0·6 in. internal diameter), drawn to a point at the lower end which contains a small plug of cotton wool. A slurry of alumina in isohexane is passed into the column and packed to a height of 6 in. A circular disc of filter paper is laid on top of the alumina and the solvent level left a few inches above the alumina. A plug of tightly rolled cotton wool ($\frac{1}{2}$ in. long) is then inserted into the column to within $\frac{3}{4}$ in. of the alumina, the space between containing solvent. Another 6-in. column of alumina is then prepared on the cotton wool support and the above procedure repeated until the final column consisted of three lengths of alumina (each 6 in. long), separated by two spaces (each $1\frac{1}{4}$ in. long) containing solvent and cotton wool plugs.

The residue A is dissolved in a mixture of ethyl acetate (1·5 ml.) and light petroleum (28·5 ml.), and slowly added to the alumina column. The flask is washed out with 1 : 19 ethyl acetate-isohexane mixture (2 × 5 ml.), and the washings added to the column. The column is developed with a mixture of these solvents (1 : 14) until the Cinerin I and Pyrethrin I 2,4-dinitrophenyl-hydrazone bands have been eluted ($4\frac{1}{2}$ h.). The Cinerin II and Pyrethrin II bands are at this time half-way down the column and are eluted with a 1 : 7 mixture of the same solvents (2 h.). The separately collected fractions are evaporated and made up with isohexane to a volume of 100 ml. Aliquots (5 ml.) of these solutions are evaporated, dissolved in spectroscopically pure ethanol (95%), made up to a volume of 100 ml. and the optical density measured on a Unicam SP 500 ultra-violet spectrophotometer at 377 mμ (1 cm. cell). The Cinerin I, Pyrethrin I, Cinerin II and Pyrethrin II contents of the preparation are calculated as described above.

Conclusion

The new method described for analysis of all four biologically active constituents of pyrethrum, in the hands of the author and assistant, has proved remarkably accurate and consistent. The 95% confidence limits of the mean are of the order of 2% of the mean for Cinerin I, Pyrethrin II and total pyrethrins and of the order of 4% of the mean for Cinerin II, furthermore the method is rapid and therefore has the great advantage of being applicable to routine work. A chemist and skilled assistant can undertake three estimations in a working day since preparation of the derivatives and the chromatographic step can be carried out simultaneously. Before any new technique can become established, however, adequate inter-laboratory trials and corroboration are necessary.

Acknowledgments

The Pyrethrum Board of Kenya
   Nakuru
   Kenya

References

[1] Brown, N. C., Hollinshead, D. T., Phipers, R. F., & Wood, M. C., *Soap, N.Y.*, 1957, **33**, (9), 87 ; (10), 91

[2] Smith, H. J., *J. Sci. Fd Agric.*, 1959, **5**, 260

[3] Brockmann, H., & Schodder, H., *Ber. dtsch. chem. Ges.*, 1941, **74**, 73

[4] Lappin, G. R., & Clark, L. C., *Analyt. Chem.*, 1951, **23**, 541

[5] Pillay, P. P., Rao, D. S., Nair, C. P. N., & Varkey, E. T., *Chem. & Ind.*, 1958, p. 258

[6] Elliott, M., *Chem. & Ind.*, 1958, p. 685

[7] Moore, B. P., *J. Sci. Fd Agric.*, 1956, **12**, 740

[8] Crombie, L., Harper, S. H., & Sleep, K. C., *J. chem. Soc.*, 1957, p. 2743

[9] Ward, J., *Chem. & Ind.*, 1953, p. 586

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

INDEX OF AUTHORS' NAMES

Run-off from pasture plots. L. E. Gard, W. C. Jacob and C. A. van Doren (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 388—391).— Pasture plots treated with fertiliser and lime showed less run-off, particularly during spring and summer, than did untreated plots over 12 years. Run-off was greater from severely grazed than from moderately grazed plots during the grazing season, but not during the non-grazing season. Run-off from all plots was greater during Jan.-Mar. than during the other three-quarters of the year. The run-off generally increased with antecedent rainfall intensity. Values obtained for the regression of run-off on amount of rainfall indicate that there were too many uncontrolled variables for the ratios to be useful. A. H. CORNFIELD.

Determination of exchangeable hydrogen in soils by a titration method. T. L. Yuan (*Soil Sci.*, 1959, **88**, 164—167).—Two methods are described, in both of which Al present is complexed with F to remove it from solution. In one method the KCl leachate from the soil is titrated with NaOH using phenolphthalein, after removal of Al, and in the other the KCl leachate is titrated with NaOH to give " exchange acidity " and then the Al is removed with NaF, liberating alkali in the process, which is titrated with HCl to give the exchangeable Al. The difference between " exchange acidity " and exchangeable Al is the exchangeable H. Values by the two methods agree well. If Fe is present in quantity a correction is necessary. T. G. MORRIS.

Soil nitrogen. V. Leaching of nitrate from soils in laboratory experiments. R. Webster and J. K. R. Gasser (*J. Sci. Fd Agric.*, 1959, **10**, 584—588 ; cf. J.S.F.A. Abstr., 1959, i, 300).—Loss of NO_3^- from a sandy loam was greater than from a clay loam when water was percolated through columns of the soils; in both soils rate of loss was initially greater from a coarse fraction (2—10 mm.) than from unseparated soil. When water was added slowly at the top of columns of unseparated soils until the bottom became wet, there was a min. concn. of NO_3^- near the bottoms of the columns. Drainage water flows initially over the structural units and not through the soil mass, so that NO_3^- is first lost from the surface of the structural units and the first drainage water has a lower NO_3^- concn. than the subsequent runnings. E. M. J.

Effect of different salts and their concentration on the rate of nitrification of ammonium sulphate [in soils]. A. Wahhab and G. Rasool (*Pakist. J. Sci. Res.*, 1959, **11**, 84—89).—Threshold concn. adversely affecting nitrification were CO_3^{2-} 0·4, HCO_3^- 0·5, Cl^- 0·5, Na_2SO_4 0·4 and $MgCl_2$ 0·5% at 30° and 12% moisture. The presence of Ca^{2+} proved beneficial to a certain extent but introduced other factors. (15 references.) C. V.

Loss of nitrogen from alkali soils. S. P. Mitra and R. Singh (*Soil & Plant Fd.*, 1958, **4**, 75—80).—Losses of N from fertilisers applied to alkali soils were in the order, urea > $(NH_4)_2SO_4$ > $NaNO_3$ and resulted from leaching, denitrification or volatilisation of NH_3 from $(NH_4)_2CO_3$ formed in these soils. The % loss of added N was greater with the smaller applications and was retarded by presence of org. matter or rock phosphate. A. G. POLLARD.

Nitrification of urea in different soils. A. Wahhab and M. Ishaq (*Pakist. J. Sci. Res.*, 1959, **11**, 81—84).—Depending on the soil, this required 21—42 days and normally 87—99% was nitrified. In deteriorated soils with high pH value only 4—8% was nitrified. (13 references.) C. V.

Ammonium lactate method for determining readily soluble phosphate in soils containing carbonates. H. Riehm (*Agrochimica*, 1958/9, **3**, 49—65).—A modified lactate-extraction method is described in which 5 g. of soil is extracted for 4 hr. with 100 ml. of a solution containing 0·1N-NH_4 lactate and 0·04N-acetic acid (pH 3·7). Phosphate in the extract is determined colorimetrically (Mo-blue). Critical values for soils are : well supplied with P, >20, adequate, 20—11, deficient, <10 mg. of P_2O_5/100 g. of air-dry soil (2 mm. sieve). Comparative data obtained by the " double-lactate " method (Ca lactate–HCl extract) are recorded. A. C. POLLARD.

Use of electrodialysis in determining the phosphate status of soils. G. Petrosini (*Agrochimica*, 1958/9, **3**, 66—82).—Comparative data from 58 soils of phosphate fraction by the methods of Ghani and of C. H. Williams, of assimilable P by Olsen's method and of electrodialysable P (I) are presented. I is regarded as readily available to plants. A. G. POLLARD.

Degree of phosphate saturation of soils as a measure of phosphate availability for plants. M. A. Islam and A. F. M. Hafizar Rahman (*Soil Sci.*, 1959, **88**, 172—178).—The % phosphate saturation was determined from the ratio of the amounts of exchangeable P to the P-fixing capacity of eight soils determined by the Piper method. Yields of four crops increased with increasing P saturation up to a certain point ; above this no further effect on the yield was found. For paddy, danta and black gram the critical point was 3—7% but

for lettuce it was 5—6%. For typical red earths with high PO_4^{3-} adsorption capacity the soil PO_4^{3-} status is best represented by the saturation %. T. G. MORRIS

Effect of product of organic matter decomposition on phosphorus availability. K. N. Goel (*Res. J. Hindi Sci. Acad.*, 1959, **2**, 169—174).—A note. (English summary.) C. V.

Influence of organic matter additions on rock phosphate availability to crops. L. F. Seatz, A. J. Sterges and J. C. Kramer (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 374—376).—Supplements of org. matter with rock phosphate increased the yields of successive crops of two grasses and two crops of red clover as compared with rock phosphate alone. The effect was attributed mainly to the additional P supplied by the org. matter rather than to any beneficial effect of the org. matter on P availability from the rock phosphate. A. H. CORNFIELD.

Reactions of monocalcium phosphate monohydrate in soils. III. Studies with metastable triple-point solution. W. L. Lindsay, J. R. Lehr and H. F. Stephenson (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 342—345).—The metastable triple point solution [solution saturated with respect to $Ca(H_2PO_4)_2,H_2O$ and the metastable hydrolysis product $CaHPO_4,2H_2O$] upon reaction with successive samples of soil dissolved appreciable quantities of Al, Fe, Ca, Mn and K. Filtrates removed following each of these reactions later precipitated cryst. $CaHPO_4,2H_2O$, $CaHPO_4$ and $H_6K_3Al_5(PO_4)_8, 18H_2O$. A. H. CORNFIELD.

Preparation of crystalline ferric phosphates. W. E. Cate, E. O. Huffman and M. E. Deming (*Soil Sci.*, 1959, **88**, 130—132).— Techniques are described for the crystallisation of strengite and calcium ferric phosphate. The crystallographic properties of the materials produced are given. T. G. MORRIS.

Effect of phosphate topdressing on a soil from andesitic volcanic ash. III. Phosphate retention and pH. W. M. H. Saunders (*N.Z. J. agric. Res.*, 1959, **2**, 659—665).—The New Plymouth black loam was investigated at low, moderate and high P status. Exchangeable Ca plays no part in phosphate retention which is due to a high content of active Al, probably derived from the amorphous clay mineral allophane AB. E. G. BRICKELL.

Potassium in alluvial soils. J.-P. Ancellin, A. Foisil and G.-C. Redlich (*C. R. Acad. Agric. Fr.*, 1959, **45**, 491—498).—The exchangeable K content of a soil varies with the crop previously cultivated, the effect of which may exceed that of the fertiliser which is added. Exchanges take place between the " assimilable " K and the non-exchangeable K in the soil and plants are not fed solely at the expense of the " assimilable " K. Additions of K must take account of the actual needs of the plants which may be greater than the amount absorbed. J. M. JACOBS.

Release of fixed potassium as a diffusion controlled process. M. M. Mortland and B. Ellis (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 363—364).—Rate of release of fixed K from vermiculite was studied by leaching with 0·1N-NaCl in an attempt to characterise the rate-limiting process. Of the processes considered, film diffusion satisfied most criteria as rate limiting. The activation energy of the release of K by 0·1N-NaCl in the system was about 3550 cal. per mole, a value of the order frequently obtained for diffusion processes. A. H. CORNFIELD.

Potassium availability in surface and subsoil horizons as measured by plant uptake and chemical extraction. C. G. Wells (*Dissert. Abstr.*, 1959, **20**, 451—452).—Exchangeable K was less in subsoil than in surface soil. Drying increased exchangeable K, to an extent increasing with depth of soil. Exchangeable K determined on moist or dried samples reliably indicated K available to plants in soils which showed little change in exchangeable K on drying ; where the change was great, determinations on moist samples were more reliable. Exchangeable K determined on moist or dry samples did not reliably measure available K in soils containing much fixed K. Fixed K was available to plants, though more slowly than available K. Subsoils fixed more K against extraction by NH_4 acetate than did surface soils. The order of the effectiveness of cations in extracting K was NH_4 > Na > Ca > Mg (in inverse order of hydrated diameters. Very little K was contributed by subsoil to a crop of maize). Exchangeable K in the surface soil gave the best prediction of the K content of a crop of lucerne. Exchangeable K in the subsoil was correlated more nearly with yield than with K content of lucerne. Soil tests for K could be more logically interpreted if figures were given for release of K on drying, fixed K in surface soil, and available K in subsoil. M. D. ANDERSON.

Mobilisation of potassium from illite by solutions of phosphate. A. Malquori, L. Radaelli and S. Cecconi (*Agrochimica*, 1958/9, **3**, 16—28).—Illite reacts with phosphate solutions with release of K and SiO_2 (" phosphatolysis ") ; it does not react with sol. acetates. The extent of phosphatolysis increases with $[PO_4^{3-}]$ over the range

0·25—1·0M, with temp. 20—80° (3—15 days to equilibrium) and with fall in pH (8—4). Under optimal conditions 100 g. of illite yielded 7·85 mequiv. of K and 22 mmol. of SiO_2. Fixation of PO_4^{3-} by illite followed a course parallel to that of the release of K.
A. G. POLLARD.

Solubility of calcium carbonate in calcareous soils. S. R. Olsen and F. S. Watanabe (*Soil Sci.*, 1959, **88**, 123—129).—Solubilities were determined by shaking suspensions of soil or of calcite under various partial pressures of CO_2. The results indicate that data based on calcite cannot be applied to any calcareous soil. In some soils the calcareous material is more sol. than calcite at a given p_{CO_2}. The value changes with the ratio of soil to water in the suspension. When IR-120 resin was added to the mixture the Ca solubility was unaffected but when $CaCO_3$ was precipitated in the presence of clay by the action of CO_2 on $Ca(OH)_2$ it was more sol. than calcite. [HCO_3^-] should be measured in addition to pH.
T. G. MORRIS.

Extractable sulphate in Florida soils in relation to amount of clay in the profile. J. R. Neller (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 346—348).—The Morgan-extractable SO_4^{2-} content of the sandy-textured surface soils of the area was usually very low, whilst that of the lower horizons, which were usually higher in clay, was much higher. With the exception of some fine sand profiles, which contained relatively high SO_4^{2-} in spite of low clay content, there was a highly significant correlation between SO_4^{2-} and clay contents for the profile samples of 13 soils.
A. H. CORNFIELD.

Availability of sulphur in Norfolk loamy sand and Leadvale silt loam as measured by cotton growth. O. E. Anderson and R. H. Webster (*Agron. J.*, 1959, **51**, 675—677).—Cotton growing on Norfolk sandy loam (1 p.p.m. Morgan-extractable SO_4^{2-}-S in 0—12 in. depth, with higher levels at lower depths) made no yield responses to $CaSO_4$ applications (4—32 lb. S per acre) during the first 4 years, but during the fifth year yields increased with rate of application of S. On Leadvale silt loam (128 p.p.m. Morgan-extractable SO_4^{2-}-S in 0—12 in. depth) no responses in yields were made to S applications over 5 years.
A. H. CORNFIELD.

Anion elution patterns from soils and soil clays. W. A. Berg and G. W. Thomas (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 348—350).—Creedmoor clay, which has a relatively high proportion of expanding-lattice type minerals, produced a normal anion elution curve when Cl^- and SO_4^{2-} were eluted through it, indicating poor retention of these anions. Clays and soil which were predominantly kaolinitic produced a skewed elution pattern indicating attraction for the two cations; these materials were also high in free Fe and Al oxides. SO_4^{2-} was adsorbed more strongly than was Cl^-.
A. H. CORNFIELD.

Humic acid investigations. III. Chemical properties of certain humic acid preparations. C. B. Coulson, R. I. Davies and E. J. A. Khan (*Soil Sci.*, 1959, **88**, 191—195).—Humic acid from peat was hydrolysed by acid. The hydrolysate, after neutralisation and deionisation, was chromatographed under various conditions to demonstrate the presence of sugars and phenolic compounds. Only traces of glucose, galactose, arabinose and xylose were found; the bulk of the phenolic compounds appeared as polymers. Humic acid from clay fractions of soil did not show any single spot. Catechol was probably present.
T. G. MORRIS.

Amounts of hexosamines found in various soils and methods for their determination. F. J. Sowden (*Soil Sci.*, 1959, **88**, 138—143).—Eastoe's (*Nature*, 1954, **173**, 540—541) and Elson and Morgan's (*Biochem. J.*, 1944, **27**, 1824—1828) methods for the determination of hexosamines were compared in six soils. Agreement between the two methods was good. A correction for loss of hexosamine during the initial hydrolysis is necessary. The glucosamine/galactosamine ratio varied between horizons of the same soil and also between soils. Podsols tend to have highest ratios.
T. G. MORRIS.

Titration curves of soil organic matter. R. S. Beckwith (*Nature, Lond.*, 1959, **184**, 745—746).—Fresh evidence shows that, contrary to author's previous conclusion (*Aust. J. agric. Res.*, 1955, **6**, 685), (i) there is no general proton release ($2H^+ \rightleftharpoons Cu^{2+}$) when small amounts of Cu are added to soils, and (ii) transition metals (Fe, Al) can be complexed by soil org. matter, the bonding sites being carboxyl and phenol or hydroxyl groups. Provided that purified org. matter extracts are used, the end-points of curves obtained by titration with NaOH in presence of Cu are sharp and the curves resemble those for chelating hydroxy-acids. Martin and Reeve's results are confirmed (cf. *J. Soil Sci.*, 1958, **9**, 89).
W. J. BAKER.

Studies on the decomposition of organic matter in soil using radioactive carbon. V. Decomposition of cellulose and lignin. J. Mayaudon and P. Simonart (*Plant & Soil*, 1959, **11**, 181—192).—Use of ^{13}C-labelled cellulose and lignin showed that lignin decomposed in soil three times faster than did the cellulose. 5·9% of the

cellulose-C and 34·2% of the lignin-C was found in the humic acid fraction. The bulk of the radioactivity in the humic acid from lignin decomposition occurred in the non-hydrolysable fraction, whilst that from cellulose decomposition occurred in the hydrolysable fraction. The distribution of radioactive C after decomposition of separate lignin constituents (vanillin, syringaldehyde and *p*-hydroxybenzaldehyde) was similar to that occurring after decomposition of lignin.
A. H. CORNFIELD.

Carbon–nitrogen relationships in soil. F. J. Stevenson (*Soil Sci.*, 1959, **88**, 201—208).—Soil profiles representative of the great soil groups were examined for C, N, fixed and exchangeable NH_4^+ contents. From 3·5 to 7·9% of the N in the surface soil occurred as fixed NH_4^+ and this relative amount increased with depth, due primarily to a decrease in org. matter content with depth. For all soils the C/N ratio decreased with increasing depth. In most soils the ratio C/org. N narrowed with depth; this being due to the presence of non-proteinaceous constituents of the fulvic acid fraction of the soil org. matter.
T. G. MORRIS.

Effect of sawdust on crop growth and physical and biological properties of Cecil soil. A. W. White, jun., J. E. Giddens and H. D. Morris (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 365—368).—Ploughing-in pine sawdust (3—20 tons per acre) had no effect on yields of maize or tomatoes even when extra N was applied to allow for N fixed by the sawdust. A sawdust mulch (20 tons per acre) increased yields of maize and tomatoes only at high levels of applied inorg. N. Mulching increased available soil moisture and reduced soil temp. and NO_3^- content. Soil microbial population was unaffected by mulching but was increased by ploughing-in the sawdust.
A. H. CORNFIELD.

Fungal flora of Iraqi soils. II. Central Iraq. Y. Al-Doory, M. K. Tolba and H. Al-Ani (*Mycologia*, 1959, **51**, 429—439).—One hundred and fifty species of fungi were isolated. The majority belonged to the Fungi *Imperfecti* and the chief genera were *Hormodendrum*, *Aspergillus*, *Fusarium*, *Alternaria*, *Penicillium*, *Humicola*, *Mucor* and *Pythium*. The abundance of soil fungi was not related to the content of org. matter and was greatly reduced when the content of sol. salts was high.
L. G. G. WARNE.

Biological fixation of nitrogen. E. R. Roberts (*Fertiliser Soc.*, 1959, Prepr., 31 pp.).—History and recent work covering the possible reactions involved, reduction, oxidation, direct reaction with org. substances and hydrolysis are reviewed. Some substances have the ability to stimulate fixation; hydrogenase seems to be intimately associated with the fixation process. (42 references.) E. M. J.

Microbiological filaments in soils. R. D. Bond (*Nature, Lond.*, 1959, **184**, 744—745).—Very fine to coarser org. filaments strongly enmeshing the grains in some S. Australian sands or forming a stable network within crumbs (<2 mm.) of associated sandy soils are described. These filaments necessitate ignition of all sands before sieving for particle-size analysis.
W. J. BAKER.

Electrolytic rocking percolator. D. J. Greenwood and H. Lees (*Plant & Soil*, 1959, **11**, 87—92).—An electrolytic method for measuring O_2 consumption at any constant partial pressure of O_2 is described for use in conjunction with the rocking percolator (*Plant & Soil*, 1956, **7**, 253).
A. H. CORNFIELD.

Deep tillage in Hawaii. I. Subsoiling. A. C. Trouse, jun. and R. P. Humbert (*Soil Sci.*, 1959, **88**, 150—158).—The use of subsoiling units in sugar-cane soils is described and discussed.
T. G. MORRIS.

Action of mineral fertilisers as dependent on the amount and on the seasonal cycle of biological activity in soil. F. Alten, C. M. Florian, E. Latzko and K. Mechsner (*Agrochimica*, 1958/9, **3**, 1—15).—Experimental data and a discussion emphasise the view that biological activity in soils and the efficiency of mineral fertilisers are largely controlled by the C/N ratio of the soils and the amount and time of application of org. manures.
A. G. POLLARD.

Dependence of the solubility of nitrogen in urea/acetaldehyde complexes on soil reaction. H. Kuntze (*Z. PflErnähr. Düng.*, 1959, **86**, 120—123).—The relation between solubility and soil reaction is similar to that found for urea–formaldehyde complexes and in acid soils these complexes are even more sol. than some common N fertilisers. Large differences in solubility between complexes are found only in neutral soils.
M. LONG.

Solubility of slightly soluble urea/acetaldehyde condensates (Urea-Z) with regard to their use as slow-acting nitrogenous fertilisers. H. Kuntze (*Z. PflErnähr. Düng.*, 1959, **86**, 131—141).—Control of solubility is achieved by the following conditions which permit close control of the reaction: an initial molar ratio of approx. 1, a faintly acid reaction medium, moderate concn., cooling of the reaction mixture and drying of the product at low temp. Replacement of formaldehyde by acetaldehyde favours the formation of low-mol. wt. products.
M. LONG.

Ammonia volatilisation losses from nitrogen fertilisers when applied to soils. C. B. Kresge (*Dissert. Abstr.*, 1959, **20**, 448—449).—Laboratory and field experiments indicated that there is little fear of volatilisation of NH_3 when growing crops are top-dressed with urea at less than 100 lb. of N per acre, and soil pH $<6\cdot3$. Larger applications of urea can be made without loss of NH_3 when the urea is mixed with the soil, or when top dressings can diffuse into the soil before drying occurs. Significant losses of NH_3 can occur if urea is not uniformly distributed on the surface of the soil.
M. D. ANDERSON.

New organo-mineral microfertilisers and their application. M. E. Shishniashvili (*Dokl. Akad. Nauk SSSR*, 1959, **126**, 421—423).—Microfertilisers prepared by the oxidative destruction of polymeric carbohydrates are investigated. These are non-ionising complexes, chemically resembling certain chelates but affecting the plants in a different way. They are easily available and readily assimilated by the plant, adsorbed by the soil to a smaller degree than the ions of their constituent metals, and resistant to relatively high pH. Their application to diseased vine and tobacco plants is found beneficial.
L. GROCHOWSKI.

Transformations of calcium cyanamide in soils and in plants. O. T. Rotini (*Agrochimica*, 1958/9, **3**, 101—107).—Possible modifications of the generally accepted view of the mechanism of cyanamide transformations are based on the concept of the isomeric change of urea into $NH_4 \cdot CNO$ and the effects thereon of soil enzymes.
A. G. POLLARD.

Properties of rock phosphates and their manurial action. L. Gisiger and H. Pulver (*Agrochimica*, 1958/9, **3**, 165—189).—The solubility and consequently the fertiliser value of rock phosphates depends on their crystal size and d, the F content being of only secondary importance. Phosphates from N. Africa and Florida contain more F than is commensurate with the presence of fluoropatite; the apatite of Kola phosphate contains less than the corresponding amount of F. $CaCO_3$ present in N. African and Kola phosphates is occluded between the phosphate crystals; that in Florida phosphate occurs in a form isomorphous with the phosphate.
A. G. POLLARD.

Diammonium phosphate. C. K. Pearson (*Iron & Steel Engr*, 1959, **36**, No. 10, 122—125).—The production is discussed with reference to its availability as fertiliser containing available N $20\cdot5$—21 and P_2O_5 53—54%. The granules show little tendency to break down on handling.
C. V.

Laboratory and greenhouse tests with monocalcium, mono-ammonium and diammonium phosphates. D. R. Bouldin and E. C. Sample (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 338—342).—Movement of P over 3—5 weeks from pellets of $Ca(H_2PO_4) \cdot H_2O$ (**I**), $NH_4H_2PO_4$ (**II**) and $(NH_4)_2HPO_4$ (**III**) placed on the surface of an acid (pH $5\cdot2$) and a calcareous soil was studied. Fertiliser P moved about $2\cdot5$ cm. in the acid and $1\cdot5$ cm. in the calcareous soil and there was little difference in movement between the three sources of P or between 3 and 5 weeks. Water-sol. fertiliser P was higher in the acid than in the calcareous soil. In the acid soil more fertiliser P was extracted by water when **III** than when **I** was added, whilst the reverse was true in the calcareous soil. Water-sol. P measurements explained most of the variation of plant uptake of P with the different fertilisers in greenhouse tests. **III** was the best source of P in the acid soil, whilst **I** was the best in the calcareous soil.
A. H. CORNFIELD.

Evaluation of phosphorus fertilisers varying in water solubility. II. Broadcast applications for maize. J. R. Webb and J. T. Pesek, jun. (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 381—384).—In 16 trials on soils of pH $5\cdot5$—$7\cdot1$ there were little differences in yields from broadcast application of 13 sources of P (0—92% P in water-sol. form) applied at rates of 20—80 lb. of available P_2O_5 per acre. In some tests residual effects on a succeeding crop of maize or oats also showed no differences between source of P. In three trials there were no differences in yields between $Ca(PO_3)_2$ and concentrated superphosphate used as P sources at equiv. available P_2O_5 rates, either in autumn or spring.
A. H. CORNFIELD.

Mechanical movement of superphosphate in soil resulting from cultural operations; use of radioactive phosphorus. A. D. Kofold (*Tidsskr. Planteavl*, 1959, **63**, 285—306).—After a 1-year cultivation cycle ^{32}P-labelled superphosphate had spread up to $4\cdot5$ in. outside the treated area and up to $7\cdot5$ in. after 6 years' cultural operations. The bearing of these results on the width of buffer areas needed between experimental plots is discussed.
A. G. POLLARD.

Determination of sulphate in superphosphate. A. G. C. Morris and S. J. Bozaler (*Analyt. chim. Acta*, 1959, **21**, 215—221).—The effects of $BaCl_2$ and HCl concn., and the solution vol. on the gravimetric determination of sulphate as $BaSO_4$ have been examined. With the final method 20 determinations on 10 samples of super-

phosphate containing $40\cdot1\%$ of sulphate gave a standard deviation of $0\cdot08$.
W. T. CARTER.

Fixation of potash fertilisers. P. Boischot and G. Simon (*Chim. et Industr.*, 1959, **82**, 189—192).—In normal cultivated soils the greater part of the K_2O is fixed by the soil. When fertilisers of various K_2O concn. are added to the soil the amounts of K_2O which pass into solution are always low ($\sim5\%$ of the quantity added). The concn. of K_2O in the solution of the soil thus depends to a much greater extent on the ease with which the K_2O initially present can be extracted by water than on the order of magnitude of the fixation of the K_2O added in the fertilisers.
J. M. JACOBS.

Radiometric estimation of potassium in combined fertilisers. S. Havelka and M. Rakovič (*Chem. Prům.*, 1959, **9**, 509—511).—A laboratory-constructed instrument is described for carrying out this estimation and studying the effects of I and Br. (11 references.) (From English summary.)
C. V.

Effect of farmyard manure on fertiliser responses. D. A. Boyd (*J. agric. Sci.*, 1959, **52**, 384—391).—In manurial trials interactions between fertiliser nutrients were large in absence of farmyard manure but small in its presence. In the manuring of potatoes on soil of average nutrient status the same ratio of plant nutrients was suitable whether or not farmyard manure was applied, due allowance being made for the amounts of nutrients in the dung. A. G. POLLARD.

Nitrogen, phosphorus and potassium content of poultry manure and some factors affecting its composition. M. B. Parker, H. F. Perkins and H. L. Fuller (*Poultry Sci.*, 1959, **38**, 1154—1158).—The moisture, total N, P and K, available P and water-sol. K of manure samples from 82 broiler houses and 31 hen houses are reported. Variability in the nutrient content of the manures was not related to type of housing or management practice.
A. H. CORNFIELD.

Fertilisers. Lummus Co. (B.P. 804,292, 16.3.56. U.S., 29,3,55). —A fertiliser product, especially suitable for use in the cultivation of legumes, is obtained by treating a phosphate (e.g., K, Na or Ca metaphosphate) with a strong base, viz., a K or Na base (especially naturally occurring pearl ash) in presence of water, then curing the product. Thus, water ($22\cdot23$) containing 85% KOH ($31\cdot38$) is stirred into Ca metaphosphate ($46\cdot49\%$) during 45 sec., temp. rising to 117°, to give a damp crumbly solid. After 2 days the product is hard and dry, and analyses as H_2O $2\cdot85$, P_2O_5 $40\cdot15$ (insol. P_2O_5 $3\cdot15$, sol. P_2O_5 37) and K_2O 29%.
F. R. BASFORD.

Granular fertilisers. Scottish Agricultural Industries Ltd. and Imperial Chemical Industries Ltd. (Inventors: I. A. Brownlie, J. Ames and E. K. Pierpoint) (B.P. 804,053, 6.4.56).—Caking of a granular fertiliser (especially material containing N) is minimised by coating with $0\cdot001$—$0\cdot5\%$ of a water-sol. salt of 2-aminonaphthalene-3,6-disulphonic acid and/or its ω-methanesulphonate.
F. R. BASFORD.

Manufacture of granular materials, e.g., fertilisers. Fisons Ltd. (Inventor: K. Sharples) (B.P. 803,437, 24.11.55).—The granulator comprises a rotary drum which is provided with one or more chains fixed, at least at both ends, within the drum.
I. JONES.

Compositions for improving the soil. Dow Chemical Co. (B.P. 803,052, 20.10.54. U.S., 29.10.53).—A composition for use in improving soil in arable land (especially for making available to plants metals which are present in soil) comprises a compound $NRR' \cdot (X \cdot NR)_n \cdot X \cdot NRR''$ (X is divalent aliphatic or *cyclo*aliphatic group or $\not> 7$; R is $CH_3 \cdot CO_2M$ or $\cdot [CH_2]_2 \cdot CO_2M$; M is H, alkali metal or NH_4; R' is R, H, alkyl or aralkyl, optionally substituted by alkoxycarboxy, ester, SH, OH, phosphoric acid or SO_3H group; R'' is R or R'). The compound may be largely present in the form of its Fe complex, and may be used in admixture with an inorg. carrier (vermiculate, Al_2O_3 or SiO_2 gel) or fertiliser (garbage, sewage sludge, animal residue, blood, proteinaceous matter or artificial manure). Chelating agents specially claimed include EDTA, N-(2-hydroxyethyl)-$NN'N'$-tri(carboxymethyl)-, and NN'-di-(2-hydroxyethyl)-NN'-di(carboxymethyl)-ethylenediamine.
F. R. BASFORD.

Plant Physiology, Nutrition and Biochemistry

Plant responses to differences in soil moisture. M. B. Russell (*Soil Sci.*, 1959, **88**, 179—183).—A review with suggestions for further work.
T. G. MORRIS.

Effects of soil moisture conditions on the uptake of plant nutrients by barley and on the nutrient content of the soil solution. S. Y. Metwally and A. G. Pollard (*J. Sci. Fd Agric.*, 1959, **10**, 632—636).—Soil moisture levels of $\sim\frac{1}{2}$ and $\frac{1}{3}$ of the water-holding capacity were maintained throughout the experiment. Differences in concn. of

individual nutrients in the displaced soil solution at the two water levels were small, whereas the total amounts of dissolved nutrients were increased at the higher water level. The % increases differed for each nutrient (NO_3^- > P, K > Ca) and with manurial treatments. The uptake of nutrients by barley per unit wt. of soil and the dry matter produced in the seedlings were greater with the higher water supply, the proportional (%) increase differing with the nutrient (19—77%) in the order Ca > K, Mg > P > N. (26 references.)
                                                                    E. M. J.

Enzyme activity in wheat grains in relation to water content. Glutamic acid–alanine transaminase, and glutamic acid decarboxylase. P. Linko and M. Milner (*Plant Physiol.*, 1959, **34**, 392—396).—Moisture levels as low as 18% activate both enzyme systems; activity increases rapidly with moisture up to that required for germination. Transamination of α-ketoglutarate with alanine occurred at moisture levels as low as 15%. At higher levels, transamination is followed by rapid decarboxylation of glutamate.
                                                                E. G. BRICKELL.

Effect of carbon dioxide on respiration of excised onion root tips in high-oxygen atmospheres. W. E. Norris, jun., J. D. Wiegand and L. Johanson (*Soil Sci.*, 1959, **88**, 144—149).—The respiration rate of freshly excised onion root tips has been measured in a Warburg manometer in atm. of O_2 with increasing amounts of CO_2. Increasing amounts of CO_2 depressed respiration and in a 1 : 1 $CO_2 : O_2$ atm. it was almost inhibited. When the roots were exposed to 100% O_2 and then to 1 : 9, $CO_2 : O_2$ the rate of respiration was decreased but the depression continued when the atm. was again changed to pure O_2. Addition of glucose to the substrate did not prevent this effect but the depression in the second O_2 period was much less than in the absence of glucose.   T. G. MORRIS.

Influence of magnesium, potassium and nitrogen nutrition on phosphoenolpyruvate-stimulated carbon dioxide fixation. G. W. Thomas, N. T. Coleman and W. A. Jackson (*Agron. J.*, 1959, **51**, 591—594).—Homogenates from leaves of sweet potato plants grown in solutions low in K, Mg and N showed a reduced capacity for fixing CO_2 in the presence of phosphoenolpyruvate. Addition of Mg to the assay restored activity to Mg-deficient leaves, but addition of K to extracts of K-deficient leaves did not.   A. H. CORNFIELD.

Root metabolism and the assimilation of ammonia by phosphorus-deficient plants. A. Kursanov and O. Kulaeva (*Agrochimica*, 1958/9, **3**, 29—38).—Products of photosynthesis in young pumpkin plants are translocated to roots largely as sucrose, from which org. acids and amino-acids are synthesised and carried upwards in sap. P deficiency lowers the intensity of the Krebs' cycle reaction and the dark fixation of CO_2 and glyoxylic acid accumulates. A supply of NH_3 to P-deficient roots results in the abnormal production of amides, guanidine derivatives and allantoin, protein synthesis from which is less satisfactory. In such treated roots addition of P rapidly restores normal metabolism.   A. G. POLLARD.

Method for measuring short-term nutrient absorption by plants. III. Nitrogen. J. D. DeMent, G. Stanford and C. M. Hunt (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 371—374).—Oats were grown for 15 days in sand in containers with removable bottoms without addition of N. The bottomless pot was then placed on the soil under test and N uptake measured from 1 to 14 days thereafter. No significant N uptake occurred during the first day. N uptake during 3, 5 and 7 days was similar from addition of $(NH_4)_2SO_4$ (**I**), $NaNO_3$ or urea to the test soil, whilst ureaform supplied only about 33% of the N supplied by the other fertilisers. There was a sigmoid relationship between fertiliser-N uptake and time (up to 14 days). In 7 days recovery of N applied in **I** ranged from 62% to 93% and after 14 days from 93% to 94% (roots and tops). The method showed differences between soils with respect to availability of native N. In both fertilised and unfertilised soils N uptake increased with soil moisture to a max. at the moisture equiv., but then decreased with higher soil moisture. Since there was a very high correlation between N uptake in tops and that in tops + roots, analysis of the tops only should give sufficiently precise data for comparing relative N uptakes.   A. H. CORNFIELD.

Effect of nutritional stress on plant composition. I. Interaction of added nitrogen with varying sulphur supply. V. V. Rendig and E. A. McComb (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 377—380).—In culture tests yields of lucerne tops increased rapidly with increasing level of SO_4^{2-} (S up to 0·8 p.p.m.) in the solution, and continued to increase at a slower rate with further increasing SO_4^{2-} (S up to 8 p.p.m.). Yields were higher at all levels of S where NO_3^- than where NH_3 was the source of applied N, and were substantially lower where no combined N was supplied. Where the S supply was limiting there were greater changes in amide and sugar contents than in the S content of the plants. At low S level amide was high and sugar was low, whilst the reverse held at high S level. The effects were similar whether N was supplied as NO_3^- or NH_3 or made available through fixation.   A. H. CORNFIELD

Phosphorus and the biochemistry of photosynthesis. D. I. Arnon (*Agrochimica*, 1958/9, **3**, 108—139).—The rôle of P in photosynthesis is examined. Evidence is presented to show that CO_2 assimilation by plants depends on a preceding phosphate–phosphate interaction resulting in the production of adenosine triphosphate utilising light energy independently of the process of respiration. (80 references.)
                                                                A. G. POLLARD.

Absorption and translocation of phosphorus [by plants] as examined with 32-phosphorus. E. Baldacci and E. Betto (*Agrochimica*, 1958/9, **3**, 83—99).—Movement of ^{32}P-labelled phosphate following intake (alone or supplemented with polyethylene glycol or indolylacetic acid) *via* leaves, from nutrient solutions in vermiculite cultures *via* roots or from lanoline paste (with or without surfactant) *via* stems is examined. Losses of P from roots and the accumulation of P in damaged green tissue are discussed
                                                                A. G. POLLARD.

Function of potassium in the metabolism of energy-rich phosphates in plants and animals. E. Latzko (*Agrochimica*, 1958/9, **3**, 148—164).—Utilisation of P in the process of aerobic phosphorylation in plant and animal cells is increased specifically by K. In the phosphorylation stage in photosynthesis K probably plays a part resembling that of Mg.   A. G. POLLARD.

Metabolism of ^{14}C-bicarbonate, ^{32}P-phosphate or ^{35}S-sulphate by lettuce seed during germination. A. H. Haber and N. E. Tolbert (*Plant Physiol.*, 1959, **34**, 376—380).—^{14}C was detected in sol. compounds as early as 1 hr. after the beginning of inhibition, suggesting fixation by carboxylations into org. acids. Neither ^{32}P nor ^{35}S were metabolised by intact seeds until after radicle protrusion (15 to 18 hr. after inhibition) but punctured seeds metabolised the radioactive salts within 3 hr. Within this time punctured seeds could esterify phosphate and reduce sulphate to the level of sulphydryl.   E. G. BRICKELL.

Effect of soil solution aluminium and calcium on root growth. J. L. Ragland and N. T. Coleman (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 355—357).—The quantity of exchangeable Al and the % Al saturation of subsoils in the Norfolk catena (pH 4·4—5·0) increased with decreasing natural drainage. The growth of sorghum roots decreased with increasing % Al saturation. Root growth was very poor when exchangeable Al exceeded 2 mequiv. per 100 g. soil. Liming to pH 5·5 (approx.) decreased exchangeable Al to <0·66 mequiv. per 100 g. in all soils and resulted in satisfactory root growth. Addition of KCl or $CaCl_2$ to acid soils increased the Al concn. in the soil solution and reduced maize and sorghum root growth. Addition of the neutral salts to limed soils did not increase soil solution Al concn. and did not reduce root growth.   A. H. CORNFIELD

Rubidium–potassium relationships in the soil–plant system. M. Fried, G. Hawkes and W. Z. Mackie (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 360—362).—The ratio of the uptakes of K and of Rb by millet from resin–sand culture was very similar to the ratio of the two cations in the substrate over the range 42 to 1360 lb. K per acre. Uptake of K by millet in six soils increased with K supply and uptake of Rb increased with Rb supply. However, uptake of K or Rb was not affected by the rate of supply of the complementary ion. The six soils showed marked differences in ability to fix added Rb in non-exchangeable form, but the extent of fixation was not affected by the level of added K. The % of added Rb fixed by the soils decreased with level of added Rb.   A. H. CORNFIELD.

Accumulation of some minor elements in maize plants grown at different levels of hydrogen ion concentration. Yuan-Pin Chou (*Dissert. Abstr.*, 1959, **20**, 440—442).—Maize was grown in gravel, solution and soil cultures, at 3 pH levels, and 15 elements were determined in the plants: Zn, Co, Sr and Fe by tagging, and Mn, Cu, Al, Ca, Mg, B, P, Pb, Si, Ag and Sn spectrographically. In general, minor elements accumulated more at low pH, and mainly in the upper portions of young plants, shifting to the lower leaves as the plant aged, and to the margins of etiolated and dead leaves. Co, B, Si and Al accumulated in leaf margins and organ tips; Mn, Fe and Cu in nodes, margins and tips; Zn, Ca, Sr and Mg usually in nodes, and in leaf margins in unfavourable growth conditions. The distribution of the elements in the various plant organs is determined and the influence of varying levels of supply are examined.
                                                                M. D. ANDERSON.

Occurrence of free galacturonic acid in apples and tomatoes. J. H. McClendon, C. W. Woodmansee and G. F. Somers (*Plant Physiol.*, 1959, **34**, 389—391).—An acid fraction isolated from 70% 2-propanol extracts of apples and tomatoes contained a component identical in R_F and aniline colour test with galacturonic acid; guluronic, glucuronic and mannuronic acids were not found. In addition the apple samples contained a minor, but complex, uronic acid component which increased at least 10-fold upon the softening of the fruit but was still less than the amount of D-galacturonic acid bound in pectin.   E. G. BRICKELL.

Effects of artificial increases in sugar content on frost hardiness. J. Levitt (*Plant Physiol.*, 1959, **34**, 401—402).—Infiltration of frost-hardened cabbage leaves with dextrose or fructose resulted in an increased frost hardiness equal to the calculated increase on the basis of a purely osmotic effect. D-Ribose produced no greater effect than either of the hexoses.   E. G. BRICKELL.

Chemistry and physiology of metabolically important acids. III. Paper chromatographic method of detection of isocitric acid in plant materials. R. Pohloudek-Fabini, C. Wollmann and H. Wollmann (*J. Chromatography*, 1959, **2**, 525—536).—Isocitric acid (I) may be separated from citric acid (II) and other acids by descending chromatography with a water-saturated mixture of isoamyl alcohol-CHCl₃-85% formic acid (4 : 1 : 1) as solvent. The R_F values are 0·12 and 0·14 for I and II respectively. The chromatogram is dried at room temp., sprayed with Schweppe's reagent, dried at 125° and the acids show as brown spots. I has been identified in various plant extracts by this method.   A. G. ROGERS.

Inhibition of root growth and cation uptake by antibiotics. A. G. Norman (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 368—370).—Of 20 antibiotics tested 7 caused 50% repression of root elongation of cucumber at concn. ranging from 0·2 to 8·5 µg. per ml. of nutrient. The inhibitng concn. was of the same order as that for NaN_3, but was much less than that for 2,4-D. Root growth of barley seedlings (24-hr. old) occurred with concn. of antibiotics similar to those inhibiting cucumber root elongation. Significant reduction in K uptake by excised 5-day-old barley roots generally occurred at concn. of antibiotics many times greater than that required to reduce root growth.   A. H. CORNFIELD.

Extension-growth activities of cyclopropane derivatives, a new class of antiauxin. N. P. Kefford (*Aust. J. biol. Sci.*, 1959, **12**, 257—262).—From ten substances tested, 2,3-dihydrobenzofur-2,3-yleneacetic acid, 1,2-dihydro-1,2-naphthyleneacetic acid, and *cis*- and *trans*-2,3-dihydrothionaphthen-2,3-yleneacetic acid inhibit competitively auxin-induced growth of *Avena* coleoptile sections. The structural difference between these antiauxins and related auxins is discussed with reference to structural requirements for antiauxin activity.   S. G. AYERST.

Changes in endogenous growth substances during flower development. H. Harada and J. P. Nitsch (*Plant Physiol.*, 1959, **34**, 409—415).—Data are presented for a long-day plant, *Rudbechia speciosa*, a cold-requiring plant, the Japanese chrysanthemum var. Shuokan, and a short-day plant, the Shasta chrysanthemum. The existence of both quant. and qual. changes in the pattern of endogenous growth substances are indicated. Data on the nature and properties of these active substances are given. E. G. BRICKELL.

Morphogenetic effects of the gibberellins. P. W. Brian (*J. Linn. Soc.*, 1959, **56**, 237—248).—A review with an extensive bibliography.   L. G. G. WARNE.

Gibberellic acid and nodulation of legumes. W. W. Fletcher, J. W. S. Alcorn and J. C. Raymond (*Nature, Lond.*, 1959, **184**, 1576).—Different genotypes of plants, presumably of varying endogenous gibberellin-levels, react differently to applications of this substance. The seeds of *Trifolium repens* (I), *T. hybridum*, *T. pratense*, *T. incarnatum*, *T. subterraneum* and *Medicago sativa* (II) were examined. K-gibberellate (500 p.p.m.) (III) with Rhizobia cultures were added to seedling cultures. III had no effect on I and II but reduced by 50% nodule numbers in the other species.   C. V.

Inverse effects of gibberellin on peroxidase activity and growth in dwarf strains of peas and maize. D. C. McCune and A. W. Galston (*Plant Physiol.*, 1959, **34**, 416—418).—Gibberellin increases the growth rate and decreases the peroxidase activity per unit protein N of dwarf maize. Similar results were shown with the dwarf pea, Progress # 9, but not in the tall variety Alaska.   E. G. BRICKELL.

Effect of gibberellin, sodium hypochlorite, light and planting depth on germination of guayule seed. B. L. Hammond (*Agron. J.*, 1959, **51**, 621—623).—Both embryo and inner seedcoat dormancy of freshly harvested achenes of guayule were completely broken by continuous exposure to daylight for 3 weeks. Gibberellin treatment of the achenes broke dormancy in the absence of light whilst NaOCl treatment was effective only with a supplementary 4-day light period during germination.   A. H. CORNFIELD.

Growth responses to gibberellic acid. M. Y. Stant (*J. Linn. Soc.*, 1959, **56**, 249—250).—Various species of plants (at Kew) were given weekly sprays of gibberellic acid (100 p.p.m.). All the species showed an increase in shoot height and in internode length, the increases being greatest for two tropical plants—*Cannabis sativa* and *Gossypium hirsutum*. Stem diameter was generally decreased and leaf area increased.   L. G. G. WARNE.

Occurrence, effectivity and fermentative conversion of indol-3-ylacetonitrile [IAN] in plants. E. Libbert and G. Ballin (*Naturwissenschaften*, 1959, **46**, 532—533).—The detection, effect as a growth factor and conversion to indol-3-ylacetic acid (IAA) of IAN was studied. Of the plants investigated, only *Pisum sativum* failed to react to IAN. IAN is either converted into IAA by hydrolysis (as in *Brassica*, *Triticum*), or exerts auxin-activity. The result in each case is increased cell size.   W. H. KEMP.

Synthesis of isomeric quinoloxyacetic acids. J. Moszew and J. Mirek (*Roczn. Chem.*, 1959, **33**, 365—369).—Five deriv. of quinoline were prepared. Of these, 6-quinoloxyacetic acid (I), 5-chloro-6-quinoloxyacetic acid (II) and 5-chloro-6-hydroxyquinoline (III) retarded the germination, sprouting and further development of oats, millet, flax and mustard. I led to the abnormal thickening of sprouts ; II and III caused upward growth of flax roots.   A. L. GROCHOWSKI.

Urethane derivatives affecting growth of plants. J. Mirek (*Roczn. Chem.*, 1959, **33**, 371—377).—Ten new isopropyl and chloroethyl esters of aryloxymethylcarbamic and arylmethylcarbamic acids were synthesised and their effect on the germination of linseed and mustard seed was investigated. The only products having activity comparable with that of known agents are the isopropyl ester of benzylcarbamic acid and chloroethyl ester of β-naphthylmethylcarbamic acid. (12 references.)   A. L. GROCHOWSKI.

Crops and Cropping

Mathematical procedure for evaluating relationships between climate and wheat yields. W. C. Johnson (*Agron. J.*, 1959, **51**, 635—639).—The procedure is described.   A. H. CORNFIELD.

Physiological factors affecting the lodging of wheat and its association with glucide/protein imbalance. J. Carles, L. Soubiés, R. Gadet and F. Fourcassié (*C. R. Acad. Agric. Fr.*, 1959, **45**, 595—602).—The " lodging " of wheat is a consequence of glucide/N imbalance. With lack of N, sheaths, straws and roots overloaded with glucides develop, but the undernourished limbs turn yellow. With abundant N, growth is slower, and the plants are finally more developed. N absorbed is carried immediately to growing tissues, promoting growth and increasing the need for glucides, thus impoverishing roots, straw and sheaths. Conditions favouring " lodging " of the wheat are produced with undernourished and under-developed sheaths, straws and roots. J. M. JACOBS.

Frost injury to maturing barley. D. W. Robertson, T. E. Haus and J. C. Hoff (*Agron. J.*, 1959, **51**, 658—660).—Frost reduced malting quality, wt. per 100 kernels, and germination of barley seed when the plants were subjected to freezing temp. at the milk, soft dough, and tough dough stages. Heads subjected to freezing temp. at the " turning " stage had shrivelled kernels, reduced germination and increased N content. Exposing ripe heads to freezing caused little damage.   A. H. CORNFIELD.

Yield components in oats. II. Effect of nitrogen fertilisation. K. J. Frey (*Agron. J.*, 1959, **51**, 605—608).—Increases in yields of oat grain due to N fertilisation (20—80 lb. of N per acre) were due to production of more heads per plant and seeds per head. Seed wt. was little affected by the treatments. There were considerable varietal differences in response to N fertilisation with respect to yields, heads per plant and seeds per head. A. H. CORNFIELD.

Influence of water and nutrient supply on the husk content of some oat varieties. W. Eberhardt and G. Krzysch (*Z. PflErnähr. Düng.*, 1959, **86**, 111—120).—Pot trials indicate that an increase in NPK reduces the husk content due to improved germ development, whilst a high water supply favours husk formation.   M. LONG.

Nitrogen manuring with split applications. III. Field trials with winter rye. H. Linser and E. Primost (*Z. PflErnähr. Düng.*, 1959, **86**, 97—111).—Increasing N applications (up to 160 kg./ha.) especially when split lead to higher yields and grain/straw ratios. The N and K contents of rye increase with increasing N supply, but the P content is little affected. Utilisation of nutrients is increased by N manuring.   M. LONG.

Salt tolerance of agricultural crops at germination stage. A. Wahhab, A. Jabbar and F. Muhammad (*Pakist. J. Sci. Res.*, 1959, **11**, 71—80).—With salt concn. of 0·6% the salt tolerance of wheat, maize, barley, gram, rice and cotton increased with moisture levels in the range 15—75%. (13 references.)   C. V.

Nutrition of rice plant (*Oryza sativa, L.*). **VI. Utilization of ammonium and nitrate nitrogen by the rice plant in water-logged soil.** A. Tanaka, S. Patnaik and C. T. Abichandani (*Proc. Indian Acad. Sci.*, 1959, **50B**, 61—74).—Applications of NH_4^+- or NO_3^--fertiliser were given as planting, or split with ⅔ at planting and ⅓ later. NH_4^+

applied at any stage of growth was superior to NO_3^- for increasing yield; utilisation of N from NH_4^+ was 55—60% while from NO_3^- was 4—20%. NO_3^-, top dressed after initial NH_4^+, gave only slightly lower ear yields than did top-dressed NH_4^+ but far less straw. Single applications of NH_4^+ at any stage gave the same ear yield, but higher straw yields were obtained with applications at planting. Fertiliser applied at the boot stage only had less effect on rice yields than did earlier applications. The slight increase in ear wt. obtained with split applications of NH_4^+ was due to increase in mean panicle wt. and no. of grains per panicle resulting from top-dressing at the later stage. (21 references.)   C. V.

Re-examination of the effect of liming on paddy rice. II. Influence of liming on hardness of grain and strength of straw. M. Deguchi, Y. Ohta and Y. Tomita (*Soil & Plant Fd*, 1958, **4**, 53—56).—Liming increased the hardness of the grain and its Ca and reducing sugar content to extents which varied with the time of application. Straw strength was also increased especially with late dressings of lime. The tensile strength of the straw was correlated positively with lime and cellulose contents and stem diameter and, negatively, with the ash and SiO_2 contents.   A. G. POLLARD.

Salinity effects at several growth stages of rice. G. A. Pearson and L. Bernstein (*Agron. J.*, 1959, **51**, 654—657).—Increasing salinity from heading to maturity had little effect on rice yields. Increasing salinity from later tillering to maturity reduced yields somewhat, whilst increasing salinity from early tillering to maturity reduced yields considerably.   A. H. CORNFIELD.

Cultivation of sweet maize. M. Dessiatoff (*C. R. Acad. Agric. Fr.*, 1959, **45**, 519—522).—Seeds already germinated are sown in seed pockets, and not in rows, in freshly prepared soil.
                                                                       J. M. JACOBS.

Influence of cropping system treatment combinations and climatic factors on maize yields in the Blackland area of Texas. J. W. Collier (*Agron. J.*, 1959, **51**, 587—590).—Without irrigation, maize after sweetclover produced higher yields than did continuous maize in 5 out of 6 years. Responses to N applications were small and inconsistent. Irrigation increased yields, particularly where N was applied. N applications increased yields in continuous maize, but not in maize after sweetclover. Soil NO_3^- and leaf N were highest in the maize–sweetclover plots. There was a significant negative correlation between yields and mean max. temp. during the 3-week period after silking for the irrigated plots following sweetclover.
                                                                       A. H. CORNFIELD.

Factors affecting the nutrient content and yield response of maize to nitrogen, phosphorus and potassium fertilisation. B. L. Baird (*Dissert. Abstr.*, 1959, **20**, 431—432).—Response of maize to application of N was usually greater on (i) well-drained soils low in org. matter than on (ii) poorly drained soils high in org. matter. Yield, and N in leaves and grain, increased with increased amount of N fertiliser. Applications of P rarely increased yield on (i), and sometimes increased it on (ii); P in leaves was increased more, and more often, by applications of N than of P. Applications of K seldom increased yield, but increased the K content of leaves, and often depressed the Ca and Mg contents of leaves. Experiments with ^{15}N showed that the total N in the leaves, and the amount of N coming from fertiliser, was larger with NH_4 fertiliser than with NO_3^-.
                                                                       M. D. ANDERSON.

Maize grain yields as related to nutrient element content of leaves and to foliar spray treatments. J. B. Jones, jun. (*Dissert. Abstr.*, 1959, **20**, 448).—Increased applications of N fertiliser and larger plant populations did not affect the contents of N, P, K, Ca, Mg, Mn, B, Cu and Zn in leaves of maize, nor were these contents correlated with yield of grain at lower plant populations. At higher populations (18,000 to 20,000 plants per acre), grain yields were negatively correlated with K, Mg, Mn, B, Cu and Zn contents of leaves. The effects of spraying with trace element solutions varied with variety of maize, soil moisture, level of N fertiliser, composition of spray and time of spraying. Increased yield of grain was obtained in dry seasons, but not when soil moisture was adequate throughout the season.   M. D. ANDERSON.

Nitrogen and phosphorus composition and yield of maize as affected by fertilisation. G. A. Reichman, D. L. Grunes, C. W. Carlson and J. Alessi (*Agron. J.*, 1959, **51**, 575—578).—Yields of maize grain and forage on an irrigated loam over 5 years increased with the level of applied N up to 80 lb. per acre and there was little further increase with 120 lb. N per acre. The treatments increased N % and P % in grain, leaves and stover. N % in the leaves was positively correlated with P %. Both P % and N % in leaves at pollination were highly correlated with grain yields and with total nutrient uptake at harvest. Although leaf-P % was important, leaf-N % was the dominant indicator of yield. Grain- and forage-N % associated with max. yields varied with season.
                                                                       A. H. CORNFIELD.

Factors concerned in the growth of stolons in the potato. A. Booth (*J. Linn. Soc.*, 1959, **56**, 166—169).—Shoots of *Solanum andigena* plants grown in soil produced stolons only at the base and this was so also for plants produced from stem cuttings (not from tuber sprouts). Stolons are produced only from nodes bearing adventitious roots and the formation of both is induced high up on aerial shoots if these are wrapped in moist *Sphagnum*. Stolons remain etiolated and diageotropic when exposed to light and this appears to be due to some substance passed down from the aerial shoot. The same effect can be produced by applications of indolyl acetic and gibberellic acids together.   L. G. G. WARNE.

Effect of rate of application of superphosphate on growth and yield of potatoes. K. Simpson, R. D. Verma and J. Dainty (*J. Sci. Fd Agric.*, 1959, **10**, 588—596).—Shoot yield was stimulated by dressings of superphosphate up to 2 cwt. of P_2O_5/acre on low-P soils, and root and tuber dry matter were not further increased by applications >0·66 cwt. of P_2O_5/acre. On high-P soils superphosphate applications had little effect on shoot yield but delayed tuber development and depressed the final yield of tuber dry matter. Correlation between P uptake and yield of tuber dry matter was positive on low-P soils and negative on high-P soils. The optimum P uptake by the whole plant for tuber yield appears to be 30—35 lb. of P_2O_5/acre and when the level exceeds 35—40 lb. of P_2O_5/acre at the 12-week stage of growth, P toxicity occurs. (23 references.)
                                                                       E. M. J.

Possibilities of liquor utilisation in potato-starch factories. K. Siebert (*Ernährungsforschung*, 1959, **4**, 183—252).—A review. Potato juice and starch-factory wash-liquors are discussed with particular reference to dissolved protein. The most practicable uses are for manuring, production of fodder and production of combustible gases by microbiological processes. (192 references.)
                                                                       E. C. APLING.

Vertical distribution of top-dressed fertiliser phosphorus and potassium in relation to yield and composition of pasture herbage. E. C. Doll, A. L. Hatfield and J. R. Todd (*Agron. J.*, 1959, **51**, 645—648).—The effect of P (P_2O_5, 30—240) and K (K_2O, 60—480 lb. per acre) on growth of a fescue–orchard grass–ladino clover pasture on a silt loam over 2 years was studied. Forage yields and total uptake of N, P and K were increased by P application but not by K. Considerable amounts of non-exchangeable K were removed by the crop at the lower rates of applied K. There was little fixation of applied K in non-exchangeable form with the heavy K dressings. Most of the applied P remained in the top in. and of the applied K in the top 3 in. of soil. There was no movement of P below 3 in. or of K below 6 in.   A. H. CORNFIELD.

Growth in swards of timothy and meadow fescue. II. Effects of cutting treatments. R. H. M. Langer (*J. agric. Sci.*, 1959, **52**, 273—281; cf. *ibid.*, 1958, **51**, 528).—Pure swards of timothy and of meadow fescue were cut at different intervals. The decline in no. of tillers between early spring and late summer was diminished by frequent cutting in a wet season. Leaf wt. per unit area of ground increased up to the time of ear emergence but not subsequently. After cutting the fescue produced heavier leaves than did timothy.   A. G. POLLARD.

Effect of fertility and management treatments on the growth and early development of rhizomes of two varieties of smooth brome-grass. L. B. Hertz (*Agron. J.*, 1959, **51**, 666—668).—The no. and growth of rhizomes of bromegrass in the seedling year were greater on plots kept free of weeds than on those on which weeds were clipped or an oat companion crop was used. Southern bromegrass produced more and longer rhizomes than did northern bromegrass, the difference being greatest in the weeded plots. Application of a complete fertiliser had no effect on rhizome development.
                                                                       A. H. CORNFIELD.

Effect of pH on uptake of native and applied nitrogen, phosphorus and potassium. S. T. Than (*Dissert. Abstr.*, 1959, **20**, 450—451).—The effects were studied of soil pH, and of applications of lime, manure, and N, P and K fertilisers, on the availability of original and applied N, P and K to three successive crops of greenhouse-grown Sudan grass. Soil pH dropped sharply during the growth of the first crop, and recovered slightly by the harvesting of the third crop; manure almost prevented fall of soil pH. Lime increased uptake of N except when manure was also applied. N uptake increased more when N was applied with P than when with K; increased P uptake was greater when P was applied with K than when with N. Lime increased uptake of P from manure and from untreated control soil and the uptake of K in NPK treatments, but decreased it in NP and PK treatments. Fertilisers increased the uptake of applied N, P and K, and of soil-N and -K, but decreased that of soil-P. Lime increased the uptakes of applied N and K, and of soil N and P, but not of applied P or soil-K. Water-stable soil aggregates larger than 1·0 mm. were increased by all treatments, especially by manure.   M. D. ANDERSON.

Growth responses of lucerne and Sudan grass in relation to cutting practices and soil moisture. R. E. Dennis, C. M. Harrison and A. E. Erickson (*Agron. J.*, 1959, **51**, 617—621).—Annual forage yields of both lucerne and Sudan grass decreased with increasing frequency of cutting (6-weekly to 1-weekly intervals). Frequent cutting stimulated regrowth for a short period only, after which any new growth was definitely curtailed. Water consumed per unit of forage produced decreased with increasing length of cutting interval. Sudan grass was more efficient than lucerne in water consumption per unit of forage produced in June—Aug.   A. H. CORNFIELD.

Influence of soil potassium and phosphorus content on the cold resistance of lucerne. G. A. Jung and D. Smith (*Agron. J.*, 1959, **51**, 585—587).—Buffalo lucerne grown in sand culture with different levels of P and K was subjected to freezing temp. in early Dec. after hardening out-of-doors. When P was applied at 80 lb. per acre the % of plant survivals and amount of topgrowth after exposure to freezing temp. increased with level of applied K up to 200 lb. per acre and then decreased with larger dressings. When K was applied at 200 lb. per acre max. plant survival occurred with 40 lb. of P and max. regrowth with 80 lb. of P per acre. When the K/P supply ratio was held at 5/2 the % plant survival was fairly constant over the range 200—800 lb. of K per acre.
   A. H. CORNFIELD.

Phosphate manuring of lucerne: experiments in Tuscany. V. Morani and A. Baroccio (*Agrochimica*, 1958/9, **3**, 39—48).—Manurial trials (P with K and Mo) with lucerne on quaternary dune soils are recorded.   A. G. POLLARD.

Control of growth and development in red clover (*Trifolium pratense* L.). II. Light, temperature and the influence of growth regulators. B. G. Cumming (*Canad. J. Bot.*, 1959, **37**, 1027—1048, 1049—1062). —II. Using the methods previously described (*Canad. J. Plant Sci.*, 1959, **39**, 9), a study was made of the effects of light, temp. and genotype, on morphogenesis in Dollard red clover clones. Development was less in autotetraploid than in diploid plants. The combined effects of temp., day-length and auxin are examined. (34 references.)
IIB. Differences in morphogenesis of red clover plants were related to the content of endogenous diffusible auxin. Interactions of light and auxin production and the effects of anti-auxin considered in relation to growth responses indicate that a mechanism for the regulation of the level of free auxin exists in red clover, whereby a system for the production of auxin can be linked with a system that decreases the amount of free auxin (possibly by indoleacetic acid oxidase). (33 referehces.)
   M. D. ANDERSON.

Effect of stage of development on carbohydrate content, growth and survival of red clover. W. A. Kendall and E. A. Hollowell (*Agron. J.*, 1959, **51**, 685—686).—At harvest, plants which had set seed had lower dry wt. and total carbohydrate contents than had those at the vegetative, bud or flower stages. Plants which had set seed survived as long and grew as much in the dark as did less mature plants.   A. H. CORNFIELD.

Action of gibberellin on the compactness of bunches of grapes in two varieties of vines. M. Rives and R. Pouget (*C. R. Acad. Agric. Fr.*, 1959, **45**, 343—345).—The varieties Chasselas and Folle Blanche were sprayed when the shoots were 15—20 cm. long with aq. gibberellin (100, 50 or 10 mg./l.). In Chasselas at flowering, the lengths of the bunches were greater with larger no. and greater size of the berries than those of untreated controls.   E. M. J.

Copper and zinc deficiency in the pineapple: " crook-neck." M.-A. Tisseau (*Fruits d'outre mer*, 1959, **14**, 363—367).—This condition is reported from Queensland, S. Africa and French Guinea. In the last named country Zn deficiency is countered with a routine treatment of the leaves with a 1% spray of $ZnSO_4$ and adding aq. $CuSO_4$ (1·5—2·0%) (~50 ml.) to the soil around each plant, 3—5 cm. from the base ; the Cu must never be added to the leaves. These deficiencies are found in light sandy soils which are contraindicated for pineapple cultivation. The outlined treatment is simple and effective.   C. V.

Growth of excised roots. VIII. Growth of excised tomato roots supplied with various inorganic sources of nitrogen. D. E. G. Sheat, B. H. Fletcher and H. E. Street (*New Phytol.*, 1959, **58**, 128—141).—Excised tomato roots in culture grew with NO_2^- and grew well with NH_4^+-N as the only source of N. Hydroxylamine even at low concn. inhibited extension growth. Fe (1 p.p.m. as FeNa EDTA) satisfied the Fe needs of the excised roots in culture media with pH <7·5. With NO_3^--N the optimum pH of the medium was 4·7—4·9, with NH_4^+-N, 7·0—7·2 and with NO_2^--N 5·0—6·0.
   L. G. G. WARNE.

Growth of excised roots. IX. Effect of other nutrient ions upon the growth of excised tomato roots supplied with various nitrogen

sources. J. W. Hannay, B. L. Fletcher and H. E. Street (*New Phytol.*, 1959, **58**, 142—154).—Excised tomato roots in culture receiving all their N as NO_3^- require a supply of Mo whereas when supplied with N as NO_2^- NH_4^+ urea, casein hydrolysate or arginine + glycine, growth occurs in the absence of Mo. Tolerance of excess Mn is greater with NH_4^+ than with NO_3^- as the source of N.
   L. G. G. WARNE.

Design of variety trials with spring cabbage. M. Nieuwhof (*Euphytica*, 1959, **8**, 151—156).—Varietal differences are due partly to differences in the growth rate and partly to differences in the length of the growing season and can be estimated adequately by using a standard spacing with single plant plots arranged in a Latin square.   L. G. G. WARNE.

Effect of oxygen diffusion rate and fertiliser on growth of peas. R. A. Cline and A. E. Erickson (*Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 333—335).—The effect of varying O_2 diffusion rate (15— 330 × 10⁻⁸ g. cm.⁻² min.⁻¹), obtained by varying the depth of the water table in soil columns, on growth and nutrient uptake by peas receiving low, medium and high levels of NPK was studied. Growth, yield and nutrient uptake by peas increased with O_2 diffusion rate up to about 70—100 × 10⁻⁸ g. cm.⁻² min.⁻¹. Increasing fertiliser rates had little effect on yields at very low O_2 diffusion rates, but overcame partially the lack of O_2 at somewhat higher (but still limiting) O_2 diffusion rates. Root growth was coarse and nodulation was reduced at low O_2 levels.   A. H. CORNFIELD.

Physiological and biochemical effects of γ-radiation on tubers of Jerusalem artichoke. D. K. Salunkhe (*Bot. Gaz.*, 1959, **120**, 180—183).—High doses (2 × 10⁶ rep) caused softening and disintegration of *Helianthus tuberosus* L.; darkening of the epidermis and enzymic (oxidative) activity in the tubers was directly correlated with doses between 1 and 4 × 10⁶ rep. The amounts of reducing sugars, acidity and $KMnO_4$ values in tubers were positively, and the amounts of inulin, crude fibre and pectic substances inversely, correlated with radiation dose ; total solids and total sugars remained fairly constant. A complete hydrolysis of inulin to fructose in irradiated (60 × 10⁶ rep.) tubers was effected by treatment with N-HCl at 176°F for 10 min.   E. C. BRICKELL.

Irrigation of flax. A. Larsen (*Tidsskr. Planteavl*, 1959, **63**, 1—33).—In pot experiments increased irrigation of flax (30—95% of the water capacity of the soil) produced increases in height and diameter of the straw and in the yields of straw and seed. Drought had the reverse effects. During the stage of stem elongation drought lowered straw yields and delayed flowering and maturity. Drought during or after flowering lowered the seed yield and shortened the remaining growth period. Microscopical examination of the corresponding changes in the structure of stems and fibres is described.   A. G. POLLARD.

Effects of environment and hormone treatment on reproductive morphogenesis in the chrysanthemum. W. W. Schabe (*J. Linn. Soc.*, 1959, **56**, 254—261).—Initiation of leaf primordia occurs at the rate of 2·2—3·2 per week and increases after the plant has been chilled, but the rate is not affected by the actual growth temp. Flowering occurs after subjection to low temp. but can be induced in a proportion of plants which have not been chilled, by sprays of gibberellic acid.   L. G. G. WARNE.

Effects of spraying with maleic hydrazide and potassium sulphate on the morphine content of the capsules of the opium poppy (*Papaver somniferum nigrum*). P. Locat (*C. R. Acad. Agric. Fr.*, 1959, **45**, 592—594).—One spraying with aq. maleic hydrazide (4 g. per 1.) caused deformation of the capsules, but did not affect the height of the plants, while there was a significant increase in the morphine content. Two sprayings at an interval of 1 week sharply reduced the yield of capsules, the height of the plants and the size of the capsules which showed the same abnormal ovoid shape as after a single spraying. Flowering took place 3 to 4 days later when the plants were sprayed twice. When mixed with K_2SO_4 maleic hydrazide caused no deformation of the capsules, but there was a highly significant increase in the morphine content. The effect of spraying with K_2SO_4 alone on the morphine content appears to depend on the amount of K_2O in the soil.   J. M. JACOBS.

Inter-relationship of various ions in absorption by tobacco plants. IV. Relation of magnesium, potassium and calcium in culture solutions. T. Takahashi and D. Yoshida (*Soil & Plant Fd*, 1958, **4**, 57—61).—Symptoms of Mg deficiency and lowered Mg content of the plants were associated with high levels of Ca and K supply and with K/Mg ratio >8 in the plants. With increasing supplies of K and Ca the alcohol-sol.- and acetic acid-sol.-Mg in leaves diminished ; acetic acid-sol. Ca varied with the nutritional treatments but HCl-sol. Ca contents remained the same in all cases.
   A. G. POLLARD.

[Effect of] application of the phytohormones 2,4-D (sodium salt) to cane foliage on juice quality. S. C. Sen, J. C. Bhargava and J. P. Bansal (*J. Instn Chem. India*, 1959, **31**, 55—58).—Results indicate no significant effects. (13 references.)

C. A. SLATER.

Foliar abscission in cotton. II. Influence of age and defoliants on chemical composition of blades and pulvinoids. C. L. Leinweber and W. C. Hall (*Bot. Gaz.*, 1959, **120**, 183—186).—K, Cu and Mg accumulated gradually with increasing leaf age, but P declined after the leaves reached maturity and N in the blades dropped rapidly with senescence. Significant changes in the inorg. components of the blades did not occur during the first 10 hr. following defoliant treatment (ATA and Endothal). Carbohydrate and N fractions were influenced both by age and defoliant treatment.

E. C. BRICKELL.

Hopi cotton, a source of cottonseed free of gossypol pigments. S. C. McMichael (*Agron. J.*, 1959, **51**, 630).—The no. of glands in the kernel of cotton seed was correlated with % of total and % of free gossypol. When the variety Hopi was crossed with upland cotton a glandless selection containing <0·022% total and <0·006% free gossypol occurred.

A. H. CORNFIELD.

Fertilising of young oil palms in the Cameroons. H. N. Hasselo (*Plant & Soil*, 1959, **11**, 113—130).—Young oil palms responded to N and K but responded to P only when K or N + K was applied and to Mg only when N was applied. The plants had a greatly increased requirement for Mg when entering the reproductive phase. Increased incidence of crown disease during this period was related to deficiency of Mg. A balanced nutritional medium had a more pronounced effect on reducing the disease and increasing the sex ratio of the inflorescences than on the total no. of inflorescences produced in the first 6 months of reproductive growth.

A. H. CORNFIELD.

Pest Control

Laboratory method for evaluating the toxicity of insecticides to the garden Symphylid, Scutigerella immaculata (Newport). J. S. Waterhouse (*J. econ. Ent.*, 1959, **52**, 892—895).—Feeding instars were exposed to an acetone solution of the insecticide in moist sand over moist plaster of Paris for 72 hr. Parathion was more toxic than malathion or aldrin. No differences in susceptibility were found between the sexes or instars.

C. M. HARDWICK.

Spectra response of certain stored-product insects to electromagnetic radiation. R. A. Stermer (*J. econ. Ent.*, 1959, **52**, 888—892).—*Sitotroga cerealella*, *Ephestia cautella*, *Tribolium castaneum* and *Rhizopertha dominica* were attracted preferentially to wavebands peaked near 500 mμ and secondarily at 334—365 mμ. *Plodia interpunctella* reversed this. *Sitophilus oryza* had no preference and *Laemophloeus minutus* showed little response. The effect of intensity was investigated. More male than female *S. cerealella* and *E. cautella* were attracted to all wavebands.

C. M. HARDWICK.

Method for testing the integral and the vapour action of seed-dressing dusts and steeps. A. P. Kole and L. H. W. Tchong (*Tijdschr. PlZiekt.*, 1958, **64**, 297—300).—The integral action consisting of the sum of the direct action by diffusion and the vapour action is tested by applying fungicide to filter paper strips placed on the surface of potato-dextrose agar mixed with a conidial suspension of *Glomerella cingulata*. The width of the inhibition zone after 3 days' incubation at 23° is a measure of fungicidal action. For determination of vapour action only a piece of glass is placed between the paper strips and the agar. Dusts were applied with Loosjes' apparatus (*Versl. PlZiekt, Dienst Wageningen*, 1955, **127**, 200—204) and steeps by the method of ten Houten and Kraak (*Ann. appl. Biol.*, 1949, **36**, 394—405).

E. G. BRICKELL.

Effects of number of test insects, exposure period and post-treatment interval on reliability of fumigant bioassay. W. K. Whitney and P. K. Harein (*J. econ. Ent.*, 1959, **52**, 942—949).—Using 80 : 20 CCl$_4$: CS$_2$, least variance was found with 50 insects per cage. Insects should be kept for 10 days after treatment to allow for anaesthetic effects and delayed mortality. Exposures of up to 48 hr. are necessary for immature rice weevils.

C. M. HARDWICK.

Stickers for fungicidal sprays in the tropics. C. S. Reddy and R. G. Davide (*Plant Dis. Reptr*, 1959, **43**, 872—877).—A technique is described for measuring amounts of spray remaining on glass slides after artificial rainfall. Dosages of a no. of stickers recommended for non-tropical climates were too low to be of much value for the tropics. The best and cheapest sticker was natural rubber latex, although PEPS (polyethylene polysulphide) was almost as good.

A. H. CORNFIELD.

Mathematical theory of soil fumigation. J. B. Hemwall (*Soil Sci.*, 1959, **88**, 184—190).—The movements of fumigant in the soil is considered and an equation is derived to describe these, due allowance being made for factors such as soil porosity, temp., org. matter, water and mineral content of the soil. After modification of the equation to allow its being used on a digital computer it was applied to simulated field injections. The results are discussed.

T. G. MORRIS.

Streptomyces spp. as a cause of natural fungitoxicity in soils. J. L. Lockwood (*Phytopathology*, 1959, **49**, 327—331).—Experimental evidence presented supports the view that diffusible toxins produced by *Streptomyces* spp. in soil contribute to its fungitoxic action.

A. G. POLLARD.

Effects of some chlorinated hydrocarbon insecticides on nematode populations in soils. N. French, E. P. Lichtenstein and G. Thorne (*J. econ. Ent.*, 1959, **52**, 861—865).—A silt loam was treated with DDT (10, 100 and 1000 lb./acre), aldrin (2, 20 and 200 lb./acre) or lindane (1, 10 and 100 lb./acre) in field and laboratory tests. Changes in nematode populations are recorded.

C. M. HARDWICK.

Evaluation of off-odour in malathion-treated wheat. D. W. Walker and R. Locke (*J. econ. Ent.*, 1959, **52**, 1013).—Wheat was judged to have no objectionable odour when treated with malathion (16 p.p.m.) and stored for 1 or 68 days. More people judged wheat treated with 100 p.p.m. to be objectionable after 68 days than after 1 day.

C. M. HARDWICK.

Volatility of organo-mercury compounds. G. F. Phillips, B. E. Dixon and R. G. Lidzey (*J. Sci. Fd Agric.*, 1959, **10**, 604—610).—Saturated vapour concn. at 35° of 21 org.-Hg compounds were determined by static (for less volatile aryl compounds) and dynamic (for the more volatile alkyl compounds) methods. The corresponding partial pressures were calculated. The arbitrary temp. of 35° was adopted as representing the max. temp. likely to be encountered in U.K. practice. When the dynamic method was used, values at 25° and 45° were observed and interpolations from the usual linear relation were compared with available values in the literature. Some correlation between chemical constitution and v.p. was noted (13 references.)

E. M. J.

Effects of physical properties of derris dusts on their toxicity to Mexican bean beetle. F. H. Harries (*J. econ. Ent.*, 1959, **52**, 1017).—Larval mortality and leaf area eaten showed that dusts with the highest percentage of derris were less toxic than those containing less root. The toxicity of dusts decreased with an increase in the particle size of the pyrophyllite. Derris of low rotenone content was most improved by finer milling.

C. M. HARDWICK.

Varietal differences in the rotenoid content of Tephrosia vogelii. J. E. Irvine and R. H. Freyre (*Agron. J.*, 1959, **51**, 664—665).—Leaf rotenoid contents of 16 introductions of *T. vogelii* ranged from nil to 2·9% (dry basis) and were negatively correlated with plant height. There were also differences in plant width, leaflet-no. and size, and flower colour but not in leaf-N %.

A. H. CORNFIELD.

Polybutenes—a new control for phytophagous mites. R. W. Fisher (*J. econ. Ent.*, 1959, **52**, 1015).—Indopol H-1500 with a viscosity of 15,000 sec. was sprayed on to infested foliage as a 5% emulsion. The motile mites were trapped in it and control was complete after eggs had hatched. The emulsion is non-volatile and insol. in water and therefore has a long residual action. Sprayed half leaves were protected for 11 days, from the other infested half.

C. M. HARDWICK.

Effect of the polyene antibiotic, fungichromin, on the free and combined amino-acids of Verticillium albo-atrum. J. P. Ross (*Phytopathology*, 1959, **49**, 422—425).—Treatment with fungichromin (10 and 30 p.p.m.) inhibited the growth of the fungus, caused the disappearance of all sol. amino-acids from its mycelium and altered the amino-acid composition of the bulk protein. Smaller concn. (2 p.p.m.) of the antibiotic, although not affecting the growth of the fungus or the % composition of the protein, increased the proportion of certain free amino-acids (notably proline, leucine, arginine and lysine) in the hyphae.

A. G. POLLARD.

Chemical and biological studies of a reaction between captan and the dialkyldithiocarbamates. R. J. Lukens (*Phytopathology*, 1959, **49**, 339—343).—Captan reacts with the Na salt of dimethyldithiocarbamic acid (I) converting the latter into methylthiuram mono- and di-sulphides together with CS$_2$ and Cl⁻ but no H$_2$S. The reaction mixture is as toxic as is I to *Saccharomyces pastorianus*. Possible mechanisms of the reaction are discussed.

A. G. POLLARD.

Reversal of fungitoxicity by L-histidine. S. Rich (*Phytopathology*, 1959, **49**, 321).—The toxic action of captan on *Monilinia fructicola* was reversed by histidine applied 24 hr. later. L-Cystine was similarly effective when applied 6 hr., but not when 24 hr. after the captan treatment.

A. G. POLLARD.

Persistence of Phosdrin. D. E. Donley (*J. econ. Ent.*, 1959, **52**, 1015—1016).—The mortality of daphnids and oakworms indicated that Phosdrin persisted in the leaves of pin oaks 48—72 hr. after trunk application.   C. M. HARDWICK.

Effect of ionisation upon penetration of organophosphates to the nerve cord of the cockroach. R. D. O'Brien (*J. econ. Ent.*, 1959, **52**, 812—816).—TEPP, which is unionised, penetrated equally rapidly into intact or excised nerve cord of *Periplaneta americana*. " Quaternarised " Tetram [the iodide of $(C_2H_5O)_2P(O)\cdot SCH_2\cdot CH_2\cdot N(C_2H_5)_3$] which is ionised penetrated the excised cord well, but intact cord only slightly. Tetram [R-6199, oxalic acid salt of $(C_2H_5O)_2(PO)\cdot SCH_2\cdot CH_2\cdot N(C_2H_5)_2$] ionised by a low pH, penetrated the intact cord poorly and the unionised form penetrated well. No difference was found with excised cord. Probably the intact cord has an ion barrier. (15 references.)
                                                        C. M. HARDWICK.

Bioassays of weathered residues of several organophosphorus insecticides. B. G. Hightower (*J. econ. Ent.*, 1959, **52**, 840—842).— The reduction in toxicity of Guthion residues to *Anthonomus grandis* due to rainfall was not increased by high temp. or intense light. Sevin was unaffected by all these conditions. Temp. >100°F for 4—6 hr. without bright sunlight did not affect methyl parathion or malathion. Toxaphene gave variable results. The toxicity of low dosages of malathion was increased by the addition of toxaphene.
                                                        C. M. HARDWICK.

Synthesis of compounds of the malathion type. Chen Ju-Yu and Yang Hua-Tsen (*Acta chim. sinica*, 1959, **25**, 292—294).—Five compounds of the type $(RO)_2PS\cdot S\cdot CH(COOC_2H_5)_2$ have been synthesised and it is shown in preliminary tests that where R = C_2H_5 the insecticidal effect was one-third that of malathion.   C. V.

α-Chloro- and αα-dichloro-arylacetic derivatives. M. Julia and M. Baillargé (*Bull. Soc. chim. Fr.*, 1959, 850—853).—Et phenyl- and *p*-chlorophenyl-αα-dichloroacetates were prepared by alcoholic hydrolysis of R·CO·CN (R = aryl) and treatment with PCl₅, or, more conveniently, by Friedel–Crafts reaction of ClCO·CO₂Et with the appropriate substituted benzene. The glyoxylic acids formed are re-esterified. Action of PCl₅ on the appropriate ester affords Et *p*-methoxyphenyl-, *p*-tolyl-, *p*-chlorophenyl- and *p*-bromophenyl-αα-dichloroacetate. Et 2,4-dichlorophenyl-αα-dichloroacetate is prepared by converting 2,4-dichlorobenzaldehyde to the 2,4-dichloromandelic acid, oxidising this with permanganate and treating with PCl₅. Attempted saponification of the esters usually leads to hydrolysis of the α-chloro-groups as well. Substituted-phenyl-α-chloroacetates are obtained by the action of PCl₅ on the corresponding mandelic acid, followed by esterification. The insecticidal activity against *Calandra granaria* of the esters was small. The dichloro-deriv. showed no plant-growth activity in the maize-root test. (21 references.)   E. J. H. BIRCH.

Volumetric spore trap for sampling pastures. P. J. Brook (*N.Z. J. agric. Res.*, 1959, **2**, 690—693).—The spore trap is based on that of Gregory (*Trans. Brit. mycol. Soc.*, 1954, **37**, 390—404) and uses sticky microscope slides prepared in the same way.
                                                        E. G. BRICKELL.

Field sampling of lucerne for estimation of Guthion residues. P. A. Dahm, J. Gurland, E. T. Hibbs, W. H. Orgell, W. O. Pfaeffle and I. Lee (*J. econ. Ent.*, 1959, **52**, 791—798).—Single, composite and cross-composite samples of lucerne, sprayed with Guthion (1 lb./acre), and analysed colorimetrically and by bioassay gave similar results, after 1, 3 and 7 days. Residues 14, 21 and 28 days after spraying were too low for exact analysis. (24 references.)
                                                        C. M. HARDWICK.

Determination of residues of O-2,4-dichlorophenyl OO-diethyl phosphorothioate (V-C 13 Nemacide) by cholinesterase inhibition. G. R. Boyd (*J. agric. Fd Chem.*, 1959, **7**, 615—617).—V-C 13 Nemacide is determined by a modification of the cholinesterase-inhibition method of Giang and Hall, after oxidation with HNO_3 to produce the O analogue. Analyses of 16 vegetables and fruits showed the highest residues in root crops, smaller residues in leaf vegetables and beans, and insignificant amounts in fruits.
                                                        M. D. ANDERSON.

An electrically operated micro dispenser. J. Brezner (*J. econ. Ent.*, 1959, **52**, 1019—1020).—The basic mechanism is a synchronous motor operated through a timer which rotates a micrometer for a pre-set number of seconds. A full description and a wiring diagram are given.   C. M. HARDWICK.

Detection and estimation of Citicide. K. Krishnamurthy, K. S. Srinivasan and S. K. Majumder (*J. sci. industr. Res.*, 1959, **18B**, 333—335).—A method, based on the colour reaction of Citicide (insecticidal product obtained by chlorinating turpentine) with pyridine and aq. KOH, is developed for its detection and estimation. The specific orange colour developed by the reagents with Citicide

differentiates it from toxaphene and chlordane. Citicide can be estimated in concn. as low as 30 μg. (10 references.)
                                                        I. JONES.

Relation between reaction to Race 15B of stem rust and reducing sugars and sucrose in wheat. W. E. Lyles, M. C. Futrell and I. M. Atkins (*Phytopathology*, 1959, **49**, 254—256).—An association between resistance to the rust and a relatively higher reducing sugar content of the plants was established in several wheat varieties. In one variety treatment with maleic hydrazide lowered the reducing sugar content of the plants and increased the susceptibility to the disease.   A. G. POLLARD.

Granulated insecticides for control of sweet maize pests in New Jersey. J. P. Reed (*J. econ. Ent.*, 1959, **52**, 972—974).—The chief pests are *Pyrausta nubilalis*, *Heliothis zea* and *Laphygma frugiperda*. Experiments over 4 seasons showed that heptachlor or parathion were best if applied when most of the eggs had hatched and again after 2 weeks. Endrin was effective against *Pyrausta nubilalis* but was phytotoxic. Sprays or dusts are necessary at the ear stage.
                                                        C. M. HARDWICK.

Control of fall armyworm in sweet maize. F. P. Harrison, R. M. Coan and L. P. Ditman (*J. econ. Ent.*, 1959, **52**, 838—840).—In 1957 up to 5 applications of granulated DDT did not decrease no. of *Laphygma frugiperda* below 33%. The use of granules and sprays in 1958 gave further reduction, but yields did not increase. An increase in spray vol. increased control slightly.
                                                        C. M. HARDWICK.

Measurement of pathogenesis by the amount of toxic substance produced in lucerne by a snow mould substance. J. B. Lebeau, M. W. Cormack and J. E. Moffatt (*Phytopathology*, 1959, **49**, 303—305).—Development of crown rot in lucerne under snow is accompanied by HCN production only when mycelial growth begins in the crown bud. Periodic determinations of HCN serve to mark the incidence of the disease.   A. G. POLLARD.

Relation of host nutrition to the development of bacterial wilt in lucerne. H. J. Walters and E. M. Cralley (*Phytopathology*, 1959, **49**, 320).—In two varieties examined increased susceptibility to bacterial wilt (*Corynebacterium insidiosum*) was associated with low-K and high N- and P-levels of nutrition.   A. G. POLLARD.

Observations in Wyoming on lucerne weevil and its control. W. D. Fronk (*J. econ. Ent.*, 1959, **52**, 939—942).—Granulated heptachlor gave better control of *Hypera postica* than did granulated dieldrin. There was a greater increase in hay yields from treated fields at the first cutting. Sprays of malathion and dieldrin lowered weevil counts in mould infestations, but org. P compounds were usually superior.   C. M. HARDWICK.

Insecticide-induced population changes in four mite species on lucerne. E. C. Klostermeyer (*J. econ. Ent.*, 1959, **52**, 991—994).— Within 4—6 weeks of the application DDT increased no. of *Tetranychus telarius* and reduced those of *Typhlodramus cucumeris* and *Tydeus* sp. Dieldrin and endrin caused increases of *T. cucumeris* and decreases of *T. telarius* and *Tydeus* sp. Schradan and other org. P compounds increased populations of *Tydeus* and reduced the other species. *Tarsonemus confusus* was present in only one season ; demeton caused it to increase and dieldrin to decrease.
                                                        C. M. HARDWICK.

Effectiveness of three organophosphorus compounds against larvae of painted lady in lucerne. G. D. Peterson, jun. (*J. econ. Ent.*, 1959, **52**, 1017—1018).—Five days after spraying parathion or Phosdrin (4 oz./acre) >95% of *Vanessa cardui* larvae were dead. Dylox was not satisfactory.   C. M. HARDWICK.

Control of insects injurious to birdsfoot trefoil in New York. R. L. Ridgway and G. G. Gyrisco (*J. econ. Ent.*, 1959, **52**, 836—838).—Sprays of parathion gave outstanding control of *Sparaganothis xanthoides*. Phosdrin was also effective but not economically competitive. *Philaenus leucophthalmus* was controlled by lindane and Thiodan. All produced substantially increased yields.
                                                        C. M. HARDWICK.

Datura stramonium, **L. as a quantitative bioassay host for the brome-grass mosaic virus.** Ren-jong Chiu and W. H. Sill, jun. (*Plant Dis. Reptr*, 1959, **43**, 690—694).—The no. of lesions produced on leaves of *D. stramonium* was directly related to the concn. of virus in leaf sap from bromegrass infected with mosaic virus when the sap was diluted more than 100 times. Two types of lesions were produced from 15 collections of the virus.   A. H. CORNFIELD.

Effectiveness of new insecticides on potato leafhopper and the influence of leafhopper control and potato variety on tuberworm infestations. R. N. Hofmaster (*J. econ. Ent.*, 1959, **52**, 908—910). —Of foliage sprays tested for control of *Empoasca fabae*, Delnav (2,3-*p*-dioxandithiol *SS*-bis-(*OO*-diethylphosphorodithioate), Sevin and Thiodan at 0·2 lb./acre gave 98% reduction for 7 days. Ethion, Guthion, Trithion and DDT needed 0·5 lb./acre. Other org. P com-

pounds had a high initial but no residual activity. Control of leaf-hoppers also reduced damage by *Gnorimoschema operculella*.

C. M. HARDWICK.

Factors affecting growth of *Phytophthora infestans*. I. *P. infestans* on living potato leaves. P. H. Lowings and I. G. Acha (*Trans. Brit. mycol. Soc.*, 1959, **42**, 491—501).—High N may increase the resistance of Majestic potato leaves to infection by *P. infestans*. In glasshouse experiments fungal growth increased after the onset of senescence in the host. The effect of high N may be only one of delaying senescence of the leaves of the host plant.

L. G. G. WARNE.

Field evaluation of demeton in the control of beet yellows virus. E. S. Sylvester, V. E. Burton and R. B. Duncan (*J. econ. Ent.*, 1959, **52**, 910—917).—Differences in yield and in percentage of sugar were associated with the reduction in no. of *Myzus persicae*. Spraying with demeton delayed 100% virus infection for 3 weeks.

C. M. HARDWICK.

Apple pest control. P. Garman (*J. econ. Ent.*, 1959, **52**, 826—828).—Insecticides and fungicides were compared on the basis of pest control, safety and cost. Guthion–captan gave best results, followed by Sevin–Kelthane–captan, methoxychlor–Glyodin–ferbam and Pb arsenate–malathion–captan. The characteristics of each are discussed.

C. M. HARDWICK.

Effect of amino-acids on susceptibility of apple varieties to scab. J. Kuc, E. Barnes, A. Daftsios and E. B. Williams (*Phytopathology*, 1959, **49**, 313—315).—Infusion of certain amino-acids through mid-ribs of apple leaves increased the resistance of the trees to infection by *Venturia inaequalis*. D- and DL- but not L-phenylalanine were notably active ; D-alanine, DL-α-aminobutyric acid and D- and DL-leucine were less active.

A. G. POLLARD.

Arthropod fauna found during the first-season trial of a selective spray schedule in a New Jersey apple orchard. H. A. Thomas, H. B. Specht and B. F. Driggers (*J. econ. Ent.*, 1959, **52**, 819—820). —Weekly records showed that a Glyodin–ryania spray schedule gave satisfactory control of *Carpocapsa pomonella* and phytophagous mites. Predaceous arthropods reappeared within one season of the discontinuation of DDT sprays. More apples were damaged by *Conotrachelus nenuphar* than by all other arthropods.

C. M. HARDWICK.

European red mite control and population studies on apple in Wisconsin. E. R. Oatman (*J. econ. Ent.*, 1959, **52**, 871—877).— A pre-blossom application of Genite (2,4-dichlorophenyl benzene-sulphonate) provided best control of *Panonychus ulmil*. Mitox (*p'*-chlorobenzyl *p*-chlorophenyl sulphide) and Ovex were also satisfactory. Summer foliage sprays of Aramite, chlorbenzilate, demeton, Kelthane and Mitox also reduced mite populations. Population curves for 3 years are analysed.

C. M. HARDWICK.

Use of plum curculio in toxicological studies. E. H. Smith and B. J. Fiori (*J. econ. Ent.*, 1959, **52**, 921—928).—A laboratory strain responded similarly to a naturally occurring strain which oviposits, but not to an unhibernated strain which does not oviposit, in topical application and feeding tests. Dosage mortality curves are given for topical application of 10 insecticides. Residue tests on field-sprayed foliage were carried out for 17 days.

C. M. HARDWICK.

Control of *Sanninoidea exitiosa graefi*, (Hy. Edw.) on apricots. H. F. Madsen and J. B. Bailey (*J. econ. Ent.*, 1959, **52**, 804—806).— Counts of pupal cases and cocoons during the season after treatment showed that *p*-$C_6H_4Cl_2$, propylene dichloride and tetrachloroethane were more effective than ethylene dichloride when applied as crystal or an emulsion around the tree trunks. Tetrachloroethane was phytotoxic. Good control was also given by trunk sprays of Thiodan and endrin, monthly or bimonthly, and Guthion, monthly. DDT gave poor control and dieldrin was unsatisfactory. (10 references.)

C. M. HARDWICK.

Reduction of decay in stored grapes by field applications of captan. J. M. Harvey (*Plant Dis. Reptr*, 1959, **43**, 889—892).—Three applications of captan to the vines at monthly intervals before rainfall gave good control of decay of grapes at harvest and also during storage for 3 months at 0°.

A. H. CORNFIELD.

Effects of naphthenic and paraffinic petroleum composition at a comparable molecular weight or viscosity on photosynthesis of Eureka lemon leaves. L. A. Riehl and R. L. Wedding (*J. econ. Ent.*, 1959, **52**, 883—884).—No differences in the effect on photosynthesis were noted for differences in mol. wt. of 306—308 at η of 70. For deposits of 300—600 μg./sq. cm., initial inhibition of photosynthesis is similar for naphthenic and paraffinic fractions but recovery is faster with naphthenic oils.

C. M. HARDWICK.

Efficiency of Ethion in oil spray against California red scale and citrus red mite. L. A. Riehl, J. P. LaDue and J. L. Rodriguez, jun. (*J. econ. Ent.*, 1959, **52**, 857—860).—Ethion (I) sprays were very

effective against eggs of non-resistant *Panonychus citri* but resistant mites required a 15-fold increase in dosage. Malathion (II) was better than I against adult female *Aonidiella aurantii*. The effect of using medium-grade spray oil instead of kerosene as solvent is tabulated. The effect of scale density on efficiency varied with the spray used. Trial deposits of I and II stopped young scales settling. (12 references.)

C. M. HARDWICK.

Spider mites on walnut in northern California. A. E. Michelbacher (*J. econ. Ent.*, 1959, **52**, 936—939).—Spraying with Tedion or Kelthane + Sevin in May gave good control of *Panonychus ulmi* for the whole season. An application of Tedion in Aug. was less effective than in May. Schradan gave excellent control of walnut aphid but stimulated mite populations ; if these were there then sprayed with Tedion, best quality walnuts were obtained. Ethion and Guthion also gave good results. Evidence suggests that mites may be developing a resistance to trithion. (19 references.)

C. M. HARDWICK.

Vegetable disease control in Delaware in 1958. D. F. Crossan, W. H. Johnson and M. R. Siegel (*Plant Dis. Reptr*, 1959, **43**, 732—734).—Dithane M-22 and Phaltan (3 lb.) were somewhat more effective in controlling anthracnose in tomatoes than was Dyrene (4 lb. per acre). Dithane Z-78 and Manzate (3 lb. per acre) were equally effective in controlling ripe-rot of pepper. Dyrene (4 lb.) and Dithane M-22 (3 lb. per acre) gave the most effective control of *Alternaria* leaf spot of cantaloupe. Dithane M-22 (3 lb.) and Dyrene (4 lb. per acre) gave the best control of stem anthracnose of lima bean.

A. H. CORNFIELD.

Control of downy mildew of broccoli with fungicides and fungicide–streptomycin combination sprays. J. J. Natti (*Plant Dis. Reptr*, 1959, **43**, 735—740).—" Copper-Zinc," " Copper-Zinc " + streptomycin, maneb + streptomycin, and Agrimycin 500 were the most effective of the materials tested for control of downy mildew, *Peronospora parasitica*, of broccoli. These materials were about equally effective during the spraying period (weekly), but the presence of streptomycin gave better control after spraying had been discontinued. The incidence of infected broccoli heads was less in plots sprayed prior to the development of heads than in plots sprayed only during the period of head development. A. H. CORNFIELD.

Insecticidal control of insects infesting broccoli and cabbage. A. L. Steinhauer, L. P. Ditman and R. C. Wiley (*J. econ. Ent.*, 1959, **52**, 816—818).—The effect of 13 different sprays on numbers of *Trichoplusia ni, Pieris rapae* and *Brevicoryne brassicae* is given. Dimethoate was most promising, followed by malathion with Perthane or toxaphene. There was no phytotoxicity or off-flavours at harvest.

C. M. HARDWICK.

Chemical control of carrot rust fly, *Psila rosae* (F.), in western Washington. A. J. Howitt and S. G. Cole (*J. econ. Ent.*, 1959, **52**, 963—966).—In 1954 heptachlor, dieldrin, aldrin, endrin and chlordane as foliage sprays controlled *P. rosae* on carrots and parsnips. By 1958, of a group of org. P compounds only diazinon granules were effective.

C. M. HARDWICK.

Effect on honey bees of DDT and Thiodan applied from the air as sprays to chou moellier. T. Palmer-Jones, I. W. Forster and G. L. Jeffery (*N.Z. J. agric. Res.*, 1959, **2**, 481—487).—A DDT spray (at 2 lb. of 100% *pp'*-DDT per acre), if applied before bees visit a flowering brassica crop, will cause only slight mortality. Thiodan should not be employed.

E. G. BRICKELL.

Hexachlorobenzene for control of onion smut. R. Duran and G. W. Fischer (*Plant Dis. Reptr*, 1959, **43**, 880—888).—Treating onion seed with $C_6H_6Cl_6$ (I) and a sticker gave excellent control of onion smut, *Urocystis colchici*, in seedlings in infested soil. Proprietary formulations of I varied greatly in their efficacy for smut control, and some were markedly phytotoxic.

A. H. CORNFIELD.

Chemical control of onion maggot in onions grown from seed in various types of soil in northwestern North America in 1955 and 1956. D. G. Finlayson, H. H. Crowell, A. J. Howitt, D. R. Scott and A. J. Walz (*J. econ. Ent.*, 1959, **52**, 851—856).—In four localities thiram in combination with isodrin, heptachlor or dieldrin reduced damage by *Hylemya antiqua* to a greater extent than did malathion. In 1956 some areas still responded to chlorinated hydrocarbons, others to org. P compounds and in other areas none were effective. This was not related to soil type. Some seedling emergence was delayed by drenches but not by dusts or wettable powders. (14 references.)

C. M. HARDWICK.

Field test for control of *Trichoplusia ni* (Hbn.) on celery with several insecticides and *Bacillus thuringiensis*, Berliner. A. A. Grigarick and Y. Tanada (*J. econ. Ent.*, 1959, **52**, 1013—1014).—Celery plants having a high population of loopers in Oct. were dusted with malathion + Perthane or DDT + toxaphene + S. This controlled

all instars for at least 14 days. A dust of *B. thuringiensis* spores was better than a spray and similar in effectiveness to Thiodan, parathion and Phosdrin. 　　　　　　　　　　C. M. HARDWICK.

Virus susceptibility increased by soaking bean leaves in water. C. E. Yarwood (*Plant Dis. Reptr*, 1959, **43**, 841—844).—Soaking the primary leaves of Pinto beans in water for several hr. prior to inoculation with a no. of viruses increased the no. of local lesions resulting. The susceptibility varied with soaking period and time of day at which inoculation was made. The increased susceptibility due to soaking was much less when the inoculum was suspended in 1% K_2HPO_4 than when suspended in water. 　　A. H. CORNFIELD.

Polybutenes for control of powdery mildew. R. W. Fisher (*Plant Dis. Reptr*, 1959, **43**, 878—879).—Spraying cucumber plants with a 5% emulsion of polybutenes (Indopol L-10 and Indopol H-50) gave excellent protection against infection with powdery mildew, *Erysiphe cichoracearum*, for one month. 　　A. H. CORNFIELD.

Effect of plant bed temperature and fungicide treatment on the occurrence of Java black rot disease in sweet potato sprouts. R. H. Daines (*Phytopathology*, 1959, **49**, 252—254).—Java black rot (*Diplodia tubericola*) in plant beds developed more freely at higher temp. in the range 75—90°F. Among fungicides examined to control the disease the relative efficiencies were, Hg prep. (notably Semesan Bel) > Dyrene = captan > carbamates. 　　A. G. POLLARD.

Influence of bedding stock source, plant bed temperature and fungicide treatment on the development of black rot of sweet potato sprouts and on the crop during storage. R. H. Daines (*Phytopathology*, 1959, **49**, 249—251).—In plant beds at 75°F black rot, *Ceratocystis fimbriata*, in inoculated roots was not controlled by the customary chemical dips. At 85° and, especially, at 90°F development of the rot was much restricted and the dips reduced the loss to small proportions. Of fungicides tested for this purpose Hg prep. were the most and carbamates the least effective. 　　A. G. POLLARD.

Control of bacterial spot, Xanthomonas vesicatoria, on field-seeded tomatoes. R. E. Stall (*Plant Dis. Reptr*, 1959, **43**, 725—728).—Good control of bacterial spot of field-seeded tomatoes was given by sprays of Cu materials (tribasic copper sulphate, Cu salt of Omadine, Cu–Zn–chromate complex) and streptomycin. Dyrene and Nabac were ineffective. 　　A. H. CORNFIELD.

Tomato disease control in relation to amount of water applied and method of application. W. T. Schroeder, G. L. Mack, J. L. Brann and W. W. Gunkel (*Plant Dis. Reptr*, 1959, **43**, 719—724).—Field tests over 5 years with tomatoes showed that, providing fungicide dosage per acre was the same, the extent of disease control was similar whether the material was applied by hydraulic application in 50—200 gal., commercial air-blast application in 50—100 gal. or concentrate applicator in 20 gal. of water per acre. 　　A. H. CORNFIELD.

Maneb injury to tomato and pepper seedlings grown under glass. C. D. McKeen (*Plant Dis. Reptr*, 1959, **43**, 729—731).—When greenhouse tomato seedlings 2—3 in. high were sprayed with maneb materials (Manzate or Dithane M-22, 1·5 lb. per 100 gal.) characteristic injury symptoms developed. Even though some of the affected seedlings recovered, subsequent growth of plants was seriously checked. Young pepper seedlings sprayed with maneb materials showed injury similar to that appearing on tomato seedlings. 　　A. H. CORNFIELD.

Evaluation of candidate insecticides and insect pathogens for tobacco hornworm control, 1956—1958. F. E. Guthrie, R. L. Rabb and T. G. Bowery (*J. econ. Ent.*, 1959, **52**, 798—804).—Laboratory and field tests showed that endrin, Thiodan, Shell SD4402, Sevin and Guthion as dusts or sprays gave similar control after 9 days although speed of action and persistence varied. Weathering reduced residues of Sevin, Guthion and Thiodan to 10—16 p.p.m. after 15 days and Dipterex was less persistent. Primary and flue curing reduced these by ~90 and 99% respectively. Only Sevin affected the flavour of the tobacco. *Bacillus thuringiensis* and *B. sotto* were as effective as insecticides against *Protoparce sexta* but slower in action. (14 references.) 　　C. M. HARDWICK.

Streptomycin for control of wildfire, Pseudomonas tabaci, in tobacco plant beds. L. Shaw, G. B. Lucas and J. H. Wilson, jun. (*Plant Dis. Reptr*, 1959, **43**, 753—754).—Weekly sprays of streptomycin (200 p.p.m.) as sulphate or nitrate on Burley tobacco plant beds gave excellent control of wildfire. When treatment was started one week after artificial infection at least two weekly sprayings were required for control of the disease. 　　A. H. CORNFIELD.

Effect of humidity and atmospheric pressure on virus infection of local lesion hosts. J. D. Panzer (*Plant Dis. Reptr*, 1959, **43**, 845—848).—*Nicotiana glutinosa* and *Phaseolus vulgaris* plants inocu-lated with tobacco mosaic virus and lucerne mosaic virus respectively showed reduced local lesion infection under a high humidity post-inoculation environment. Bean plants inoculated with lucerne mosaic virus developed fewer lesions at low and high than at intermediate humidities. Much less infection developed when inoculated plants were submerged in water. Varying atm. pressures 0—20 lb. per sq. in. above normal had no effect on extent of infection. 　　A. H. CORNFIELD.

Field experiments for control of late-season infestations of several cotton insects. C. B. Cowan, jun., C. R. Parencia, jun., and J. W. Davis (*J. econ. Ent.*, 1959, **52**, 975—977).—Various mixtures of org. phosphates and DDT reduced injury by bollworms and boll weevils. Seven org. phosphates reduced spider mite populations considerably. Sprays for control of *Alabama argillacea* are listed. 　　C. M. HARDWICK.

Response of cotton and cotton pests to Thimet seed-treatment. W. J. Mistric, jun., and E. J. Spyhalski (*J. econ. Ent.*, 1959, **52**, 807—811).—The reduction in emergence due to Thimet seed treatment was not significant after thinning except where there were other adverse factors. Thrips, cotton aphid and spider mites were controlled for several weeks, and boll weevils throughout the season. Blooming was always delayed and the crop was therefore affected by late season bollworms and climate deterioration. Seed treatment produced increased yields only when there was a damaging infestation present amongst controls. 　　C. M. HARDWICK.

An inhibitor of Verticillium albo-atrum in cotton seed. R. H. Garber and B. R. Houston (*Phytopathology*, 1959, **49**, 449—450).—Cotton seed coats contained a substance (probably fungistatic) inhibiting the growth of the fungus. 　　A. G. POLLARD.

Control of sugarcane borer with insecticides. W. H. Long, E. J. Concienne, S. D. Hensley, W. J. McCormick and L. D. Newsom (*J. econ. Ent.*, 1959, **52**, 821—824).—Eight weekly or four biweekly aerial applications of 2% endrin granules reduced the percentage of joints bored by *Diatraea saccharalis* to ~5% and increased yields by 6 tons/acre. Endrin dust was less effective. Ryania and toxaphene dust or granules also reduced damage and increased yields. Small plot experiments showed that Thiodan was promising. DDT decreased yields. 　　C. M. HARDWICK.

Treatment of soya-bean seed in Minnesota. T. D. Wyllie and R. W. Goth (*Plant Dis. Reptr*, 1959, **43**, 898—902).—Treating soya-bean seed with thiram (2 oz. per bushel) improved stands and yields to a greater extent when seed was planted at 3 in. than at 1 in. depth. In 68 trials at a no. of locations stands were increased in 74% of the locations by seed treatment. 　　A. H. CORNFIELD.

Root and stalk rot of soya-beans caused by Phytophthora megasperma, Drechsler var. sojae var. nov. A. A. Hildebrand (*Canad. J. Bot.*, 1959, **37**, 927—957).—The disease prevalent in S.W. Ontario since 1954, is identical with that attributed in U.S.A. to *Phytophthora cactorum* or to a new sp. *P. sojae*. Infection is easily transmitted by soil in which infected plants have grown; spreading from inoculated seedlings to control seedlings growing 4 in. away. Steamed soil inoculated with the fungus transmitted the disease actively; in non-steamed inoculated soil, the activity of the fungus was inhibited to a considerable extent. Tests with common weeds of soya-bean fields, and with numerous crops, showed that beans only were susceptible. (33 references.) 　　M. D. ANDERSON.

Control of the sting nematode, Belonolaimus longicaudatus, with 1,2-dibromo-3-chloropropane. W. E. Cooper, J. C. Wells, J. N. Sasser and T. G. Bowery (*Plant Dis. Reptr*, 1959, **43**, 903—908).—Yields of soya-beans, groundnuts and maize were increased 500%, 400% and 100% respectively by application, two weeks before planting, of 1,2-dibromo-3-chloropropane (I) (1·0—1·5 gal. per acre in granulated formulation). Soil treatment one month after planting gave somewhat lower yield increases of soya-beans and groundnuts, but had no effect on yields of maize. Sting nematode populations were reduced by all treatments. Br content of groundnut foliage increased with level of I applied. Shelled groundnuts contained no Br with application of up to 1·0 gal. I per acre, but contained 16—39 p.p.m. Br with the 1·5 gal. rate of I. 　　A. H. CORNFIELD.

Effectiveness of non-dirting cultivation and soil-surface applications of pentachloronitrobenzene in controlling groundnut stem rot, Sclerotium rolfsii, in Virginia. K. H. Garren (*Plant Dis. Reptr*, 1959, **43**, 750—752).—Application of pentachloronitrobenzene (12—15 lb. per acre) usually reduced incidence of stem rot and increased groundnut yields when used in conjunction with conventional cultivation, but had little effect when used with non-dirting cultivation (groundnuts planted on a layer of org. matter and cultivation such that no soil was brought into contact with the plants). Non-dirting cultivation gave higher yields in only one of two years. 　　A. H. CORNFIELD.

Control of resistant spider mites on greenhouse roses. E. A. Taylor, T. J. Henneberry and F. F. Smith (*J. econ. Ent.*, 1959, **52**, 1026—1027).—Weekly sprayings with Aramite + Tedion or schradan gave satisfactory control of highly resistant *Tetranychus telarius*. Tedion, Ovex or Aramite + demeton were less satisfactory. Some phytotoxicity was encountered with a few varieties of roses.

　　　　　　　　　　　　　　　　　　　　C. M. HARDWICK.

Systemic insecticides for citrus whitefly control on gardenia. L. L. Hyche and B. W. Arthur (*J. econ. Ent.*, 1959, **52**, 1008—·1010).—The effectiveness of several org. P compounds as soil dusts and sprays and foliage sprays for controlling *Dialeurodes citri* is tabulated.　　　　　　　　　　　　　　　　C. M. HARDWICK.

Control of root rot of Croft lilies. W. W. Willis, C. T. Rogerson and W. J. Carpenter (*Plant Dis. Reptr*, 1959, **43**,·745—749).—Treatment of the lily bulbs or soil with Terraclor, captan and copper Omadine gave only partial control of soil-borne fungus diseases. Soil treatments were usually superior to bulb treatment for control of the two most prevalent fungi, *Cylindrocarpon radicicola* and *Fusarium solani*.　　　　　　　　　　　　A. H. CORNFIELD.

Prevention of bark beetle transmission of *Ceratocystis ulmi* **(Buis.), Moreau with the systemic insecticide Chipman R-6199.** A. F. Al-Azawi and D. M. Norris, jun. (*J. econ. Ent.*, 1959, **52**, 902—904).— A solution containing 10, 20 or 30 g. of insecticide was applied to four holes bored into the trunk 6 in. from ground level. Infected beetles in cages were put on a terminal branch each week for 10 weeks. No treated trees developed dutch elm disease but 30% of controls did. Insecticidal treatment reduced the depth and no. of feeding niches and so reduced the chance of infection by >90%.

　　　　　　　　　　　　　　　　　　　　C. M. HARDWICK.

Toxicity of oak heartwood and oak heartwood water extracts to the oak wilt fungus, *Ceratocystis fagacearum*. J. D. Bilbruck (*Plant Dis. Reptr*, 1959, **43**, 936—941).—A substance toxic to the oak wilt fungus occurred in water extracts of the heartwood of red, black, northern pin and bur oaks (the fungus does not grow in the heartwood of these species). Properties of the toxic substance, which does not appear to be a resin, pigment or alkaloid, are described ; it may be tartaric acid, which is toxic to the oak wilt fungus at concn. of 0·6% or greater.　　　　　　　　　　　　　A. H. CORNFIELD.

Pre-emergent herbicidal activity of some substituted amides and related compounds. J. S. Pizey and R. L. Wain (*J. Sci. Fd Agric.*, 1959, **10**, 577—584).—Series of related aliphatic and aromatic amides were tested on wheat, cabbage and rye-grass. The importance of the *ortho*-substituent in the benzamide and phenylacetamide series was established, but no correlation was observed between structural characteristics of the amides and their toxicity or selectivity. Max. selectivity against wheat is shown by compounds XCH₂·CO·NR₂ where R is alkyl, X is phenyl or Cl. Cabbage seedlings probably lack, or have only in part, an enzyme capable of hydrolysing such compounds. (14 references.)　　　E. M. J.

Max. selectivity against wheat is shown by compounds $XCH_2 \cdot CO \cdot NR_2$ where R is alkyl, X is phenyl or Cl.

2,4-D [2,4-dichlorophenoxyacetic acid] weed-killer and derivatives. H. J. Sanders and R. F. Prescott (*Industr. Engng Chem.*, 1959, **51**, 974—980).—A survey of manufacture of 2,4-D and its salts and esters.　　　　　　　　　　　　　　　　　　O. M. WHITTON.

Effects of irrigation on toxicity of 2,4-D and IPC applied pre-emergence. H. P. Cords (*Dissert. Abstr.*, 1959, **20**, 442—446).— Applied to crops of barley and safflower, 2,4-D delayed emergence, increasingly so with increased supply of water ; and, especially in safflower, reduced stands, caused abnormalities of growth and reduced yields. IPC had less marked effects on barley, and little or no effect on safflower ; yields were not reduced. Neither chemical affected seed wt. Treatment with 2,4-D reduced the yield of silage from sorghum when irrigation followed treatment, but not when irrigation was delayed until emergence.　　　M. D. ANDERSON.

Herbicides from phenols of pyrolysed wood resins. V. Kovalev and D. Tishchenko (*Zh. prikl. Khim.*, 1958, **31**, 1708—1715).— Powerful selective herbicides and plant growth stimulators, with 28—30% Cl content, were prepared from phenol fractions of b.p. 180—210° (from pyrolysed wood resins) with guaiacol contents from 33% to 43%. They were best prepared by condensation with Na chloroacetate and chlorination of the phenoxyacetic acids to equiv. wt. 238—256 (the dichloro-acid stage). The products were comparable with 2,4-dichloro- and 4-chloro-2-methylphenoxyacetic acid but had improved growth-stimulating activity. They contained ~18% chlorophenols and ~82% chlorophenoxyacetic acids.

　　　　　　　　　　　　　　　　　　　　A. L. B.

Autoradiography of radioactive dalapon. A. S. Crofts and C. L. Foy (*Down to Earth*, 1959, **14**, No. 4, 2—6).—Use of autoradiography in tracing pathways of translocation of growth-regulators and herbicides, applied *via* leaves or roots of plants, is discussed and recent work on dalapon is summarised.　　　A. G. POLLARD.

Respiratory and associated responses of carrot discs to substituted phenols. B. K. Gaur and H. Beevers (*Plant Physiol.*, 1959, **34**, 427—432).—Respiratory and concomitant glucose uptake were studied. All the substituted phenols acted as uncoupling agents, the efficiency being in the order 2,4-DNP followed by 2,4-DCP, *p*-nitrophenol, the bromophenols, *m*- and *p*-chlorophenol, *m*- and *o*-nitrophenol, *o*-chlorophenol and phenol itself, which induced at best only 20% stimulation.　　　　　　　　　　E. G. BRICKELL.

Effects of herbicides on cereal germination, yield and quality. H. I. Petersen (*Tidsskr. Planteavl*, 1959, **63**, 197—284).—Extensive trials are recorded of the effects of various formulations of MCPA, DCPA and MCPB on winter- and spring-sown cereals. Germination, growth, morphological characteristics, yields of grain and straw and the quality and germinative capacity of the grain produced are examined. (70 references.)　　　　　　A. G. POLLARD.

Weed control in soya-beans. F. S. Pearse (*Down to Earth*, 1959, **14**, No. 4, 7—8).—Successful use of Premerge (dinitrobutylphenol) (**I**) is recorded. The soya-bean is tolerant to **I** up to the stage when the first true leaves are well developed (1 in.). Control of weeds, especially if these include grasses, is more successful the later in the " tolerant " stage **I** (3—4 lb. as amine, in 25—40 gal./acre) is applied.　　　　　　　　　　　　　　　　A. G. POLLARD.

Sod subjugation with herbicides and other cultural practices for pasture renovation. J. D. Harrington (*Dissert. Abstr.*, 1959, **20**, 433—434).—Kentucky bluegrass was more effectively suppressed by 3-amino-1,2,4-triazole and Na 2,2-dichloropropionate, at 10 and 15 lb. per acre respectively, than by Na 2,2,3-trichloropropionate or Na trichloroacetate. Applications were less effective in spring than in July—Sept., and less effective in July than in Aug.-Sept. Moisture conditions affected the activity of the herbicides. When birdsfoot trefoil and timothy grass were sown in the pastures, separately or together, yields were related to the degree to which the bluegrass had been suppressed. Ploughing was more effective than application of herbicides, both in suppressing bluegrass and in increasing the yield of the spp. sown.

　　　　　　　　　　　　　　　　　　　　M. D. ANDERSON.

Control of Johnson grass (*Sorghum halepense***, L. Pers.) by herbicides and cultural practices.** E. O. Burt (*Dissert. Abstr.*, 1959, **20**, 438—440).—Johnson grass has seeds of which 26 to 49% germinated after 2 years in the soil. The effectiveness of pesticides and cultural practices in controlling Johnson grass depended on the extent to which root reserves were decreased. Johnson grass weakened by grazing, and disc-ploughed in July, showed 84% reduction in stand the next year. The effectiveness of Na trichloroacetate (TCA) or NaClO₄ was increased by ploughing before application, and by enough rain to leach the herbicides into the top 6 to 8 in. of soil. TCA at 20 lb. per acre was effective if applied in Mar., and maize could be sown 60 days later. Polybor-chlorate was ineffective at 100 to 400 lb. per acre, and was seriously toxic to maize in the following year. Maleic hydrazide at 12 lb. per acre was effective if ploughing followed within a few days. Pre-emergence application to maize of 2,4-D at 2 or 4 lb. per acre gave fair control of Johnson grass seedlings without damaging the crop. Dalapon at 10 lb. per acre, and TCA at 20 lb. per acre, gave selective control of Johnson grass in mixtures with lucerne. 3-*p*-Chlorophenyl-1,1-dimethyl-urea at 80 lb. per acre almost eradicated Johnson grass, but even at 64 lb. per acre was present in soil down to 24 in., 2 years later, in amounts lethal to soya-beans.　　　　　M. D. ANDERSON.

Bindweed control and seedling emergence as affected by tillage, 2, 4-D and competitive crops. A. F. Wiese and H. E. Rea (*Agron. J.*, 1959, **51**, 672—675).—On fallow areas bindweed was controlled over 5 years by sweep cultivation 10—15 days after emergence or two annual applications of 2,4-D (ester or amine). Winter wheat with three fallow cultivations gave only moderate control, whilst application of 0·5 lb. 2,4-D to the wheat in spring in addition gave 99% control. Annual sorghum alone or with cultivations during fallow periods gave relatively poor control of bindweed. Emergence of bindweed seedlings was reduced to a low level only on plots where 2,4-D was used exclusively.　　　　　　A. H. CORNFIELD.

Fungicidal compositions. Upjohn Co. (B.P. 803,409, 6.3.57. U.S., 2.4.56).—Cycloheximide (I) is compounded with pentachloronitrobenzene (15—140 pt.), to provide a fungicidal composition, especially effective in the control of *Pythium*-caused diseases and large brown patch (*Rhizoctonia solani*). The composition may also contain FeSO₄, a surface-active agent and a non-alkaline carrier.

　　　　　　　　　　　　　　　　　　　　F. R. BASFORD.

Fungicidal supermetallic associates and compositions containing them. N.V. de Bataafsche Petroleum Maats. (B.P. 804,507, 23.4.56. Neth., 22.4.55 and 29.3.56).—A solution of an org. carboxylic or sulphonic acid [especially a naphthenic acid or an alkylbenzene- or alkylnaphthalene-carboxylic acid (or -sulphonic acid)],

or a salt thereof in a hydrocarbon (or $\not> 10$ C) is treated in presence of alkanol ($\not< 95\%$ of $\not< 3$ C) with a hydroxide of a metal of atomic no. 24—31 (Cu) formed *in situ* to give a metal complex. The latter (useful in fungicidal compositions) is precipitated in finely divided form by adding a hydrocarbon-miscible fluid of dielectric constant $\not< 6$ (e.g., an alkanol of $\not> 3$ C), preferably in presence of a surface-active agent.　　　　　　　　　F. R. BASFORD.

Antiparasitic agents. J. R. Geigy A.-G. (B.P. 804,186, 7.5.56. Switz., 5.5.55).—Compounds $R_1 X \cdot R_2 \cdot CO \cdot NR_3 \cdot CH_2 \cdot CH_2 \cdot OH$ (R_1 is alkyl of $\not< 8$ C which may be interrupted by O or S, R_2 is alkylene of $\not> 3$ C and R_3 is H, Me or $C_6H_4 \cdot OH$, X is O or S) have strong fungistatic, fungicidal and antiparasitic action. Among examples are given the uses of decylthioacetic acid diethanolamide as a dust when mixed with talc and as a spray when mixed with kaolin and sulphite waste liquor.　　　　　　　　　H. S. R.

Fungicidal compounds. Plant Protection Ltd. (Inventor: A. R. Kemble) (B.P. 804,444, 6.1.56).—A hot (conc.) aq. solution of o-ONa·C_6H_4·CO·NHPh is mixed with a boiling (saturated) aq. solution of HgPH·OAc, to give *phenylmercuri-salicylanilide*, m.p. 136—138°. The product is a fungicide and may be compounded, e.g., with Lubrol E (10·8) and Sextone B (77·1%), to provide a seed-dressing composition.　　　　　　　　　F. R. BASFORD.

Improved fungicide. R. T. Vanderbilt Co. (Inventors: A. A. Somerville and C. E. Bradley) (B.P. 804,477, 23.4.56).—A composition for use in the control of fungus diseases of fruit and foliage of fruit trees comprises manganous dimethyldithiocarbamate (**I**) and a suitable carrier (e.g., water). **I** may be obtained by adding an aq. solution of alkali metal or alkaline-earth metal dimethyldithio-carbamate to an aq. solution of a sol. Mn^{II} salt (optionally in presence of a small amount of the alkali metal salt of 2-mercapto-benzthiazole, viz., 8·1 pt. per 91·9 pt. of the dithiocarbamate), then filtering off the pptd. **I**, and washing with water until the content of sol. salts is $< 0·25\%$. The latter treatment affords a paler product.　　　　　　　　　F. R. BASFORD.

Dicyclohexyl(alkyl)phenols. Dow Chemical Co. (Inventor: H. B. Rickert) (B.P. 802,884, 20.6.57).—Compounds, useful as parasiticides (especially active against Southern army worms and Mexican bean beetles), comprise 2,6-dicyclohexylphenols substituted in the 4-position by alkyl of 2—5 C. The prep. of 4-*ethyl*-2,6-*dicyclohexylphenol*, b.p. 151—159°/0·1 mm., is detailed.　　　　　　　　　F. R. BASFORD.

Liquid concentrates of sodium pentachlorophenoxide. Monsanto Chemicals (Australia) Ltd. (B.P. 804,257, 31.7.56, Aust., 12.8.55). —Na pentachlorophenoxide ($\not< 20$ wt.-%) is dissolved in a solvent mixture (53—80 wt.-%) consisting of water (25—95) and a water-miscible org. solvent (5—15 wt.-%) in which the phenoxide is sol., e.g., an aliphatic alcohol, ketone and/or ketoalcohol (MeOH, PriOH, acetone, diacetone alcohol). The resulting solution is stable at 0°.　　　　　　　　　F. R. BASFORD.

Thiophosphonic acid esters. Farbenfabriken Bayer A.-G. (B.P. 804,538, 15.5.57., Ger., 19.5.56).—The esters of the formula $(R_3O)(R_4O)PX \cdot S \cdot CH(CH_2 \cdot SR) \cdot CH_2 \cdot NR_1R_2$ where R is an alkyl or aromatic radical, R_1—R_4 are alkyl radicals of 1—4 C, or R_1 and R_2 together with N form a cyclic compound which may contain further hetero atoms, and X is O or S, are prepared by reacting salts of OO-dialkyl phosphoro-thiolic or -thiolthionic acid with 1-(substituted amino)-3-(substituted mercapto)-2-halogen propanes. The products are useful as insecticides and have systematic action. The prep. of OO-*diethyl* S-1-*dimethylamino*-3-*phenylthio*)-*prop*-2-*yl phosphorothiolate* is detailed.　　　　　　　　　I. JONES.

Phosphorus-containing esters with sulphur groups. Farbenfabriken Bayer A.-G. (B.P. 804,141, 5.9.55. Ger., 4.9.54).—Compounds $OR(OR') \cdot PY \cdot X \cdot [CH_2]_n \cdot SO_2R''$ (R and R' and 1—4-C alkyl, R'' is aryl, aralkyl or preferably as R, X is O, S or a direct bond, Y is O or S, n is 1—4) are prepared by oxidation of the corresponding mercapto-compound for use as insecticides. Details are given for methyl (2-ethylsulphonylethyl)phosphonate prepared in 80% yield.　　　　　　　　　H. S. R.

Production of halogenobenzyl esters of thiophosphoric acid. Farbenfabriken Bayer A.-G. (B.P. 803,446, 27.4.56. Ger., 3.5.56).—Compounds $(OR)_2 PX \cdot S \cdot CH_2R'$ (R is alkyl of 1—4 C; R' is phenyl substituted by 1—3 halogen; X is O or S), useful as acaricides with only a slight effect on warm-blooded animals, are obtained by interaction of a salt of $(OR)_2 PX \cdot SH$ with a halogenobenzyl halide. The prep. by conventional means of OO-*dimethyl* S-*p*-*chlorobenzyl thiothionophosphate*, b.p. 98—100°/0·01 mm., is detailed.　　　　　　　　　F. R. BASFORD.

Thiophosphoric acid esters. Farbenfabriken Bayer A.-G. (B.P. 804,761, 9.5.56. Ger., 13.5.55).—Compounds $(OR)_2 PX \cdot S \cdot [CH_2]_2 \cdot NR'R''$ are claimed (R is alkyl; X is O or S; R' and R'' together with N comprise a radical of a cyclic dicarboxylic acid imide or of

benztriazole); they are characterised by high acaricidal and aphicidal activity. The prep. of OO-*diethyl* S-(2-*succinimidoethyl*) *phosphorothiolate* is outlined.　　　　　　　　　F. R. BASFORD.

Thiophosphoric acid esters. Farbenfabriken Bayer A.-G. (B.P. 803,441, 9.2.56. Ger., 10.2.55).—Compounds $(OR)_2 PX \cdot X \cdot CHR' \cdot CO_2R''$ are claimed (R and R'' are aliphatic or aromatic radicals; R' is H, aliphatic or aromatic radical, or benzyl; one X is S and the other X is O); they are characterised by insecticidal properties. The prep. by conventional means of Me_2 S-(α-*ethoxycarbonylbenzyl*) *thiothionophosphate*, b.p. 122—125°/0·01 mm., is detailed.　　　　　　　　　F. R. BASFORD.

Production of cycloheximide by fermentation. Upjohn Co. (B.P. 800,170, 27.11.56. U.S., 26.1.56).—In the production of cycloheximide by fermentation with *Streptomyces griseus*, an improved yield is obtained by use of aq. culture medium containing soya-bean meal ($\not< 14$), KH_2PO_4 (0·15—0·25 g. per l.), and glucose (~ 4 pt. per pt. of soya meal).　　　　　　　　　F. R. BASFORD.

New sulphonamidophosphoric esters. Olin Mathieson Chemical Corp. (B.P. 804,052, 4.11.55. U.S., 5.11.54).—Compounds $(OR)_2 PX \cdot NH \cdot SO_2R'$ (R is alkyl of 1—8 C; X is O or S; R' is hydrocarbon radical optionally substituted by halogen, NO_2, alkoxy, CO_2H, esterified CO_2H, NH_2 or acetamido), useful as insecticides (especially active against aphids and mites), are obtained by interaction of $R \cdot SO_2NHM$ with $(OR)_2 PX \cdot Y$ at 60—110° in an inert solvent (M is alkali metal; Y is halogen). The prep. of p-*toluenesulphonamido* Et_2 *phosphate* (Et_2 N-*p*-*toluenesulphonyl-phosporamidate*) is detailed.　　　　　　　　　F. R. BASFORD.

New vinylphosphoric acid ester. Farbenfabriken Bayer A.-G. (B.P. 804,080, 25.7.56. Ger., 29.7.55).—Dichloroacetaldehyde is condensed with Me_3PO_3 or a salt of Me_2HPO_3, to give Me_2 2-*chlorovinyl phosphate*, b.p. 38—40°/0·01 mm., useful as an insecticide.　　　　　　　　　F. R. BASFORD.

γ-(4-Chloro-2-methylphenoxy)- and γ-(2,4-dichlorophenoxy)-n-butyric acid. G. W. Kitchingman, A. C. Tucker, and Imperial Chemical Industries Ltd. (B.P. 804,565, 31.8.56).—The compounds (in the form of their alkali metal salts) are obtained by interaction of alkali metal salt of $OH \cdot [CH_2]_3 \cdot CO_2H$ with 4-chloro-2-methyl or 2,4-dichloro-phenol in inert liquid medium, preferably water-insol. org. solvent, b.p. 100—210°, with azeotropic removal of water.　　　　　　　　　F. R. BASFORD.

Systemic herbicide compositions. British Rubber Producers' Research Ass. (B.P. 803,772, 3.8.54).—A composition especially suitable for use in the treatment of *Hevea* (to stimulate yield of rubber and/or bark renewal) comprises a solution of a low-alkyl (1—5 C) 2,4,5-trichlorophenoxyacetate (1%) in vegetable oil or a mixture of the latter and palm oil sludge or mineral grease. The preferred vegetable oil is palm oil.　　　　　　　　　F. R. BASFORD.

1-Ethynylcyclohexyloxyalkanols. Dow Chemical Co. (B.P. 802,798, 17.7.57. U.S., 2.8.56).—Compounds $OR \cdot ([CH_2]_n)_m \cdot H$ are claimed (R is 1-ethynylcyclohexy-1-yl radical substituted in the 2-, 3- or 4-position by Me; m is 1—2; n is 2—3). The products are useful as plant growth materials and herbicides. As an example of prep., a mixture of 1-ethynylcyclohexanol, ethylene oxide and NEt_3 is heated at 70—175°/150 lb. per sq. in. during 6 hr., then distilled to give 2-1'-*ethynylcyclohexyloxyethanol*, b.p. 73—74°/1 mm., n_D^{15} 1·4811.　　　　　　　　　F. R. BASFORD.

Preparations for combating weeds in flax. N.V. Philips Gloeilampenfabrieken (B.P. 804,309, 9.4.57. Neth., 12.4.56).—The prep. comprises a solution of MCPA (4-chloro-2-methylphenoxyacetic acid) (1) and DNBP (2,4-dinitro-6-s-butylphenol) (3—4 pt.) and/or their salts in water and optionally on auxiliary solvent, e.g., MeOH or EtOH.　　　　　　　　　F. R. BASFORD.

1-Ethynylcyclohexyl ethyl carbonates. Dow Chemical Co. (B.P. 803,203, 19.7.57. U.S., 2.8.56).—Compounds $OR \cdot CO \cdot OEt$ (R is 1-ethynylcyclohexyl, optionally substituted in the 2-, 3- or 4- position by Me), useful as plant growth-control agents, are obtained by interaction of $Cl \cdot CO_2Et$ with an alkali metal salt of ROH. Details are given for the prep. of Et 1-*ethynylcyclohexyl carbonate*, b.p. 95°/3 mm., n_D^{15} 1·4578.　　　　　　　　　F. R. BASFORD.

Animal Husbandry

Fish meal. B. H. Schneider (*Pakist. J. Sci.*, 1959, **11**, 77—87).— A review relating to animal foods. The question of "taint" is discussed. (56 references.)　　　　　　　　　C. V.

Development of the digestive system of the young animal. I. Tissue weights, dry matter of tissues, total acidity and chloride content of stomach contents in the young pig. II. Carbohydrase enzyme development in the young pig. D. M. Walker (*J. agric. Sci.*, 1959, **52**, 352—356, 357—363).—I. From birth until five weeks of age the

pH of the pig stomach contents was >3·4, of the duodenum 6·5 and of the small intestine 6·4. The total acidity and NaCl content remained unchanged over the period. No free HCl was detectable in the stomach.

II. Over the experimental period the pancreatic amylase, sucrose and maltase increased progressively. The level of lactase at birth and of small-intestine amylase at one week did not change over the rest of the period. Anaemia did not affect the activity of the enzymes although maltase production was retarded. Pancreatic amylase was adequate to digest all likely levels of starch in pig rations. Maltase might become a limiting factor in the early stages of growth.   A. G. POLLARD.

Oestrogens in British pasture plants. G. S. Pope, M. J. McNaughton and H. E. H. Jones (*J. dairy Res.*, 1959, **26**, 196—202).—Oestrogenic activity was detected in 4 of 4 spp. of *Medicago*, in 4 of 6 spp. of *Trifolium*, and in 6 of 14 spp. of grasses, all frequently found in British dairy pastures, but the amounts present were probably insufficient to affect the composition of milk from cows on pasture.   S. C. JOLLY.

Oestrogen-like substances in certain legumes and grasses. I. Quantitative determination of such substances in red clover and oats. W. D. Kitts, E. Swierstra, V. C. Brink and A. J. Wood (*Canad. J. Animal Sci.*, 1959, **39**, 6—13).—A bioassay method is described and, with diethylstilboestrol as reference, a dose response curve was constructed. Samples from first- and second-year growth of red clover possessed considerable oestrogenic activity, the level being highest in the spring and decreasing towards autumn. Victory oats possessed little or no activity at any time during the growing season.   E. G. BRICKELL.

Photosensitivity diseases in New Zealand. XV. Chemical procedure for the detection of facial eczema toxicity in pasture. D. D. Perrin (*N.Z. J. agric. Res.*, 1959, **2**, 266—273).—Traces of a white material present in toxic, but not in non-toxic pasture were isolated. A method based on presence or absence of this material is described and appears to differentiate qual. between normal and facial-eczema-producing pastures.   E. M. J.

Selection for toxicity in single plants of *Indigofera endecaphylla* by biological assay. E. J. Britten, A. L. Palafox and H. Matsumoto (*Agron. J.*, 1959, **51**, 651—654).—The gain in wt. to 2 weeks of age, of chicks receiving diets containing 5% of ground *Indigofera endecaphylla* varied widely depending on the individual plant used. There was a highly significant negative correlation between wt. gains and % of 3-nitropropionic acid (**I**) in the plant. No reduction in wt. gains occurred with <0·36% of **I** in the plant (5% of **I** in the diet). The toxic factor in the plant is probably also related to unknown environmental effects as well as to genetic differences.   A. H. CORNFIELD.

Influence of growth hormone on growth in young cattle. P. J. Brumby (*N.Z. J. agric. Res.*, 1959, **2**, 683—689).—Daily injection of 5 mg./100 lb. body wt. of growth hormone for 12 weeks increased live wt. and height. L-Thyroxine (0·5 mg./100 lb. live wt.) increased height but lowered the gain in wt.; blood-sugar levels increased by 20—30%.   E. G. BRICKELL.

Grazing behaviour of dairy cattle in relation to milk production, live weight and pasture intake. P. J. Brumby (*N.Z. agric. Res.*, 1959, **2**, 797—807).—Free grazing Jersey and Friesian cattle were studied throughout their lactation period. There was a positive, although small, relationship between both grazing and rumination times, milk production and pasture intake, but differences in live wt. had little effect on grazing and rumination time. Grazing time required per unit of pasture intake was appreciably greater in the Jerseys than the Friesians, whereas the feed intake per lb. of fat-corrected milk showed the reverse order.   E. G. BRICKELL.

Effect of stocking upon a comparison of break and rotational paddock grazing for dairy cows. I. A. M. Lucas (*N.Z. J. agric. Res.*, 1959, **2**, 707—718).—Neither rate of stocking nor grazing management affected milk or butterfat yields per cow but those which were break-grazed had 4—5% lower feed intakes and 7—10% better gross efficiencies of conversion of feed into milk than those in paddock. Stocking rate had a stronger influence upon production per acre than did grazing method, the 32% higher rate causing increases of about the same in milk and butterfat yields per acre and an increase of about 10% in yield of digestible org. matter.   E. G. BRICKELL.

Effect on milk composition of feeding spring grass to cows. R. Waite, M. E. Castle and J. N. Watson (*J. Dairy Res.*, 1959, **26**, 173—181).—Compared with good quality winter rations, a diet of cut spring grass had no specific effect on the yield or composition of milk from cows maintained indoors. The increase in milk-protein content which normally occurs soon after the change from winter ration to spring grazing probably results from an improved plane of

nutrition and not specifically from an increase in sol.-carbohydrate intake. Increases in total N content of the milk were accounted for equally by increases in the casein, total albumin and β-lactoglobulin fractions.   S. C. JOLLY.

Grass silage as sole roughage for dairy cows. N. D. Dijkstra (*Versl. Landbouwk. Onderz.*, 1959, 65.14, 47 pp.).—Feeding trials showed that, compared with a hay-fed group, the faeces of the cows given grass silage were often too soft, the condition of the cows fell off and their live wt. decreased. Milk production was lower and the % of fat, solids-not-fat and protein in the milk distinctly lower. A supplement of other roughage, e.g. hay, is recommended.   E. G. BRICKELL.

Relationship between milk production and forage production and consumption by cows. H. M. Austenson, F. R. Murdock, A. S. Hodgson and T. S. Russell (*Agron. J.*, 1959, **51**, 648—650).—On orchardgrass–ladino clover and orchardgrass + inorg. N (120— 210 lb. annually) plots over 2 years, milk production per acre was highly correlated with both forage dry matter production and dry matter consumption by the cow. Although dry matter production and consumption per acre were higher for the orchardgrass + N plots than for the orchardgrass–ladino clover plots, the reverse held for milk production per cow-day and financial returns.   A. H. CORNFIELD.

Effect of concentrates of high or low starch equivalent, both fed at two levels, on the milk production of dairy cows. M. E. Castle, D. S. Maclusky, J. Morrison and J. N. Watson (*J. dairy Res.*, 1959, **26**, 1—8).—Milk yield and live wt. were increased significantly when the amount of concentrate (15% total digestible crude protein) was increased from 2·6 to 4·6 lb. per gal. of milk produced; the starch equiv. of the concentrate (63 or 79) did not affect these increases. Solids-not-fat contents varied from 8·53 to 8·77%, with rise in starch level of the concentrate and rate of feeding; the fat content of the milk (3·84%) and wt. of dry matter in the basic ration consumed daily were similar on all four rations.   S. C. JOLLY.

Secretion of milk of low fat content by cows on diets low in hay and high in concentrates. VII. Effect of administration of volatile fatty acids to cows giving normal milk and milk of low fat content. C. C. Balch and S. J. Rowland (*J. dairy Res.*, 1959, **26**, 162—172).—Administration of 0·5 to 1·5 kg. of acetate daily to cows in which the milk fat % had been reduced by low-hay–high-concentrate diets usually restored both the % and Reichert value of the fat; addition of 0·5 kg. of Na acetate to normal diets had no effect on milk fat %. Daily administration of 0·3 to 0·5 kg. of butyrate, but not of propionate, appeared to be as effective as was acetate. The fat % on diets containing either 50 lb. of silage as the sole roughage or 60 lb. of fodder beet and only 6 lb. of hay was the same as on a normal diet containing 16 lb. of hay.   S. C. JOLLY

Use of animal fat in concentrate mixtures for dairy cows. N. D. Dijkstra (*Versl. Landbouwk. Onderz.*, 1959, 65.15, 31 pp.).—Addition of 5% of stabilised destructor fat to concentrate mixtures was unobjectionable and led to a small increase in milk production and in milk fat content, coupled with a slight decrease in protein and solids-not-fat content. The butterfat showed a rise in I val.   E. G. BRICKELL.

Grazing of crop forages by sheep. III. Intake, maintenance and weight-gain requirements of wethers grazing rape. A. F. Greenall (*N.Z. J. agric. Res.*, 1959, **2**, 639—648).—Intake of units of starch equivalents was 8% higher than that calculated from Wood and Woodman (1930) feeding tables. Maintenance requirements were 20% higher and wt.-gain needs 30% lower than standard values. Rate of wt.-gain increased as grazing progressed, there being a linear increase in intake in successive blocks. (26 references.)   E. G. BRICKELL.

Comparison of vitamin B₁₂ and cobalt contents of livers from normal lambs, cobalt-dosed lambs and others with a recent history of mild cobalt deficiency disease. E. D. Andrews, L. I. Hart and B. J. Stevenson (*N.Z. J. agric. Res.*, 1959, **2**, 274—282).—Co deficiency in individual lambs is not associated with liver vitamin B_{12} concn. >∼0·30 μg./g., but concn. of 0·20—0·30 μg./g. could be consistent with a recent history of mild Co deficiency. Co in the livers of normal lambs on Co-sufficient pasture was in the form of vitamin B_{12}; in the livers of Co-dosed lambs, the Co was in some other form. (14 references.)   E. M. J.

Influence of the amount of protein and energy in the ration of replacement ewe lambs on body weight gains and wool production. F. Whiting, S. B. Slen and L. M. Bezeau (*Canad. J. Animal Sci.*, 1959, **39**, 64—70).—Increasing the amount of protein resulted in an increase in apparent digestibility, but no change in the % protein retained or in digestibility of dry matter and gross energy. The average digestible crude protein requirements of a ewe lamb weighing 85 lb., and consuming 1·3 lb. of T.D.N. was 0·13 lb. (0·16 lb. when wool production was considered).   E. G. BRICKELL.

Effect of thyroxine on lactation in ewes. D. S. Hart and N. Laffey (*N.Z. J. agric. Res.*, 1959, **2**, 666—676).—Evidence of lactation response is reported from (i) mature ewes implanted with L-thyroxine (*a*) 6 weeks before lambing, (*b*) 2/3 days after lambing, and (ii) 2-tooth ewes implanted about the time of mating. (18 references.)　　　　　　　　　　　　　　E. G. BRICKELL.

Effects of bran and cellulose on the water relationships in the digesta and faeces of pigs. I. Effects of including bran and two forms of cellulose in otherwise normal rations. II. Effects of adding different levels of fibrous cellulose to a highly digestible purified ration. III. Effect of the level of water intake and level of cellulose in the ration on the dry matter content of faeces. P. H. Cooper and C. Tyler (*J. agric. Sci.*, 1959, **52**, 332—339, 340—347, 348—351).— I. Addition of bran or fibrous cellulose to a pig ration lowered the % of dry matter in the faeces but tended to increase the variability of this value. Powdered cellulose had substantially no effect on the water balances and caused hard stools.

II. Starch was replaced by fibrous cellulose in a purified ration. The subsequent distribution of dry matter, cellulose and water throughout the digestive tract is recorded.

III. Differences in the water intake of pigs on a definite ration affected faecal dry matter to only a limited extent.
　　　　　　　　　　　　　　A. G. POLLARD.

Influence of strain and sex on the relationship of protein to energy in the rations of growing and finishing bacon pigs. J. P. Bowland and R. T. Berg (*Canad. J. Anim. Sci.*, 1959, **39**, 102—114).—Rate of live-wt. gain tended to be highest in pigs fed high energy-high protein rations throughout. Males gained more rapidly than females. Strain × sex interactions in rate of gain were present in both the growing and finishing period with a ration × strain interaction present in the growing period. Carcasses from female pigs excelled those from male pigs in all factors measured except carcass length. Strain differences in carcass characteristics existed but no appreciable strain × ration interactions were noted.　　　E. G. BRICKELL.

Rapeseed oil meal as a protein supplement for swine and rats. I. Rate of gain, efficiency of food utilisation, carcass characteristics and thyroid activity. II. Energy and nitrogen digestibility and nitrogen retention. N. Hussar and J. P. Bowland (*Canad. J. Anim. Sci.*, 1959, **39**, 84—93, 94—101).—I. A 10% level of the meal depressed rates of live-wt. gain and in some cases reduced efficiency of food utilisation ; food consumption was not adversely influenced. Total wt., histological sectioning, and ^{131}I turnover rate of the thyroid gland indicated hypertrophy and other abnormalities in animals fed 10% meal ; the 2% level did not exert consistent effects on the criteria measured. The nutritional quality of the diet fed to rats tended to alter the response to toxicity. Swine carcass characteristics were not markedly affected.

II. The 10% level of the meal depressed apparent digestibility of dry matter, energy and N with significant effects occurring only in rats ; the 2% level had no significant effect on digestibility. Retention of digestible N was not altered by the rapeseed level.
　　　　　　　　　　　　　　E. G. BRICKELL.

Effects of levels of dried apple pomace in swine rations on growth rate, feed efficiency, carcass quality and size of certain organs. D. M. Bowden and J. C. Berry (*Canad. J. Anim. Sci.*, 1959, **39**, 26—33).—At levels up to 20% pomace did not affect daily gain in wt. of pigs, dressing %, carcass quality or wt. of heart, liver, spleen or small intestine but increasing the level to 40% resulted in significantly slower growth, lower dressing %, greater feed consumption per unit gain, leaner carcass, heavier liver, lighter stomach, and heavier large intestine.　　　　　　　　　E. G. BRICKELL.

Unrestricted whey for fattening pigs, including the effect of omitting antibiotic from the diet during the later stages of fattening. R. Braude, K. G. Mitchell, A. S. Cray, A. Franke and P. H. Sedgwick (*J. Dairy Res.*, 1959, **26**, 63—71).—Pigs fed 3 lb. (reduced to 2 lb. at 13 weeks of age) of meal daily with oxytetracycline (**I**) and unrestricted amounts of whey grew significantly more slowly and utilised their feed significantly less efficiently than did pigs fed only ≯6 lb. of meal and **I** daily. They also had significantly lower dressing %, but longer and less fat carcasses. For efficiency of feed utilisation, 1 gal. of whey replaced approx. 0·7 lb. of meal. Omission of **I** from either diet after the pigs reached 130 lb. live wt. had no significant effect on growth rate, efficiency of feed utilisation or any carcass measurement.　　　　　　S. C. JOLLY.

Chlortetracycline and protein level in rations for market hogs. I. Effect of rate of gain and efficiency of feed utilisation. II. Effect on carcass quality. S. E. Beacom (*Canad. J. Anim. Sci.*, 1959, **39**, 71—78, 79—83).—I. For the over-all feeding period (weaning to market wt.), the addition of Aureomycin caused statistically significant increases in rate of gain at all protein levels. Protein level also affected rate of gain significantly and the effect of the " Protein × Antibiotic " interaction on rate of gain was also significant. Aureo-

mycin improved feed efficiency at all protein levels, especially at low and medium levels. Over-all feed consumption was increased only at the standard protein level.

II. Aureomycin had no significant effect on length of carcass, or on the area of the eye of the lean, at any of the four levels of protein tested, but depth of back fat, though not of shoulder or loin fat, was significantly increased. Protein level had no significant effect except to increase the area of the eye of lean.　　　E. G. BRICKELL.

Availability to pigs of nicotinic acid in *tortilla* baked from maize treated with lime water. E. Kodicek, R. Braude, S. K. Kon and K. G. Mitchell (*Brit. J. Nutr.*, 1959, **13**, 363—384).—In maize almost all the nicotinic acid (**I**) exists in bound form, is unavailable as nutrient and is only partly usable by micro-organisms. Treatment with 1% lime water followed by baking liberates **I** ; this is the normal practice in Central America in the preparation of *tortilla*. The details of the animal tests are given. (69 references.)　　　C. V.

Growth and feed conversion of turkeys reared on range and in confinement. J. D. Wyne, R. D. Carter, M. G. McCartney and V. D. Chamberlin (*Poultry Sci.*, 1959, **38**, 1003—1005).—The performance of turkeys from 8 weeks to 24 weeks of age was compared on ladino clover range plots and on confinement in a pole shelter. Both groups received a 20% protein diet to 16 weeks followed by a 16% protein diet to 24 weeks of age. Males, but not females, made better growth on range than in confinement. There was no difference in feed efficiency between the two systems of rearing.
　　　　　　　　　　　　　　A. H. CORNFIELD.

Turkeys grown in confinement and on range. L. F. Payne (*Poultry Sci.*, 1959, **38**, 1087—1094).—Range-reared male turkeys averaged 1·50 lb. more and female turkeys 0·94 lb. more at 26 weeks of age than corresponding birds in pole-type houses. Feed efficiency was only slightly higher for the range group, whilst mortality was similar for both groups. The range birds graded higher when dressed than did the housed birds.　　　　　　　　A. H. CORNFIELD.

Broiler pigmentation as influenced by dietary modifications. R. G. Ratcliff, E. J. Day and J. E. Hill (*Poultry Sci.*, 1959, **38**, 1039—1048).—The xanthophyll in yellow maize was much more effectively utilised by chicks for pigmentation than was that in dehydrated lucerne meal or maize gluten meal. Varying the kg.-cal./protein ratio of the diet from 35 to 60 or addition of 4% of fat or 2% of lecithin had no influence on pigmentation. Efficiency of xanthophyll utilisation was less when the kg.-cal./protein ratio was <40. Addition of a commercial broiler pigmenter, which contained appreciable amounts of xanthophyll to the diet, had no effect on carotenoid deposition.　　　　　　　A. H. CORNFIELD.

Availability of phosphorus in soft phosphate and phosphoric acid and the effect of acidulation of soft phosphate. J. D. Summers, S. J. Slinger, W. F. Pepper, I. Motzok and G. C. Ashton (*Poultry Sci.*, 1959, **38**, 1168—1179).—Assuming the P in $CaHPO_4$ to be 100% available to chicks, bone ash values and wt. gains of chicks receiving soft phosphate showed that the P in the material was about 48% available. The P in H_3PO_4 was approx. 125% available. The availability of P in soft phosphate was increased by mixing it with 1·0 or 0·5 parts of H_3PO_4 and the material produced was of suitable physical condition for mixing with the diet. Mixing soft phosphate with 0·5 part of HCl increased the availability of P in the material, but the product was wet and sticky.　　　　A. H. CORNFIELD.

Discrimination between carbohydrates by the fowl. M. R. Kare and W. Medway (*Poultry Sci.*, 1959, **38**, 1119—1127).—During the day chicks were given free choice of water and carbohydrate in solution (2·5% to 25% concn.). The % acceptance [(sugar solution taken/total fluid intake) × 100] was similar for all concn. of glucose, sucrose and maltose but decreased to low values with increasing concn. of xylose. Sweetness, viscosity, refractive index, osmotic pressure and density of the solutions were not related to acceptance. The *in vitro* effect on the motility of a segment of intestine was not related to acceptance.　　　　　　　　A. H. CORNFIELD.

Amino-acid requirements of the chick. II. Effect of total essential amino-acid level in the diet on the arginine and lysine requirements. J. O. Anderson and D. C. Dobson (*Poultry Sci.*, 1959, **38**, 1140—1150).—Chick trials with diets containing varying levels of casein or other proteins and amino-acids providing the same essential amino-acids as casein indicated that the chick's requirement for arginine, lysine and probably other amino-acids increased as the level of the other essential amino-acids found in the diet in balanced proportions increased. Ration protein level *per se* had little effect on the requirement for arginine or lysine.　　　　　　A. H. CORNFIELD.

Use of Micro-Cel-Fat (MCF) in chick diets. H. W. Titus, A. L. Mehring, jun., D. Johnson, jun., L. L. Nesbitt and T. Tomas (*Poultry Sci.*, 1959, **38**, 1114—1119).—Micro-Cel-Fat (MCF) is a blend of tallow and Micro-Cel, a highly adsorptive synthetic Ca silicate, and has the advantage over tallow and fats in that it is easily mixed

with other feeding-stuffs. In trials with chicks to 10 weeks of age the tallow in MCF was as well utilised as plain tallow. The N-free extract in the diet containing MCF appeared to be more digestible than that in the diet containing tallow and the former also contained more metabolisable energy, per kg.-cal. of heat combustion, than did the latter.   A. H. CORNFIELD.

Effect of thiouracil and thyroxine on chick embryo development. J. C. Rogler, H. E. Parker, F. N. Andrews and C. W. Carrick (*Poultry Sci.*, 1959, **38**, 1027—1032).—The injection of 0·002 g. of thiouracil into the albumin of eggs prior to incubation reduced embryo size after 10 days. The treatment also reduced hatchability, delayed hatching time, and increased thyroid size in the embryos and chicks which hatched. Injection of 2—16 µg. of thyroxine into the albumin before incubation, followed in some cases by an additional injection into the air cell or allantoic sac after 17 days of incubation had little effect on time of hatch or chick thyroid size. Thiouracil treatment of the egg increased the total I_2 content of the thyroid of 20—23-day-old chicks, but I_2 concn. in the thyroid was reduced by the treatment.   A. H. CORNFIELD.

Effect of drug additives upon the vitamin B_6 requirement of chicks. H. L. Fuller and W. S. Dunahoo (*Poultry Sci.*, 1959, **38**, 1150—1154). —Chick growth from 7 to 14 days of age was depressed by addition of nitrofurazone 0·011 + furazolidone 0·0016 + arsanilic acid 0·01% to a diet deficient in vitamin B_6 and also that of chicks receiving added vitamin B_6 (0·0005—0·0020 g. of pyridoxine per lb. of feed). Furazolidone + arsanilic acid depressed growth only in the absence of added pyridoxine. The growth-depressing effect of nitrofurazone was not overcome by addition of pyridoxine to the diet. In general, the presence of 0·0015 g. pyridoxine per lb. of feed was sufficient for max. growth and feed efficiency.
                                                    A. H. CORNFIELD.

Factors affecting the vitamin K requirement of chicks. T. S. Nelson and L. C. Norris (*Poultry Sci.*, 1959, **38**, 1094—1102).— Addition of 0·100—0·125% of sulphaquinoxaline (**I**) to the diet of chicks (reared on vitamin K-low diets) at 30—34 days of age increased the blood-clotting time, incidence of haemorrhages and mortality and reduced the wt. gains. In the absence of **I**, menadione-NaHSO₃ (**II**) (0·0005 g. per 100 g. feed) prevented the haemorrhages and resulted in normal blood-clotting time. In the presence of **I, II** corrected only the prolonged blood-clotting time. The bad effects of **I** were not overcome even when **II** was supplied at 50 times the chick's normal requirement. Addition of nicarbazin (0·0125), arsanilic acid (0·01), Aureomycin (0·0055) or arsonic acid (0·005)% slightly increased blood-clotting times with the vitamin-K-low diet, but had no effect when **II** was added. Infectious bronchitis increased the clotting time of chicks fed vitamin-K-low diets, but not of those receiving adequate **II**.   A. H. CORNFIELD.

Fractionation of soya-bean oil-meal for growth and anti-perotic factors. I. Non-phospholipid nature of the factors. F. H. Kratzer, P. Vohra, R. L. Atkinson, P. N. Davies, B. J. Marshall and J. B. Allred (*Poultry Sci.*, 1959, **38**, 1049—1055).—An org. growth-promoting and anti-perotic factor(s) present in soya-bean oil-meal was extractable with MeOH but was insol. in acetone. The activity was not due to lecithin, cephalin, choline or linoleic acid. Liver powder, brain powder, crude soya phospholipids and egg yolks also exhibited growth-promoting activities.   A. H. CORNFIELD.

Molybdenum in chick diets. R. A. Teekell and A. B. Watts (*Poultry Sci.*, 1959, **38**, 1127—1132).—The effect of Mo supplementation of the diet of chicks from control and W-supplemented dams was studied. Chicks, from W-supplemented dams, fed purified or practical rations made slower wt. gains than did chicks from non-supplemented dams. Addition of Mo (1—100 p.p.m.) to the diet of chicks from control dams had no effect on growth, but when added to the diet of chicks from W-supplemented dams wt. gains were increased. The greatest wt. gains were made by chicks from W-supplemented dams, receiving Mo (10—50 p.p.m.), indicating a synergistic effect between Mo and W for growing chicks. Chicks from control dams tolerated higher levels of added Mo (~500 p.p.m.) in their diet without adverse effect of growth than did chicks from W-supplemented dams, which showed reduced growth rates with Mo at 500 p.p.m.   A. H. CORNFIELD.

Mercury retention by chickens. V. L. Miller, G. E. Bearse and K. E. Hammermeister (*Poultry Sci.*, 1959, **38**, 1037—1039).—After injection of phenyl Hg acetate there were differences in kidney Hg retention in strains of chickens selected for leucosis resistance and susceptibility and their reciprocal crosses. The first generation of cross chicks resembled more closely the parent that retained Hg poorly than they did the one retaining large amounts of Hg. There were no significant differences between sexes in Hg retention.
                                                    A. H. CORNFIELD.

Effect of route of administration upon growth response to penicillin by turkey poults. J. R. Jowsey, F. D. Cook and H. I. MacGregor

(*Canad. J. Anim. Sci.*, 1959, **39**, 21—25).—Results indicate that growth response to injected penicillin, both intramuscularly and intraperitoneally, and to penicillin administered in the feed is similar in so far as sufficient penicillin from injection reaches the gut to cause typical suppression of lactobacilli.   E. G. BRICKELL.

Mineral metabolism of pullets. XII. Effects of protracted treatment with oestrogen and with oestrogen plus androgen on retention of sodium. K. A. McCully, W. A. Maw and R. H. Common (*Canad. J. Anim. Sci.*, 1959, **39**, 1—5).—Na retention by sexually immature crossbred pullets was not affected by their treatment with either oestradiol benzoate, 0·5, or oestradiol benzoate, 0·5 + testosterone propionate, 0·4 mg. per day. The average daily retention was 37 mg.
                                                    E. G. BRICKELL.

Effect of environment on reproductive characters and endocrine organs of New Hampshire chickens. B. Glick, J. Griffin and A. van Tienhoven (*Poultry Sci.*, 1959, **38**, 1078—1087).—Egg production and fertility were higher when mean summer max. temp. was maintained at about 21·1° by using insulated air-conditioned houses than when conventional or open houses were used in which the temp. was about 30°. Temp. control had no effect on % hatch of fertile eggs or on age of embryonic mortality.   A. H. CORNFIELD.

Flavour of modern- and old-type chickens. H. L. Hanson, A. A. Campbell, A. A. Kraft, G. L. Gilpin and A. M. Harkin (*Poultry Sci.*, 1959, **38**, 1071—1078).—Birds representative of breeds in commercial production in 1930 and in 1956 were reared on diets typical of their particular year and compared for flavour after five different methods of cooking. In 600 comparisons at two locations there were no differences in flavour between the birds of the two periods.
                                                    A. H. CORNFIELD.

Efficiency of food utilisation for egg production by pullets and yearling hens. W. Bolton (*J. agric. Sci.*, 1959, **52**, 364—368).— Egg production by both classes of chickens was slightly higher on a low-energy than on a high-energy ration. The gross food intake was greater on the low-energy ration but the consumption of digestible protein, non-protein digestible energy and metabolisable energy was identical with both rations. The efficiency of utilisation of digestible energy and protein fell slightly from the pullet stage until the following year.   A. G. POLLARD.

Substances in plants of the order *Malvaceae* causing pink whites in stored eggs. F. S. Shenstone and J. R. Vickery (*Poultry Sci.*, 1959, **38**, 1055—1070).—Two fatty acids, malvalic and sterculic, which occur in plants in the order *Malvaceae* produced typical symptoms of the pink whites in eggs when fed to laying hens at 0·025 g. per hen daily. 20—25% of the ingested acids were incorporated in the yolks. These acids were the only constituents of the oils extracted from the leaves and/or seeds of *Malva* spp. which give the Halphen colour test. The fatty acids remaining after extraction of these acids did not give the Halphen test or produce the pink-white condition. The active acids contain a cyclopropene ring, which is probably responsible for their activity, since their hydrogenated derivatives (cyclopropane ring) were inactive. Egg production was not affected by daily doses up to 0·05 g. per hen, whilst 0·25 g. of sterculic acid per day rapidly caused cessation of egg production. Other disorders associated with the pink-white condition were also produced by ingestion of the cyclopropene acids.   A. H. CORNFIELD.

Value of sunflower seed oil meal as a protein supplement for laying hens. E. D. Walter, G. S. Lindblad and J. R. Aitken (*Canad. J. Anim. Sci.*, 1959, **39**, 45—49).—In rations containing 2·0—2·5% fish meal, the complete replacement of other supplementary protein sources with sunflower seed oil meal had no influence on mortality, egg production, egg wt. or body wt. maintenance but feed consumption tended to be higher when meat meal was replaced by its protein equivalent of sunflower seed oil meal, and by an equivalent amount of mineral supplement.   E. G. BRICKELL.

Enzyme supplementation of barley diets for laying hens. L. R Berg (*Poultry Sci.*, 1959, **38**, 1132—1139).—Addition of fungal or bacterial enzyme prep. or malt barley (replacing some of the ordinary barley) or use of water-treated instead of ordinary barley had no effect on egg production, feed efficiency with respect to egg production or egg quality factors of White Leghorns fed barley rations. Water treatment of the barley increased feed efficiency slightly. The fungal prep. decreased litter moisture. Both enzyme prep. improved growth and feed efficiency in young chicks fed barley rations.   A. H. CORNFIELD.

Variability of the blood plasma-cholesterol of laying chickens. D. Johnson, jun., A. L. Mehring, jun. and H. W. Titus (*Poultry Sci.*, 1959, **38**, 1109—1113).—There were no significant differences in the cholesterol content of the blood plasma of caged birds receiving tallow ranging from 3·6 to 14·5% of the diet (isonitrogenous, isocaloric diets), or between these birds and birds kept on grass range and receiving a diet containing no added fat.   A. H. CORNFIELD.

Adrenal ascorbic acid content of moulting hens and the effect of ACTH on the adrenal ascorbic acid content of laying hens. M. Perek and B. Eckstein (*Poultry Sci.*, 1959, **38**, 996—999).—Adrenal ascorbic acid depletion was elicited in laying hens by ACTH injections as readily and to the same extent as in mammals. The treatment had no effect on 3-month-old pullets. Untreated moulting hens showed a depletion in adrenal ascorbic acid similar to that in ACTH-treated laying hens.   A. H. CORNFIELD.

Effect of high levels of chlortetracycline on egg weight and shell quality during hot weather. B. W. Heywang and M. G. Vavich (*Poultry Sci.*, 1959, **38**, 999—1003).—Addition of chlortetracycline HCl (50—200 g. per ton of feed) to the diet of laying hens for 35 days during hot weather had no effect on egg wt. or shell quality.
                    A. H. CORNFIELD.

Genetic and nutritional effects on the incidence of the avian leucosis complex. J. Biely and B. E. March (*Poultry Sci.*, 1959, **38**, 1103—1109).—Of four strains studied two were susceptible and two relatively resistant to avian leucosis. With all strains incidence of leucosis was greater when birds were on a high than on a low plane of nutrition.   A. H. CORNFIELD.

Dimethoate for systemic control of cattle grubs. R. O. Drummond (*J. econ. Ent.*, 1959, **52**, 1004—1006).—Cattle were treated orally, intramuscularly and dermally with doses of 5—20 mg./kg. and with dermal sprays of up to 1%. 90% control of *Hypoderma lineatum* and *H. bovis* occurred only with the higher dosages, and these caused poisoning.   C. M. HARDWICK.

Ronnel sprays for systemic control of cattle grubs. R. O. Drummond and B. Moore (*J. econ. Ent.*, 1959, **52**, 1028—1029).—100% and 63% control of grubs was obtained in two herds after a single spray with Ronnel. The same total amount of insecticide was applied on several occasions at 0·25, 0·5 and 0·75% concentrations. Only those treated four times with 0·75% Ronnel showed any considerable degree of control.   C. M. HARDWICK.

Free-choice administration of Ronnel in a mineral mixture for control of cattle grubs. W. M. Rogoff and P. H. Kohler (*J. econ. Ent.*, 1959, **52**, 958—962).—An intake of ∼9 mg./kg./day of a salt-bone meal mixture containing Ronnel, for 66 days gave 100% control of *Hypoderma* spp; 2 mg./kg./day gave 82% control. Access for 28 days gave poor results. Cholinesterase depression was >50% at 9 mg. dosage but none was found at the lower dosage. (16 references.)   C. M. HARDWICK.

Low-level feeding of Trolene for the control of the cattle grubs *Hypoderma lineatum,* **De Vill. and** *H. bovis,* **L.** J. Weintraub, C. O. M Thompson and M. C. Qually (*Canad. J. Anim. Sci.*, 1959, **39**, 58—63). —Cattle were fed individually for 18 days on a ration of crushed oats treated with Trolene to give a daily dosage of 10 mg./kg. This treatment produced 94% mortality of grubs, which was not significantly different from 97% mortality obtained with a single treatment by boluses at 100 mg./kg. The only symptom of toxicity was mild diarrhoea. In a field experiment with treated range blocks, averages of 7·7 and 4·2 mg. of Trolene/kg. for 93 and 64 days showed 95% and 85% mortality of the grubs. By comparison treatment with boluses at 110 mg./kg. showed 80% mortality. No symptoms of toxicity were seen in the calves of the two low-level-treated groups.
                    E. G. BRICKELL.

Timing the treatment of cattle with Trolene for systemic control of the cattle grubs, *Hypoderma lineatum,* **De Vill. and** *H. bovis,* **L. in Alberta and British Columbia.** J. Weintraub, G. B. Rich and C. O. M. Thompson (*Canad. J. Anim. Sci.*, 1959, **39**, 50—57).—Oral treatment (100 mg./kg.) at Lethbridge and Kamloops gave effective control if administered in Nov., Jan. or Mar. at the former and Dec., Jan. and Feb. at the latter station. Slight symptoms of toxicity, in the form of lethargy and reduced food consumption at Kamloops, and ataxia of the hindquarters at Lethbridge, were observed in the calves treated in Dec. and Jan. respectively, but these disappeared within 48 hr. of treatment without the use of antidotes. E. G. BRICKELL.

Co-Ral sprays for systemic control of the cattle grubs, *Hypoderma bovis,* **L. and** *H. lineatum,* **De Vill.** M. A. Khan, C. O. M. Thompson and W. L. Pelham (*Canad. J. Anim. Sci.*, 1959, **39**, 115—120).— Sprays containing 0·75% Co-Ral [*OO*-diethyl *O*-(3-chloro-4-methyl-7-coumarinyl) phosphorothionate] reduced the no. of grubs in treated calves by approx. 88% but there was no difference in larvicidal effects between 0·25 and 0·5%, both of which reduced the no. of grubs by 60 to 70%. Neither the surfactants used nor the pressures employed had any effect on larvicidal properties. None of the treated calves showed signs of org. P poisoning, but an outbreak of shipping fever occurred.   E. G. BRICKELL.

Effectiveness of aerosol formulations containing methoxychlor and other insect-repellents against biting flies on cattle and analyses of milk from treated animals. T-H. Cheng, E. H. Frear and H. F. Enas, jun. (*J. econ. Ent.*, 1959, **52**, 866—868).—One application a day, for 14 weeks, of an aerosol containing 1 or 2% methoxychlor with diethyltoluamide, Thanite, MGK-R-326 and MGK 264 and pyrethrins reduced *Siphona irritans* populations by >95% and *Stomoxys calcitrans* by ∼40%. The latter value was increased to 60% by the use of 4% methoxychlor. More than 50% of the flies were on the heads of the cattle which were untreated. No residues were detectable in the milk.   C. M. HARDWICK.

Detection of streptococcal mastitis by paper electrophoresis. U. Weigt (*Milchwissenschaft*, 1959, **14**, 477—481).—A shift in the serum-protein fraction occurs which enables chronic and acute forms to be clearly differentiated ; it is stated that this shift takes place before a bacteriological diagnosis becomes clearly positive. (11 references.)   C. V.

Residue studies in sheep and goats dipped in 0·025% lindane. J. B. Jackson, M. C. Ivey, R. H. Roberts and R. D. Radeleff (*J. econ. Ent.*, 1959, **52**, 1031—1032).—Details are given of modifications of the Schechter–Hornstein colorimetric method for BHC used for its analysis in fat. At each biopsy residues in sheep were higher than those in goats. Highest values were found 2 weeks after dipping and these decreased to zero at 12 weeks.   C. M. HARDWICK.

Fate of ^{14}**C-diethyltoluamide applied to guinea pigs.** C. H. Schmidt, F. Acree, jun. and M. C. Bowman (*J. econ. Ent.*, 1959, **52**, 928—930).—Six hours after ∼7 mg. of ^{14}C-diethyltoluamide per sq. in. was applied to the skin of guinea pigs, 0·97 mg. had evaporated and 1·32—3·4 mg. was absorbed. Radioactivity in the urine reached a peak 12 hr. after application and 80% of it was excreted within 24 hr. but all was changed to unknown metabolites. Only 0·75% was excreted in faeces.   C. M. HARDWICK.

Control of goat lice in 1957 and 1958. B. Moore, R. O. Drummond and H. M. Brundrett (*J. econ. Ent.*, 1959, **52**, 980—981).—Laboratory tests showed that *Bovicola caprae* and *B. limbatus* from one of two ranches had developed resistance. In field tests, the time taken for Bayer 21/199 malathion, Delav, Dipterex, Ronnel and Sevin to control lice depended on length of coat. Whole flocks must be treated.   C. M. HARDWICK.

Control of experimental caecal coccidiosis with sulphaquinoxaline-antibiotic combinations. J. L. Gardner (*Poultry Sci.*, 1959, **38**, 1032—1037).—Addition of 0·0125—0·0250% of sulphaquinoxaline to a diet containing Aureomycin (200 g. per ton) gave excellent control of experimentally-induced caecal coccidiosis in chicks. Growth compared favourably with that of uninfected non-medicated birds. Sulphaquinoxaline alone or in combination with Terramycin gave relatively poor control of the disease or inhibited growth.
                    A. H. CORNFIELD.

2.—FOODS

Carbohydrate Materials

Cereals, flours, starches, baking

Present importance and future of grain sorghums. S. S. Watson (*Cereal Sci.*, 1959, **4**, 230—233).—The structure and chemical composition of the sorghum kernel are described. It is highly nutritious for animals and human beings, but requires some protein supplement to provide a balanced food. It is processed in various ways and products obtained from it include wax, edible oil, flour, animal feed, cryst. dextrose, and starches for use in foods and in manufacturing processes. (29 references.)   S. G. AYERST.

Loss in weight and volume of wet parboiled rice during drying. R. Radhakrishnamurthy, H. S. R. Desikachar and V. Subrahmanyan (*Food Sci., Mysore*, 1959, **8**, 315—316).—Most parboiled rice of about 20% moisture content was air dried in the shade and the decrease in wt. and vol. and the increase in bulk density was measured. This data could be used as a basis for fixing the max. moisture content permissible in marketed rice, which is at present being sold in bad condition.   S. G. AYERST.

Grain hardness tester. R. Katz, A. B. Cardwell, N. D. Collins and A. E. Hostetter (*Cereal Chem.*, 1959, **36**, 393—401).—The Barcol Impressor for soft metal testing has been modified for estimating the hardness of single transverse kernel sections. The displacement of a spring-loaded stylus (measured by dial micrometer) was related to the Vickers diamond pyramid hardness (DPH). Measurements on hard red winter wheat (Ponca) showed a variation of 25—40 hardness units compared with ±½ for lead.   P. M. KINGSTON.

Treatment of wheat with ionising radiations. IV. Oxidative, physical and biochemical changes. Sing-Ping Lai, K. F. Finney and M. Milner (*Cereal Chem.*, 1959, **36**, 401—411).—γ-Irradiation up to 1 million rep on two varieties of wheat grains resulted in a marked

decrease in gelatinisation η, starch content and gluten hydration capacity of the resultant flours. At high dosages the maltose value and colour increased (possible stimulation of a browning reaction). Baking tests showed a decrease in loaf vol. (improved with $KBrO_3$), production of off-flavours, reduction in crumb softness and increased staling rate. Crumb firming on storage was improved. The effect of malt and sugar in the test formulae was also examined. (18 references.)   P. M. KINGSTON.

Rapid method of detecting germ damage in wheat and maize. C. M. Christensen and S. A. Qasem (*Cereal Chem.*, 1959, **36**, 461—463).—A known no. of kernels (e.g., 400) are boiled with 2% sodium hypochlorite until bleaching begins, whereupon the damaged grains (dark colour) may be easily counted. Not more than 15 min. is required for each determination. Accuracy is comparable with conventional methods.   P. M. KINGSTON.

Factors affecting the protein content of wheat. A. M. Schlehuber and B. B. Tucker (*Cereal Sci.*, 1959, **4**, 240—242).—From a review of the literature it appears that the protein content of wheat is affected mainly by the climate, the available N and the variety grown. (21 references.)   S. G. AYERST.

Extraction of total protein from wheaten flour as soluble derivatives. E. E. McDermott and J. Pace (*Nature, Lond.*, 1959, **184**, 546—547).—Swan's method (*ibid.*, 1957, **180**, 643) can be applied to white flour (70% extraction), the reagent (containing Cu^{2+} and $SO_2{}^{2-}$) readily dissolving all the protein, with $<3\%$ of the carbohydrate, during 1—2 hr. extraction at 25° and pH 7·5—8. The clear protein solution can be freed from Cu by dialysis. The proteins in gluten, freshly washed from flour, are also solubilised after $\sim$12 hr. extraction with Swan's reagent.   W. J. BAKER.

Analytical results on air-separated flour. H. Cleve (*Getreide u. Mehl*, 1959, **9**, 81—86).—Determinations of protein, ash, maltose-figure, water-absorption, baking quality, and extensogram results are reported for various size fractions separated from typical flours by air separation (turbo-milling). The quality of the gluten is not altered by the process and the baking quality of each fraction depends mainly on the protein content. The protein content is highest for the fractions of smallest particle size and least for those between 18μ and 45μ. The separation makes possible the production of flour with protein contents between 3% and 20%.   E. C. APLING.

Some new observations on the behaviour of rye- and wheatflour-suspensions in the amylograph. J. Hampl (*Getreide u. Mehl*, 1959, **9**, 86—92).—The effect of additions of glutamic acid on the amylograph maxima (AM) recorded for rye and wheat flour suspensions is studied. With rye suspensions the normal AM correlates well with starch damage, hardly with sol. protein and not at all with maltose-figure. Additions of glutamic acid (0·25% to 5%) strongly affect the AM, influencing the arrest of enzyme activity. The change in AM produced is correlated with the pH of the suspension and hence with the buffering capacity of the flour. Additions of glutamic acid can be used to distinguish between flours with the same normal AM. (20 references.)   E. C. APLING.

Studies with radioactive tracers. III. Effects of defatting and of benzoyl peroxide on decomposition of ^{82}Br-labelled bromate by wheat-flour doughs. C. C. Lee and R. Tkachuk (*Cereal Chem.*, 1959, **36**, 412—420).—Three grades of commercially milled Canadian flour were used to make the dough samples (100 g. of flour and 60 ml. of water containing 15 p.p.m. of labelled bromate). Both defatting and benzoyl peroxide treatment markedly decreased decomposition of bromate to bromide. From a discussion of the effect of bromate on bread making in the light of results obtained, improver action appears to be only one of its functions. (16 references.)   P. M. KINGSTON.

Consistency measurements on batters, doughs and pastes. E. B. Lancaster and R. A. Anderson (*Cereal Chem.*, 1959, **36**, 420—430).—Further results are given using the consistency recording apparatus previously described (*Cereal Chem.*, 1957, **34**, 379—388) with different models of Hobart and farinograph mixers. Flour-water batters, cake-mix batters and gluten/soft wheat flour doughs, made to standard formulae, were measured in arbitrary units. Batter curves gave more information than that obtained with standard equipment in predicting the correct flour/water ratio for control purposes. The relationship between flour protein content and batter consistency had a correlation coeff. of 0·97 with standard error of 0·104.   P. M. KINGSTON.

Potentiometric titration of sulphydryl groups in wheat gluten with iodine. W. C. Shaefer, C. A. Wilham, R. J. Dimler and F. R. Senti (*Cereal Chem.*, 1959, **36**, 431—441).—To avoid solubility and turbidity problems common to gluten sulphydryl analysis by the direct iodometric method, titrations were made with a saturated solution of I in 0·01N AcOH (N_2 atm.) recording e.m.f. to the nearest mV.

3 min. after each I addition. Tests with glutathione and 2-mer-captoethanol showed good agreement with theory, giving a standard deviation of 5·4% of the average titre. Values obtained for sulphydryl-containing proteins gave high results compared with those by other methods. Glutens reduced 6·4—9·8 μequiv. of I per g. of protein. No correlation appeared to exist between gluten reducing power and baking quality. (41 references.)   P. M. KINGSTON.

Modification caused in bread starch by supplementation with amylolytic enzymes. H. Beck, B. S. Miller and J. A. Johnson (*Rev. Quím. industr. Rio de J.*, 1959, **38**, No. 326, 15—19).—A discussion of the hydrolytic action of α- and β-amylase on starch chains. Amylases from different sources are shown to differ in ability to retard hardening of bread crumbs and this is related to the thermostability of the enzymes. Variations (10) in supplementation were carried out and the resulting breads analysed for sol. dextrin, glucose and maltose. α-Amylase from bacteria has greatest effect in production of sol. dextrin and in chain length of extracted dextrin, but since this is not permitted, carefully controlled quantities of α-amylase from fungi and malted wheat may be advantageously used. (23 references.)   C. A. BLAU.

Interaction of anti-staling agents with starch. E. J. Bourne, A. I. Tiffin and H. Weigel (*Nature, Lond.*, 1959, **184**, 547).—The effectiveness of anti-staling agents in respect of pptn. of starch from solution (starch 0·5, NaCl 0·05, test agent 0·005—0·075%) was in the order sucrose monostearate, glyceryl monostearate (pure) and polyoxyethylene monostearate > glyceryl monostearate (commercial) > sucrose distearate $\gg$ stearoyl tartrate. Butanol, thymol and two ionic surfactants had no pptg. effect. Relations between baking qualities of bread, anti-staling activity and starch-pptn. power are discussed.   W. J. BAKER.

Bread staling. X-ray diffraction studies on breads containing a cross-linked starch and a heat-stable amylase. H. F. Zobel and F. R. Senti (*Cereal Chem.*, 1959, **36**, 441—451).—An increased crystallisation of bread from reconstituted flours containing 40% of cross-linked starch (Vulca 100) and bacterial α-amylase was observed up to 3—4 days after baking. No corresponding increase in crumb firmness occurred, however, in the presence of the amylase. Cells of cross-linked starch showed a greater proportion of retrograded ("B") structure and ageing increased crystallinity independent of the amylase content. (16 references.)   P. M. KINGSTON.

The concept and problems of fermentation tolerance. O. Doose (*Brot u. Gebäck*, 1959, **13**, 174—177).—By fermentation tolerance is understood the property of a dough which allows an extension of fermentation time without deterioration of dough ripeness or baking quality, and depends on flour quality and yeast quantity as well as on the kneading process, dough temp. and dough consistency. Tolerance is improved by the use of low temp. and high yeast contents, and by additions of sugar, malt products and fungal amylases, although the last named often give small loaf vol. from young doughs. Addition of lecithin reduces optimum proof time and increases loaf vol. Ascorbic acid, $KBrO_3$ or ammonium persulphate reduce optimum proof time and at favourable rates of addition increase tolerance. Additions of starch cut proof time, reduce loaf vol. and improve pore distribution in the crumb. (12 references.)   E. C. APLING.

Viscous strain hardening in bread doughs. J. Glucklich, R. Schoenfeld-Reiner and L. Shelef (*Bull. Res. Counc. Israel*, 1959, **7C**, 15—16).—In a study of the deformation due to strain of doughs made from *Triticum vulgaris* and *T. durum* flour, the two differed considerably with regard to viscous strain hardening. Results show that the *vulgaris* is a "strong" flour with good baking qualities whilst *durum* is "weak."   C. A. SLATER.

Contribution of the germ to oil content of white flour. D. J. Stevens (*Cereal Chem.*, 1959, **36**, 452—461).—Chemical analysis and baking tests on laboratory milled No. 2 Manitoba northern wheat were compared with flour from the corresponding germ-free wheat. Germ was removed by infecting with adult flour beetle (*Tribolium confusum* Dev.). Milling showed a 72·0% extraction rate as compared with 69·7% for the control, while baking tests gave a paler crust loaf. From oil extractions (light petroleum) and microscopic colour tests (Crystal Violet, 2,6-dichloroquinone-4-chloroimide, etc.) 34% originated from the germ in sizings reduction (semolina) as compared with 23—27% in other milled products. (17 references.)   P. M. KINGSTON.

Changes in, and the stability of, cereal oils. D. Karp (*Getreide u. Mehl*, 1959, **9**, 93—99).—Investigations with special reference to rye and crispbread manufacture show the importance of max. content of tocopherols and their synergists in the grain for long shelf-life of wholemeal products. If the grain is damaged additions of antioxidants do not fully rectify the protective system, and lipoxidase activity can destroy tocopherols in the presence of carotenoids. The requirements of manufacturers are best met by grain

harvested soon after reaching yellow ripeness, with a moisture content of from 25 to 20%. (14 references.)   E. C. APLING.

Simplified bread-making process : experiments in a large bakery. G. Jongh and C. J. Wensveen (*Brot u. Gebäck*, 1959, **13,** 151—154).—Results obtained using a bakery process employing high speed dough mixing and a shortened fermentation period are compared with the traditional baking method. Dough mixing in the simplified process was at twice to three times normal speed and the proof time was reduced to 60 min. at 28—30°. The addition of from 0·5 to 10% of sugar is necessary, and to give good crumb texture the dough is moulded very thin. The appearance and aroma of the bread was not inferior to bread baked by the normal process, and the crumb was distinctly brighter in colour.   E. C. APLING.

Quantitative determination of mercaptan as a constituent of volatile aromas of bread and baked goods. H. D. Ocker and A. Rotsch (*Brot u. Gebäck*, 1959, **13,** 165—168).—The mercaptan content of baked goods (from 4 to 20 μg. per 100 g.) depends on the protein content, the baking time and the baking temp., and is mainly concentrated in the crust. The mercaptan compounds contribute to the aroma of the baked goods, and with good packing survive storage for some days. Mercaptans were isolated from a thin watery suspension of the ground goods with a stream of N_2, collected in 5% Hg acetate solution, and estimated by the method of Slivinski and Doty (cf. J.S.F.A. Abstr., 1958, ii, 136). (10 references.)   E. C. APLING.

Baker's yeast. Svenska Jastfabriksaktiebolaget (B.P. 804,426, 25.10.55. Sw., 25.10.54).—A method for the production of baker's yeast, which minimises the number of washing stages, comprises subjecting a yeast concentrate to its principal wash in one or more stages on a rotary or other continuous filter (after having been previously dehydrated into cake form and having had a preparatory wash).   F. R. BASFORD.

Preparation from yeast of substance having antioxidant activity. Trustees of the University of Pennsylvania, Assees of M. Forbes, P. Gyoergy and F. Zilliken (B.P. 803,898, 10.8.56. U.S., 11.8.55.)—A suspension of yeast in 90—95% aq. EtOH is cooled (e.g., to 5°), then pptd. solid is filtered off. The filtrate is freed from solvent in vac., the residue is dissolved in MeOH, and the solution is cooled, with separation of more solid. The filtered liquor is evaporated, the residue is suspended in phosphate buffer, and after adjustment of the pH to ~7 the mixture is extracted with ether. Removal of solvent from the (clarified) extract leaves a product C 67·58, H 4·54, O 27·15% ; mol. wt. ~280 ; m.p. 118°, characterised by i.r. spectrum (quoted). The substance is a powerful antioxidant (e.g., in food products), and is also effective in preventing liver necrosis in animals   F. R. BASFORD.

Bleaching of bread. Research Ass. of British Flour Millers, T. Moran, J. Pace and E. E. McDermott (B.P. 804,914, 7.4.54).—A flour improver is obtained by extracting fat from flour (e.g., with ether, $CHCl_3$, etc.), oxidising the fat (either before or after extraction) by keeping in contact with a solvent (CCl_4 or light petroleum) in presence of light and air, then recovering the solute (e.g., by concentration). If desired, the flour may be pretreated with a flour improver (NCl_3 or ClO_2). The active fraction may be separated from the product by chromatography on Al_2O_3 and used at the rate of 300 p.p.m. in untreated flour to give good bleaching effect.   F. R. BASFORD.

Ready-to-eat food products. Kellogg Co. (B.P. 804,923, 24.2.56. U.S., 18.4.55).—A ready-to-eat composite palatable flaked food product comprises baked flakes of cooked particles of rice or maize having a coherent coating of relatively high-protein-content flour (15—30%) containing >50 (70—85) wt.-% of wheat gluten, the flour being uncooked prior to the baking step.   F. R. BASFORD.

Sugars and confectionery

Exchange capacity and flocculating activity of adsorbants in sugar cane juice. M. C. Bennett (*Chem. & Ind.*, 1959, 1380—1381).—The flocculating activity (10^7 particles/mg.) and exchange capacity for Ca (mequiv./100 g.) of a no. of adsorbants are : bentonite 46, 66 ; kieselghur 5, 16 ; fine bauxite 5, 5 ; calcined fine bauxite 3, 5 ; alumina 3, 2 ; charcoal 2, 7 ; " acid-activated " montmorillonite 2, 0—120 ; kaolin 2, 2 ; fuller's earth 1, 1 ; acid-washed charcoal 1, 17 and coarse bauxite 0, 1. These suggest that adhesion of juice particles to adsorbent particles takes place through the Ca^{2+} bound at the juice-particle surface by adsorbed protein. When the Ca requirement of the added adsorbant is already satisfied, no adhesion of juice particles can take place.   C. V.

Non-enzymic browning in commercial glucose syrups. R. Schachtel, J. B. S. Braverman and W. Groag (*Bull. Res. Counc. Israel*, 1959, **7C,** 37—50).—Factors affecting the colour of glucose

syrups on storing, e.g., the origin of the raw material, its protein content, the final pH of the syrup, and treatment with activated C are reviewed. (20 references.)   C. A. SLATER

Fermentation and Alcoholic Beverages

Rapid detection of sucrose in must and wine. L. T. Kováts and R. Kolta (*Period. polyt. Budapest*, 1959, **3,** 87—94).—A modified Raybin method is used. The sample is shaken with C, the filtrate made alkaline and diazouracil added for colour development, with further addition of $MgSO_4$. A content of ~1% may be detected. (In German.)   J. L. PROSSER.

Biological acid formation in unfermented and fermented fruit and grape juices. H. Lüthi and V. Vetsch (*Mitt. Lebensm. Hyg. Bern*, 1959, **50,** 264—275).—Addition of yeast extract to the culture medium increased the growth of *Lactobacillus* and *Leuconostoc* strains responsible for malic and lactic acid fermentation of wines. The growth-promoting substances have been isolated by ion-exchange chromatography and they seem to be simple N compounds, possibly of a peptide character. (10 references.)   M. H. SAWISTOWSKA.

Influence of various salt solutions and their concentration on steeping and germination of malt. K. Schuster and H. Eppinger (*Brauwissenschaft*, 1959, **12,** 191—196).—In general, the salts present in soft and moderately hard natural waters (in concn. $\ngtr 0·01N$) have no effect on water-absorption or germination, but nitrites, even in low concn. retard germination. Water-absorption is retarded with increasing concn. (0·05—0·1N) of salts, but this tendency is counteracted by the presence of pH-increasing anions or cations. Germination is, however, retarded by a shift to the alkaline range ; this observation is explained by the partial penetration of dissolved salts through lacunae in the testa. These findings are considered from the physico-chemical and physiological points of view. (54 references.)   P. S. ARUP.

Chemically induced water-sensitivity in barley seeds. G. Jansson (*Ark. Kem.*, 1959, **14,** 279—289).—Coumarin, acetic acid, benzoxazolone, *trans-o*-coumaric acid, phthalimidine and salicylic aldehyde induced water-sensitivity, i.e., failure to germinate in the presence of large amounts of moisture, in normal barley, while inorg. enzyme inhibitors ($HgCl_2$, NaN_3, KCN) did not. Coumarin and acetic acid differed in their inhibitory action. Thus, pretreatment with $HgCl_2$ of barley treated with coumarin or acetic acid removed or accentuated the inhibition respectively. Cysteine or ferrous ions eliminated coumarin-induced inhibition but were without effect on acetic acid-induced inhibition. Peeling of the grains reversed inhibition by coumarin and acetic acid, a similar response being shown by water-sensitive barley. Probably a film of water which would otherwise prevent sufficient amounts of O_2 reaching the inhibitor-destroying enzyme is not formed. (24 references.) (In English.)   A. G. COOPER.

Barley and malt. XV. Growth substances and other compounds in relation to dormancy in barley. J. R. A. Pollock (*J. Inst. Brew.*, 1959, **65,** 334—337).—The germination of dormant barley is stimulated, under defined conditions, by 6-furfurylaminopurine (kinetin) and its analogues and by gibberellic acid. These facts are discussed in relation to the activity of H_2S and the factors concerned in dormancy. (13 references.)   C. A. SLATER.

Evaluation of diastatic activity in brewing malts. L. Weith (*Mschr. Brauerei wissen. Beil.*, 1959, **12,** 166—170).—Present-day knowledge of the formation of amylases during germination and its significance in the mashing process is summarised ; the α-amylase formed during malting is the governing factor for the diastatic quality of malts. Methods for determining diastatic activity by the Windisch–Kolbach and other procedures are discussed and criticised. It is recommended that one of the approved methods for measurement of α-amylase should supersede the Windisch–Kolbach method in the EBC-Analytica.   S. M. MARSH.

Comparison of starches from barley and malted barley. C. T. Greenwood and J. Thomson (*J. Inst. Brew.*, 1959, **65,** 346—353).—Malted-barley starch has a higher gelatinisation temp. and smaller granules than that from the original barley. The general properties of the components from malted-barley starch can be accounted for by assuming limited β-amylolysis of the amylopectin and very limited α-amylolysis of the amylose in the original barley starch. (20 references.)   C. A. SLATER.

Structure of cell wall and mechanism of flocculation of bottom yeasts. C. A. Masschelein (*Rev. Ferment.*, 1959, **14,** 87—112).—A flocculation effect (reversible on washing with water) is observed when suspensions of the isolated cell walls of a flocculating bottom yeast are treated with dil. solutions of Ca^{2+}. The effect depends directly on the concn. of Ca^{2+} and of the cell walls. This effect is

not observed for the cell walls of non-flocculating yeasts. Hydrolysates of the proteins of the cell walls contain $\not< 12$ amino-acids, chiefly serine, threonine and alanine. An inverse relationship is found between the mannosan content of the mannosan–protein complex (constituting the outer membrane of the cell wall) and the flocculating capacity. A bacterium has been isolated from air which forms an extracellular enzyme capable of decomposing the cell walls. An electron-microscopic study of the progress of the enzymic hydrolysis reveals the presence of two membranes. Flocculation probably depends on an intracellular hydrolysing mechanism in the mannosan–protein (outer) membrane which exposes mol. groupings capable of forming loose complexes with Ca^{2+}. (71 references.)   P. S. ARUP.

Dhar yeast. II. Effect of inorganic ions on growth. S. P. Mitra and N. K. Garg (*J. Inst. Brew.*, 1959, **65**, 342—346).—For good growth of Dhar yeast it is necessary to provide adequate concn. of K and Mg with traces of Cu, B and Zn. The presence of V, Hg and Co must be rigorously avoided. (30 references.)   C. A. SLATER.

Flagella-staining acid bacteria. J. L. Shimwell (*J. Inst. Brew.*, 1959, **65**, 340—341).—A modification of the Fisher and Conn staining technique has made it possible to demonstrate the peritrichous flagellation of motile *Acetobacter* strains and the polar flagellation of motile *Acetomonas* strains.   C. A. SLATER.

Participation of acetic acid in biosynthesis in beer yeasts. S. S. Rȳlkin and N. V. Pokrovskaya (*Mikrobiologiya*, 1959, **28**, 586—593).—Radioactive acetic acid, $CH_3{}^{14}COOH$, was used in fermentations of *Saccharomyces carlsbergensis* yeasts. At 0·164% acetic acid concn. the label was detected in all components of the yeast cell. The max. amount was present in the lipid fraction extracted with acetone from the hydrolysed yeasts : 80% of this fraction was formed from the acetic acid. In yeast hydrolysate three amino-acids accounted for 84% of the total activity : glutamic acid 56, proline 15·7 and ornithine 11·4%. Acetic acid was utilised by a biosynthetic process, rather than adsorbed by the yeast cells.   L. GROCHOWSKI.

Occurrence of pentoses in worts and beers. V. Arkima and P. Rintala (*Brauwissenschaft*, 1959, **12**, 182—183).—A column-chromatographic separation followed by a paper-chromatographic resolution reveals the presence of arabinose and xylose in wort, and of arabinose, xylose and ribose in the corresponding beer.   P. S. ARUP.

Rôle of trace metals in brewing. J. R. Hudson (*J. Inst. Brew.*, 1959, **65**, 321—330).—A review. (77 references.)   C. A. SLATER.

Non-biological hazes of beers. VIII. Rapid estimation of anthocyanogens in beer. G. Harris and R. W. Ricketts (*J. Inst. Brew.*, 1959, **65**, 331—333).—A method for estimating anthocyanogens in beer is presented. The anthocyanogens are adsorbed on nylon and then converted to anthocyanidins and estimated colorimetrically.   C. A. SLATER.

Amino-acid composition of some cold-trubs [of beer]. G. Biserte, R. Scriban and M. T. Pocqué (*Brasserie*, 1959, **14**, 248—250).—The influence of conditions of formation on composition of four samples of trub is examined.   P. S. ARUP.

Simplified method for measuring head retention [of beer]. W. M. Brenner, J. Siebenberg and F. Zientara (*Amer. Brewer*, 1958, **91**, 42—44 ; *Brauwissenschaft*, 1959, **12**, 183—184).—A previously described device is used for sampling the beer (at 25°) from the bottom of the bottle. The sample is forced under an excess pressure of 2 atm. through a foam-nozzle, and sufficient foam is collected to fill a 200-ml. measuring cylinder. The vol. of liquid beer formed after standing during 90 sec. (V_1) and the total vol. formed after complete destruction of the foam by Pr^iOH (V_2) are determined. A foam value is calculated from the ratio $(V_2 - V_1)/V_2$. Good reproducibility is claimed.   P. S. ARUP.

Electronic measurement of oxygen dissolved in beer. G. Silbereisen and C. Weymar (*Mschr. Brauerei wissen. Beil.*, 1959, **12**, 155—161).—Various methods (especially electrochemical) for the determination of O_2 in beer are discussed. Modified Tödt apparatus was used with various electrode combinations and types of electrode. The method compared advantageously with colorimetric and volumetric procedures for accurate quant. work. An apparatus for the industrial continuous determination of O_2 in beer is described. Conditions required are temp. control, constant stirring, regular replacement of electrodes and exact calibration and therefore experienced analytical control.   S. M. MARSH.

Brewing of beer. Ultra-Technik G.m.b.H (Inventor : J. Speight) (B.P. 803,073, 13.5.55).—In the brewing of beer, the protein formed during the boiling of the malt liquor is coagulated and thereby rendered more readily filterable, by subjecting the boiling liquor to ultrasonic vibrations derived from a piezoelectric transducer operating at 2000—3000 W.   F. R. BASFORD.

Fruits, Vegetables, etc.

Green mould of prunes. *Aspergillus mangini* : **nutritive requirements and conditions for growth.** M. Moreau (*Fruits d'outre Mer*, 1959, **14**, 315—328).—Plums infected by *Monilia* before drying show white marks after drying, but are then sterile, and comparatively resistant to infection by green mould. In conditions of high humidity, prunes of high moisture content may be attacked by common fungi such as *Rhizopus nigricans*, *Aspergillus niger* and *Penicillium crustaceum*, but the characteristic organism infecting properly dried prunes is *Aspergillus mangini* Thom & Raper. This organism grows in sucrose solutions of such high concn. that spontaneous crystallisation occurs ; it is less tolerant to high concn. of glucose. Growth on prunes depends on the R.H. of the fruit and the surrounding air, and on the temp. The fruit cannot be dried enough to prevent the growth of the fungus without spoiling its organoleptic properties ; lowering the atm. humidity also causes excessive dehydration of the fruit. Because of the difficulty of sterilising, infected prunes should be removed from the drying tunnel directly to low-temp. storage at controlled humidity. (11 references.)   M. D. ANDERSON.

Vitamin C potency and the food value of the guava. M. K. R. Siddiqui and M. A. Faroqui (*Pakist. J. Sci. Res.*, 1959, **11**, 29—32).—The guava compared with 14 other fruits possesses a high cal. value (54—66 cal./100 g.) ; niacin 1·2 mg./100 g. of expressed pulp and vitamin C 229 mg./100 g. of fresh fruit. On the basis of this comparison the value of the guava is stressed.   C. V.

Preparation of pectin from raw papaya (*Carica papaya*) by aluminium chloride precipitation. B. S. Bhatia, G. V. Krishnamurthi and Girdhari Lal (*Food Sci., Mysore*, 1959, **8**, 314).—The method is described.   S. G. AYERST.

Pectin and pectin-like products : Pectin, gelatin, their resources and utilisation. I. N. A. Khan, M. Yunus, H. Rahman and M. Q. Khuda (*Pakist. J. Sci. Res.*, 1959, **11**, 5—8).—Waste products of the citrus fruits, especially the peels of pomelo, lemon and mandarin, were used in prep. of fruit jellies, jams and marmalades as well as citric and ascorbic acids, pectin and gelatin. (18 references.)   C. V.

Polarographic determination of vitamin C in fresh vegetables and fruit. S. Krauze and Z. Bozyk (*Mitt. Lebensm. Hyg., Bern*, 1959, **50**, 228—242).—Influence of pH, nature of extracting medium and temp. of extraction on polarographic determination of vitamin C in some vegetables and fruit was investigated. Optimum conditions are given. H_2S is suggested as the best reducing agent for dehydroascorbic acid. According to the polarographic results, there was no dehydroascorbic acid in the fruit and vegetables investigated. (28 references.)   M. H. SAWISTOWSKA.

Formation of pyrrolidonecarboxylic acid in processed fruit and vegetable products. I. A. A. Mahdi, A. C. Rice and K. G. Weckel (*J. agric. Fd Chem.*, 1959, **7**, 712—714).—Pyrrolidonecarboxylic acid (PCA) is formed in some fruits and vegetables on heating. It contributes to off-flavour in purées of beetroot, and possibly in other foods. PCA and its possible precursors, glutamine and glutamic acid, were determined by partition chromatography in some fruits and vegetables before and after heat processing, and during storage for 2 years of the canned products. Before sterilisation, PCA was present only in beets, cherries and tomato juice, each of which had already undergone mild heat treatment (steaming of beets and cherries, hot-break procedure with tomatoes). In low-acid foods, processed at high temp., PCA increased during processing to an extent related to the amount of glutamine present, all of which was decomposed ; after processing, PCA remained more or less constant. In high-acid foods, processed at lower temp., only part of the glutamine present was converted to PCA during processing ; the remainder was converted during storage, at a rate increasing with storage temp. Sweet maize and lima beans contained no PCA or glutamine throughout processing and storage. Glutamic acid did not contribute to PCA. (17 references.)   M. D. ANDERSON.

The influence of storage on the moisture content and weight of packed legumes. C. Bergel (*Dtsch. LebensmittRdsch.*, 1959, **55**, 197—200).—Moisture changes in packed peas, beans and lentils during storage under various conditions of temp. and humidity over a period of seven months are reported in tabular form. The best conditions for moisture and wt. stability are temp. from 5 to 10° and R.H. of 70—80%.   E. C. APLING.

Chemical examination of *Allium cepa* L. [onion]. I. Glycosidic and sugar fractions. A. Sinha (*Indian J. appl. Chem.*, 1959, **22**, 89—91).

—Oleanolic acid has been detected in the glycoside fraction. The sol. carbohydrate fraction comprises arabinose, rhamnose, xylose and ribose.   O. M. WHITTON.

Interactions between copper ions and sweet-potato polyphenolase-oxidised substrates. J. C. Arthur, jun. and T. A. McLemore (*J. agric. Fd Chem.*, 1959, **7**, 714—716).—The formation of Cu complexes with sweet-potato polyphenolase and oxidised catechol was determined, using ^{64}Cu, and an ion-exchange method. Increase in concn. of enzyme or Cu^{2+}, or increase in oxidation time, increased the apparent amount of Cu^{2+} complexed and/or exchanged. Amount of Cu^{2+} reacting was greater with catechol as substrate than with quinol, or quinol + a trace of catechol. (10 references.)   M. D. ANDERSON.

Determination of inulin in chicory roots. W. Wöhlert and U. Freimuth (*Z. LebensmittUntersuch.*, 1959, **110**, 371—375).—Current methods are criticised. The inulin contained in aq. extracts of the roots is completely purified by a simple paper-chromatographic technique in which all the accompanying substances show R_F values, whilst the inulin remains immobile. The inulin is determined colorimetrically by the anthrone–H$_2$SO$_4$ reaction in an eluate of a square of the chromatographic paper including the starting point. The time required for development is 1—5 days, depending on the content of slowly-moving higher inulides. The average error on the mean of 20 determinations is ±0·1%. (12 references.)   P. S. ARUP.

Non-alcoholic beverages

Fruit juice concentrates. *Int. Fed. Fruit Juice Producers' Symp., Bristol*, 1958, 413 pp. **Technical aspects of the production of concentrated fruit juices.** J. Royo-Iranzo, 13—39.—The processing of citrus, apple, grape and tomato juices is described together with methods of treating the fruit prior to concentration. The techniques of vac. drying, freezing, atomisation and lyophilisation are covered for obtaining both the conc. liquid and dry powdered products, with particular reference to recovery of the volatile aroma during vac. concn. (34 references.) (In English.)

New type of concentrator. P. Dupaigne, 41—50.—A pilot scale vac. evaporator is described in which the juice is dispersed by sonic vibrations. By operating at 6000—7500 impulses per min. and at a temp. of 32°, as much as 27 l./hr. of water could be removed from the juice. (In French.)

Continuous vacuum evaporator. M. Koffler, 51—55.—This is designed so that the area of the heating surface is progressively reduced as the juice concn. increases. (In English.)

Developments in fruit-juice concentration in Jugoslavia. D. Šulc, 57—67.—The factors involved in producing high quality fruit juice concentrates by a continuous process are discussed with particular reference to pre-treatment of the whole fruit. These considerations have resulted in a new plant design for flavour recovery and a new type of thin film evaporator. (In German.)

Time, temperature and concentration of apple juice. M. de Witte, 69—77.—The rapid thermal concentration of apple juice in the Unipectine evaporator effects the removal of 1100 gal. of water/hr. without recirculation. A short contact time of 32 sec. is partly facilitated by a final circulation speed of approx. 360 ft./sec. Ageing tests show that browning is reduced at low temp. (In French.)

Solute content of liquid phase of partially frozen fruit juices. R. Gane, 79—85.—The separation of water from partially frozen apple, plum, strawberry and blackcurrant juices by hydroextractor was examined. From a study of the variation of f.p. with juice concn., the temp. for a required juice strength may be predicted. (Gane, *Food Manuf.*, 1948, **23**, 282—287.) (In English.)

Technical and economic aspects of choice of evaporator design. F. Emch, 87—112.—The question of cleaning, disinfection, etc., should be considered as well as the type of process used. Full data on the characteristics of different evaporator designs are given together with the economics for producing 44 and 77° Brix concentrates based on pilot plant studies. (30 references.) (In German.)

Combination of freezing and thin-film techniques for citrus concentrates. C. Schneider, 113—124.—After a brief description of the techniques, it was concluded that, in general, very little difference exists economically between them. The various possibilities of combining the two methods are discussed. (In German.)

Chemistry of fruit juice concentrates. W. Büchi, 125—144.—Non-enzymic reactions such as sucrose inversion occur more rapidly in fruit juice concentrates than in the original juice. The browning reaction of sugars, polyphenols etc. and the chemical changes which result with amino-acids and proteins are reviewed with particular reference to apple juice. (64 references.) (In German.)

Non-enzymic browning of glucose syrups and citrus concentrates. J. B. S. Braverman, 145—158.—Colorimetric and u.v. measurements were made under varying conditions of pH, protein and phosphate contents. Browning was a min. at pH 3 and depended on the

amount of protein present. Rapid formation of hydroxymethyl-furfural occurs at pH 1, the rate of increase falling off with a rise in pH. In citrus concentrates, SO$_2$ strongly inhibits the Maillard reaction and appears to affect the amino-acid–ascorbic acid system. (In English.)

Rôle of ascorbic acid in the browning phenomenon of fruit juices. J. C. Bauernfeind, 159—185.—The addition of 5—50 mg./100 ml. L-ascorbic acid (in particular to apple juices) delays enzymic browning by preventing conversion of the naturally occurring flavonoids to the quinone form. In closed containers it will also inhibit the oxidation of the natural colour and flavour components. Laboratory, pilot plant and commercial tests show that the quality of clarified juices of apple, grape, etc., can be substantially improved and their storage life prolonged. (57 references.) (In English.)

Browning of concentrated fruit juices: microbiological considerations. M. Ingram, 187—201.—Although heat treated concentrates cannot normally be fermented by yeasts, other factors such as N status and antimicrobial substances may be involved. Oxidation-reduction changes were not considered responsible. Fermentation studies on preheated juices showed that failure of yeasts to develop in browned orange concentrate was caused by lack of essential N-compounds (e.g. ammonium salts). With apple concentrates, inhibition was attributed to oxidation of leuco-anthocyanins and other phenols to coloured quinonoid compounds having antimicrobial properties. (15 references.) (In English.)

Cloud stability of citrus concentrates. W. Pilnik, 203—228.—The theory and causes of cloud loss are reviewed with special reference to de-esterification by pectin esterase (PE). Stabilisation by means of (1) high solid content (1 : 6 concentrates), (2) addition of Ca-chelating agents (e.g., polyphosphates, EDTA, etc.), and (3) use of PE inhibitors of the surfactant type, is discussed. (88 references.) (In German.)

Chemical alteration of fruit juice concentrates during storage at various temperatures. A. Grob, 229—243.—Apple and pear juice concentrates (of known origin and process) were stored at 0°, 10° and 20°. Analyses, over three years at one-yearly intervals, were carried out for pH, °Be′, n, η, sugars, N, tannin, acidity, etc. Changes which occurred included sucrose inversion, decrease in acidity (max. of 10% after three years at 20°), η decrease (nearly independent of temp. and concn.), CH$_2$O-tannin decrease and a greater browning and solid pptn. (In German.)

Albumin in fruit juices, its dependence on ripeness and basic technical precautions. J. Koch, 245—257.—The proteins of various grape juices have been isolated by (NH$_4$)$_2$SO$_4$ and separated (paper electrophoresis) into five albumin fractions. From the three main fractions, twelve amino-acids were identified. The effect of climate and processing on the properties and content of protein in grape juice was studied. (In German.)

Phenolics of fruit juices. A. H. Williams, 259—263.—Phenolics (tannins) identified in apples and perry pears are briefly described with special reference to cider apples. Chlorogenic acid (principal) is accompanied by p-coumaryl quinic acid, three quercetin glucosides (near skin), phloridzin (trace in pips) and idaein (in skin) as well as catechins and leuco-anthocyanins in varying amounts. Total phenolics may exceed 1% in apples, according to variety. Pears can contain more than 1% leuco-anthocyanin which is largely responsible for clots in perry juices. (In English.)

Carotenoids in fruits, juices and concentrates. J. C. Bauernfeind, 265—290.—A review on the chemistry of natural fruit pigments and the use of commercial β-carotene for colour juices and concentrates. (36 references.) (In English.)

Metal complexes in fruit juices. C. F. Timberlake, 291—301.—In a review of the structure and formation of Cu and Fe complexes with org. acids, amino-acids, proteins and phenolics under various conditions of pH, ionisation constant, etc., their effect on general juice stability is considered. (22 references.) (In English.)

Recent progress in recovery of aromas of fruit and vegetables. P. Dupaigne, 303—317.—The chemical composition of the volatile aroma of apples, grapes, oranges and strawberries is reviewed together with equipment for aroma recovery. Methods for the fixation of flavours on sugars are also covered. (39 references.) (In French.)

Estimation of fruit juice concentrate extracts : refractometric methods. W. Büchi and F. Ullmann, 319—335.—Experiments with aq. solutions of sucrose, glucose, fructose and juice concentrates show that vol. contraction is greater with the last named than with sucrose. Refractometric and pycnometric estimations of solids should thus not be made on the diluted concentrates. Discrepancies between the two methods is attributed to the action of org. acids. Coeff. of variation for solids (calculated by empirical methods) depend on acid value and may be used for correcting such discrepancies. (25 references.) (In German.)

Micro-organisms in frozen concentrated orange juice. E. R. Wolford, 337—350.—Current methods for their determination and

detection are reviewed with a discussion on off-flavour spoilage and the relationship of contamination to public health. (36 references.) (In English.)

Fermentation of diluted concentrates. A. Pollard, 351—360.— During normal commercial cider production the pectin enzymes may be derived from contamination of fruit, the fruit itself or micro-organisms present during fermentation. Experiments have established that pectin breakdown is caused by combined pectin methyl-esterase in the fruit and a polygalacturonase produced by fermentation yeast. Diluted concentrates or flash-pasteurised juices may not contain one or both of these enzymes and thus cider from this source may still contain pectins. The addition of pectin enzymes is, therefore, recommended. (18 references.) (In English.)

Surface fermentation of sugar-rich concentrates. M. Ingram, 361—372.—Controlled laboratory experiments on artificial cultures have been made (aerations, sugar concn. and sp. gr. of the cells) and an explanation of the cause of this phenomenon is advanced. Dilution of the surface layer by atm. moisture facilitates yeast growth, which in turn reduces the density by sugar uptake thus producing an equilibrium of steep concentration gradient. Sugar-tolerant yeast cells are less dense than the supporting medium and, above approx. 500 g. sugar/l., they float to the surface. Although aeration is important in accelerating initial fermentation, growth can occur anaerobically. (In English.)

Microbiology of apple juices (yeasts). F. W. Beech, 373—382.— Yeast flora from the juice and fruit of Kingston Black cider apples have been examined in relation to the fermentation problems of low acid varieties in S.W. England. The yeasts (over 20 types) were grown anaerobically on apple juice/yeast extract/agar at pH 4·8 at 25° for seven days, followed by four days' aerobic incubation. Moulds were inhibited with diphenyl, and bacteria with an actinomycin/Aureomycin mixture. Mainly asporogenous yeasts were found in cores and skin but *Saccharomyces uvarum* and *Hansenula* spp. were also isolated from the latter. Examination of sulphited press juice showed the presence of *S. uvarum* almost to the end of fermentation. Effects of pH and SO_2 on the extent of lactic acid bacterial development were studied. During fermentation of sulphited juices (pH 3·4—4·0) malic acid is rapidly synthesised by the yeasts. (15 references.) (In English.)

Fate of acetic acid bacteria in fermenting cider. J. G. Carr, 383—390.—In laboratory fermentation (aerobic and anaerobic) of Yarlington Mill apple juice, the bacteria reached their highest peak before yeast activity had fully started (by relative counts at seven-day intervals on differential media). This was followed by a second smaller bacterial growth peak after fermentation had ceased. Activity was generally more vigorous in the aerobic fermentation. A study of the growth of five individual bacterial spp. showed that *Acetomonas suboxydans* died out, during fermentation, to be replaced by *Acetobacter xylinum* and *A. rancens*. (In English.)

Causes of incomplete fermentations of browned fruit-juice concentrates. H. Lüthi, 391—401.—The storage breakdown of amino-acids and vitamins as well as the presence of hydroxymethyl furfural in concentrates is attributed to be the main cause of poor fermentation of the rediluted juice. Paper chromatographic analysis (nine amino-acids) shows a rapid disappearance of glutamic acid followed by asparagine and serine. Calcium pantothenate, thiamine and pyridoxine were likewise attacked first (microbiological identification). These inhibitory factors may be counteracted by a salt of known composition. (10 references.) (In German.)

Determination of mould count in tomato puree. K. Vas, 403—413.—An investigation into variables associated with Howard's mould count method (A.O.A.C. Methods of Analysis, 1955) has been made with particular reference to the puree concentration, staining technique, optical magnification and field diameter. A new permanent mould count slide is also described, enabling counts to be made long after sampling. (12 references.) (In English.)

P. M. KINGSTON.

Rapid determination of benzoic acid in soft drinks. E. English (*Analyst*, 1959, **84**, 465—466).—The sample is diluted to give an expected concn. of ≃4 p.p.m. of benzoic acid and is filtered with rejection of the first portion of filtrate. The extinction (x) of the subsequent portion is measured at 230 mμ. A blank measurement (y) is made with a prepared sample of the drink containing a known concn. (a) of benzoic acid. The concn. in the sample is then ax/y. The use of the reference standard prepared as described is essential because the unpreserved product, as well as having a characteristic extinction of its own at 230 mμ, has an influence on the extinction of benzoic acid.

A. O. JONES.

Analysis of soft drinks following recent Italian regulations. A. Canuti and F. Salvadori (*Chim. e Industr.*, 1959, **41**, 891—895).— Recent Italian legislation on production, trade, and sale of soft drinks, and relevant methods of analysis are discussed. Besides conventional methods of determination of residue, density and

N-containing materials, electrometric methods are suggested for determination of Cl⁻, acidity, " formol number " and chromatographic methods for the qual. detection and for a semi-quant. determination of amino-acids and sugars. Experimental data are reported from analyses of genuine fruit-juices, orange pastes, and orange-soda beverages. (27 references.)

C. A. FINCH.

Tea, coffee, cocoa

Chromatographic detection of opium in tea and other foods. P. N. Sengupta, S. N. Mitra and B. R. Roy (*J. Instn Chem. India*, 1959, **31**, 124—125).—Opium may be detected in foods by circular paper chromatography using an eluent consisting of butanol-ethanol-acetic acid and water. The opium is developed with a solution of platinic chloride and KI.

C. A. SLATER.

Milk, Dairy Products, Eggs

Dependence of oxidation–reduction potential of milk on its vitamin C content. J. J. R. Campbell, R. H. Phelps and L. B. Keur (*J. Milk. Tech.*, 1959, **22**, 346—347).—Raw milk from 30 cows examined showed an inverse relationship between the oxidation–reduction potential (**I**) and the vitamin C (**II**) content ; this held for both fresh and 5-day-old refrigerated milk. Restoration of **II** in stored milk returned the **I** value to the original level ; this indicated that the decrease in **II** content largely accounted for the change in **I**. The milk from certain cows showed an abnormally rapid **II** loss and this was accounted for by a high Cu value although no explanation was forthcoming as to the presence of this element.

C. V.

Electrophoretic examination of proteins of raw, pasteurised and sterilised milk. C. Ambrosino, E. Ghiosso, J. Liberatori and R. Tentoni (*Ric. sci.*, 1959, **29**, 1649—1657).—The electrophoretic pattern of the serum of milk pasteurised at either 73° for 15 sec. or 80° for 4 sec. was similar to that of raw milk, indicating no appreciable modification of electrokinetic characteristics. On the other hand, the serum of milk sterilised at 135° for 6 to 7 sec., followed by 117 to 118° for 15 min., showed the presence of a large new homogeneous component of low anodic mobility. Storage of the sterilised milk for 87 days either in light or dark did not appreciably affect this component but its concn. varied from sample to sample. (34 references.)

L. A. O'NEILL.

Effects of feeding low levels of insecticide residues on hay to dairy cattle on flavour and residues in milk. G. G. Gyrisco, L. B. Norton, G. W. Trimberger, R. F. Holland, P. J. McEnerney and A. A. Muka (*J. agric. Fd Chem.*, 1959, **7**, 707—711).—Hay containing up to 10 p.p.m. of aldrin, lindane, DDT, parathion or methoxychlor was fed to cows for periods up to 3 months. No parathion or methoxychlor was found in any sample of milk. No lindane was detected in milk in an experiment in 1950—51 ; in one in 1951—52, the mean content of lindane for all sampling dates was significantly greater than that for the control, but that for any single sampling date was not. Small amounts of DDT and aldrin were present in the milk after cows had received 10 p.p.m. of either for 1 month ; none was found in the milk when the dose was 2 to 4 p.p.m. No effect was noted on the health of the cows, or on their organs after slaughter, and the milks had no off-flavours or off-odours attributable to insecticide. (23 references.)

M. D. ANDERSON.

Problems created by the presence of antibiotics in milk and milk products. E. H. Marth and B. E. Ellickson (*J. Milk Tech.*, 1959, **22**, 266—272).—A review. The concn. of penicillin required to inhibit the growth of various pure and mixed cultures (51) is tabulated and the results are discussed ; chlortetracycline (28), streptomycin (7) and six other antibiotics (11) are similarly examined using the indicated number of organisms. (51 references.) C. V.

Rapid disc assay method for detecting penicillin in milk. B. Arret and A. Kirshbaum (*J. Milk Tech.*, 1959, **22**, 329—331).— Penicillin can be detected in concn. as low as 0·05 unit per ml. The test organism used is *Bacillus subtilis* ATCC 6633. (12 references.)

C. V.

Nutritive-physiological changes during manufacture of skimmed milk powder by yoghurt fermentation. H. Fink, U. Ruge and I. Benda (*Fette Seif. Anstrichm.*, 1959, **61**, 911—912).—The occurrence of liver necrosis in experimental animals fed skimmed milk powder may be caused by the partial decomposition or inactivation of essential amino-acids during the drying process. Determination of amino-acids after hydrolysis shows that such acids are unaffected during drying ; further, no amino-acid blockage occurs which cannot be subsequently released by enzymic action.

G. R. WHALLEY.

[Nutritive value of] milk powder and the drying of milk. H. Fink, I. Schlie and U. Ruge (*Milchwissenschaft*, 1959, **14**, 572—578).— Roller dried (**I**) (49) and spray dried (**II**) (11) samples were examined ;

these originated from five plants and 123 fresh bulk skim milk samples were used as controls. With young albino rats (860) over a 120-day period it was found that a 76% death rate from hepatic necrosis occurred with **I** and 40% with **II**. Controls showed no change.   C. V.

Analysis of milk and dairy products. Comparative study on detection of coli-aerogenes in milk and dairy products. K. Schätzel (*Milchwissenschaft*, 1959, **14**, 530—540, 584—593).—A general survey of methods employed. (78 references.)   C. V.

Occurrence and prevention of salmonella in milk and dairy products. O. Roemmele (*Milchwissenschaft*, 1959, **14**, 569—572).—A brief review. (15 references.)   C. V.

The stabilisation of ice cream and ice lollies. J. L. Boyle (*Food Technol. Aust.*, 1959, **11**, 543—551).—Explanations of the mode of action of stabilisers are discussed; probably they act by forming H bonds with water mol., thus reducing the amount of water available to form ice crystals. Factors which affect the texture of ice cream and should be closely controlled are, the temp. and length of freezing, the type and amount of stabiliser, and the η of the mix. The requirements for stabilisers for ice lollies are slightly different from those for ice cream.   S. G. AYERST.

Butter colour: oxidative alteration. L. Wurziger (*Milchwissenschaft*, 1959, **14**, 565—569).—Light and air affect coloration as measured by extinction and the quotient (**I**) was measured at different wavelengths. Using filters S47E and S49, with an Elko-11 unit, additional information was obtained. Fresh butter under ideal conditions gave a **I** value of 1·28 while an approach to 1·33 indicated that deterioration had already commenced.   C. V.

Staphylococcal food intoxication due to cheddar cheese. I. Epidemiology. S. L. Hendricks, R. A. Belknap and W. J. Hausler, jun. (*J. Milk Tech.*, 1959, **22**, 313—317).—A literature review. (21 references.)   C. V.

New one-flow evaporator for the continuous production of " brown cheese " (Norwegian whey cheese) and for whey evaporated feedstuffs. R. Hansen (*Milchwissenschaft*, 1959, **14**, 581—584).—Preconcentrated whey with 45—80% solids at 55—63° is used. The unit has a capacity of 500 kg./hr. with a flow rate of 80 m./sec., the product being then filled into moulds. The solidified blocks can be stored over long periods.   C. V.

Manufacture of cheese, etc. Fisons Milk Products Ltd. (Inventors : B. Reiter and M. L. Scott) (B.P. 804,647, 13.6.55).—In the production of cheese by fermentation of milk, viz., in presence of *Streptococcus cremoris* or *S. lactis*, failure of the latter to work is minimised by reducing the C^{11} content of the milk, e.g., to <20 p.p.m. This is attained by treating the milk with ion-exchange material (weakly acidic cation-exchange resin, e.g., Zeo-karb 226). Preferably the resin is so buffered that the pH of the treated milk is ~7 ; also, the treated milk is then admixed with bacterial nutrients and/or sequestering agents of C^{11}, e.g., the Na_2 salt of EDTA.   F.R . BASFORD.

Egg products. E. Strauss (Inventor : W. P. G. Seck) (B.P 803,071, 22.10.53).—Fresh, preserved or dried whole egg or egg yolk is extracted at ⊁50° with a fat solvent (ether or light petroleum) containing up to 5% of water, then the extract is removed, to leave an egg product which can be whipped up into a foam and also has the ability to emulsify and coagulate.   F. R. BASFORD.

Edible Oils and Fats

Urea complexes : Preparation of fatty acids and esters from cottonseed oil. N. A. Khan (*Pakist. J. Sci. Res.*, 1959, **11**, 9—12).—The isolation of stearolic acid by means of these is discussed. (24 references.)   C. V.

Taste reversion of soya-bean oil. H. von Pezold (*Fette Seif. Anstrichm.*, 1959, **61**, 1018—1024).—Soya-bean oil which contains fatty acids with >2 double bonds can undergo flavour reversion before true autoxidation occurs ; this is attributed to the formation of 2,4-heptadienal and/or -octadienal from the autoxidation of linolenic acid. Such primary oxidation products are easily decomposed further, and could cause flavour and colour reversion. (13 references.)   G. R. WHALLEY.

Effect of antioxidants and metal inactivators in tocopherol-free soya-bean oil. E. N. Frankel, P. M. Cooney, H. A. Moser, J. C. Cowan and C. D. Evans (*Fette Seif. Anstrichm.*, 1959, **61**, 1036—1039).—Soya-bean oil is partially or completely freed from natural tocopherols by treatment in light petroleum with a 1 : 1 mixture of C black and Celite. Marked increase in stability is observed with

tocopherol removal, with an optimum concn. of 400—600 μg./g. of oil. Flavour of partially stripped oil differed little from that of the control after storage for 4 days at 60°. Addition of Fe to C-treated oils caused an increase in oxidative deterioration, but addition of citric acid (e.g., 0·01%) markedly improved the stability of all oils ; the partially tocopherol-stripped oils were the more stable. (18 references.) (In English.)   G. R. WHALLEY.

Autoxidation of emulsified fats. M. Loncin, D. Jacqmain, J. Labarrère and J. Lefèbvre (*Fette Seif. Anstrichm.*, 1959, **61**, 1055—1058).—It is shown, by experiments with emulsions containing maize oils, that the rate of autoxidation (as measured by peroxide value) is considerably influenced by the heavy metal content (especially Cu) of the oil phase. By complexing the Cu with alanine or glycine, it can be readily transferred to the aq. phase, when oil deterioration is considerably reduced. Application of alanine allows the storage life of dried milk to be increased by 3—4 times; treated butter does not show a marked increase in stability. (18 references.)   G. R. WHALLEY.

Identifying additions of rectified oils to expressed olive oils. A. Fabris and M. Vitagliano (*Olii min.*, 1959, **36**, 313—324).—Expressed olive oils are practically free of conjugated triene compounds, although in a few cases small amounts have been found. Rectified oils A and B contain significant amounts of conjugated trienes, which appear to be formed mainly in the treatment with bleaching earth, and additions of 5 or 10% of the rectified oils to virgin olive oils may readily be detected spectroscopically. Conditions leading to the formation of conjugated triene compounds in the oils have been studied. (30 references.)   L. A. O'Neill.

Use of ultra-violet spectrophotometry for evaluation and identification of olive oils. A. Uzzan (*Olii min.*, 1959, **36**, 307—311).—The characterisation of olive oil by means of the sp. extinction coeff. at 232 and 270 mμ (K_{232} and K_{270}) is considered. Results for oils of various origin are shown in terms of the values of K_{270} and the ratio K_{232}/K_{270} (R). It is proposed that oils be classified into best and good qualities according as the values of K_{270}, R and % acidity are respectively : <0·16, <0·20 ; >10, >9 ; <1, <2.   L. A. O'NEILL.

Spectrophotometry in analysis of olive oil. II. Ultra-violet spectrophotometry for classification. A. Montefredine and L. Laporta (*Olii min.*, 1959, **36**, 325—326).—The classification of olive oils in terms of the sp. extinction coeff. (K) at 232 and 270 mμ is suggested. Typical figures for K_{232} and K_{270} for virgin olive oil, rectified A and rectified B oils are respectively : 3·0, 0·2 ; 4·0, 0·6 to 0·8 ; >4, 2·0.   L. A. O'NEILL.

Ultra-violet spectrophotometry for recognition of olive oil. V. Morani and C. Marignoli Colloca (*Olii min.*, 1959, **36**, 327—328).—Virgin olive oil may be clearly differentiated from rectified oils A or B from the sp. extinction coeff. (K) at 262, 268 and 274 mμ. Expressing the values in terms of ΔK, which is 1000 [K_{268} − 0·5(K_{262} + K_{274})], pure olive oils have a ΔK of <5, rectified A oils of ~50, and rectified B oils of >100. (12 references.)   L. A. O'NEILL.

Possibility of detecting esterified oils by infra-red spectrophotometry. F. Provvedi (*Olii min.*, 1959, **36**, 375—376).—Comparison of i.r. spectra of a virgin olive oil and an esterified oil showed the presence in the latter of distinct peaks in the 2·5—3 and the 10—10·5μ regions, which might serve as a basis of differentiation.   L. A. O'NEILL.

Physico-chemical studies on ground olive pastes. VII. Breaking of oil-alpechin emulsions. J. M. Martínez Moreno, C. Gómez Herrera and C. Janer del Valle (*Grasas y Aceites*, 1959, **10**, 170—176).—The olive-oil droplets in the alpechin (vegetation water) are protected by a colloidal membrane, which reduces the yield in extraction of the oils. The protective action can be destroyed by pptn. of sol. proteins, addition of alkylarylsulphonate, or steam-treatment of the olives before milling. Addition of protolytic enzymes does not affect the emulsifying power of the alpechin but assists the expression of the oils.   L. A. O'NEILL.

Cold process of saponification and its advantages. A. K. Mallik, S. N. Mitra and T. V. Mathew (*J. Instn Chem. India*, 1959, **31**, 122—123).—A modified cold saponification process has been found to give results as good as the usual A.O.A.C. hot process.   C. A. SLATER.

Carotenoid-containing oils. Harburger Oilwerke Brinckman & Aergell (B.P. 804, 685, 23.4.57. Ger. 21.4.56).—Carotenoid-containing concentrates are prepared from palm oil (raw or deacidified) by removing from the oil after admixture with another vegetable oil (groundnut or sunflower) the solid fatty acids by fractional crystallisation. The deep reddish oil obtained is further purified as necessary.   I. JONES.

Oral fat emulsions. Schenley Laboratories Inc. (Inventor: K. Kalish) (B.P. 803,078, 16.10.56).—A composition, suitable for use in human and animal nutrition, comprises an aq. suspension of coconut oil (especially refined oil, setting point ~76°F, of low acid val. and low I no.) (40—55), glucose, sucrose or other nutrient saccharide (5—20%), and a mixture of an emulsifying grade of glyceryl monostearate and water-sol. polyoxyethylene sorbitan monostearate (to produce an emulsion containing oil particles of 1—2µ).　　　　　　　　　　　　　　F. R. BASFORD.

Refinement of fatty acid esters. Noblee & Thoerl G.m.b.H., (B.P. 804,022, 11.8.55. Ger., 12.8.54).—Fatty acid esters, in particular oils and fats, are refined by adding to the ester a quantity of alkali at least equal to that required to neutralise the acid present, the concn. of the alkali being such that the total amount of water is 1½ times the wt. of the soap formed, agitating the reaction mixture without formation of an emulsion and, after sufficient time for a single phase soap to be produced, removing, by means of centrifugal force and without the use of washing steps, the soap and impurities present.　　　　　　　　　　　　　　I. JONES.

Rendering of animal fats. Hygrade Food Products Corp. (Inventors: W. R. Dayen and K. M. Christensen) (B.P. 804,145, 4.4.56).—In a continuous process, rendering of animal fat is effected by coarsely grinding fat-containing tissue; heating it (to melt the fat and coagulate the tissue, and to produce a fluidised tissue); further heating the fluidised product under pressure (to coagulate the protein); then rendering the tissue by grinding to a sub-cellular, non-fibrous state.　　　　　　　　F. R. BASFORD.

Meat and Poultry

Water-binding capacity and drip formation in meat. R. A Lawrie (*J. Refrig.*, 1959, **2**, 87—89).—Freezing rate increase for <1 hr. can almost eliminate drip but dimensions would have to be severely limited. Cubes (6 in.) can be cooled from +5° to −5° in 30 min. by air blast at −60°. With this volume and meat pre-slaughter injection of relaxant doses of MgSO₄ combined with speed of freezing markedly slow down adenosine-triphosphate breakdown. The corresponding times for beef in quarters, etc. are discussed (18 hr. at −40°, 1000 ft./min.) and the alteration in pH is examined since it is noted that eating quality tends to fall off where pH >6·3. The benefits of Ca-sequestration are reviewed so that the water-binding capacity of muscle protein is enhanced; such an approach is offset by difficulties in administration. The action of glycerol is suggested since it confers a resistance to damage by freezing and thawing in biological tissues; this is considered to be an interesting approach. (38 references.)　　　　　　　　C. V.

Influence of sulphite on colour and bacterial content of minced meat. B. Krol and P. C. Moerman (*Conserva*, 1959/60, **8**, 1—11).—Discoloration and bacterial multiplication are prevented during ≪3 days at 4° by the addition of sulphite (≡0·03% of SO₂) to the meat immediately before mincing. Ascorbic and nicotinic acids are ineffective. The discoloration (due to the oxidation of the myoglobin) cannot be reversed by SO₃²⁻. Approx. 60% of the SO₃²⁻ is oxidised during storage and subsequent cooking. (23 references.)　　　　　　　　　　　　P. S. ARUP.

Rôle of products of non-enzymic browning on development of mealiness in dehydrated cooked pork mince during storage in air. B. S. Bhatia (*Food Sci., Mysore*, 1959, **8**, 309—312).—Three types of mince; normal, desugared, and desugared but with the glucose replaced, were packed in cans with and without O₂. They were stored at three different temp. and examined after varying storage periods. The total reducing sugars, mealiness, browning (% reflectance) and acceptability were estimated. The relationship between mealiness and browning is discussed.　　　S. G. AYERST.

Fish

Distribution of acetic acid in fish dressing baths and its determination by steam distillation. V. Meyer (*Dtsch. LebensmittRdsch.*, 1959, **55**, 193—197).—Acetic acid diffuses not only into the tissue fluids, but also into the protein whose buffering capacity interferes with direct titration using indicators. This interference can be eliminated by steam distillation after acidification with phosphoric acid. The distribution of acid between fish and bath liquid is studied in relation to bath liquid/fish wt. ratio, and the moisture, fat and protein contents of the fish. Empirical formulae are derived for calculation of final bath acidity.　　　E. C. APLING.

Packaging effects on frozen fish palatability. J. D. Winter and S. Trantanella (*Quick Froz. Fds*, 1958, **20**, No. 12, 81—83, 159).—Two wt. polyethylene with and without antioxidants (I) and Al foils (II) were examined. There was little difference in I with

slight preference for those containing the antioxidant; after 6½ months II was preferable when stored at −15°F but at 0°F there was a definite loss of palatability.　　　　　　　C. V.

Bacterial survey of frozen breaded shrimp. R. Kachikian, C. R. Fellers and W. Litsky (*J. Milk. Tech.*, 1959, **22**, 310—312).—A large variation in the no. of bacteria was found in the examination of 144 samples (22,500—54 million per g.); 61% had <10⁶, 68% contained <100 coliform per g. while faecal streptococci were present in all samples varying from a few to 13,500 per g.　　　　　　　　　　　　　　　　　　　C. V.

Fermented meat products such as sausage. A. W. Brickman, V. Conquest, F. J. Madden, W. B. Oleson and E. T. Filbet (B.P. 804,296, 18.10.56. U.S., 14.11.55).—A fermented meat product (especially fermented sausage, e.g., cervelat) is obtained by inoculating a meat emulsion with *Pediococcus cerevisiae* at ≯pH 5 and smoking at 45—115°F.　　　　　　　　F. R. BASFORD.

Protein products from fish materials. Vogel & Co. G.m.b.H. (Inventors: K. Mohler and R. Vogel) (B.P. 804,013, 22.5.56).—Partly dehydrated fish material of <4% of fat (and ≯60 wt.-% of water), e.g., (defatted) fish meal or product obtained by drying fresh fish, is treated (at 20—80° in vacuum) with a solution of alkali, e.g., NaOH (1—10 wt.-%) in a (water-miscible) org. solvent (e.g., an alcohol, preferably EtOH; or a ketone, preferably acetone) and/or with a solution of acid in the same solvent, then the org. solvent extract is adjusted to the isoelectric point, and the pptd. protein is separated off. By subsequently treating the latter with org. solvent and/or steam (to remove flavour principles), then drying (at <60° in vacuum), there is obtained a tasteless, protein product, suitable for use as food, animal feed, etc.

F. R. BASFORD.

Spices, Flavours, etc.

Characterisation of non-carbonyl volatiles of vanilla by gas chromatography. H. P. Burchfield and E. A. Prill (*Contr. Boyce Thompson Inst.*, 1959, **20**, 217—229).—Alcoholic extracts of vanilla were treated with 2,4-dinitrophenylhydrazine to precipitate CO compounds, including vanillin, and were then extracted with isopentane. After evaporation of solvent, the residue was taken up in dichloromethane, solvent was again evaporated, and the residue was dissolved in acetone, and submitted to gas chromatography. Authentic vanilla extracts mostly gave elution patterns with four characteristic peaks; in some, peak II (in order of increasing retention time) was double, and, in a few, peak III was double. Increasing the pH of the alcohol during extraction much increased the height of peak II. Beans from Tahiti gave different patterns from Mexican and Madagascan beans. This method detects adulterations of commercial vanilla extracts that are not revealed by paper chromatography.　　　　　　　M. D. ANDERSON.

Flavoured food compositions. S. L. Ruskin (B.P. 804,293, 22.3.56).—A nutritional composition, especially a non-allergenic composition having the same flavour as natural chocolate, is obtained by heating a mixture of a furfuryl compound, sucrose, milk, a cross-linked starch, vegetable or animal fat (cocoa butter) and a protein hydrolysate mol. wt. 500—10,000 (e.g., acid-hydrolysed casein). The composition may also contain at least one amino-acid (methionine and/or lysine), edible alkaloid (caffeine or theobromine), and one or more of the following: phenol, glycine, ascorbic acid, dehydro-ascorbic acid and L-2-ketogulonic acid.　　　F. R. BASFORD.

Colouring matters

Extraction and identification of synthetic colours in sugar-containing foods. F. M. Del Bianco and G. Trabacchi (*Chim. e Industr.*, 1959, **41**, 896—898).—A rapid procedure is described for the identification of colours permitted by the new Italian laws in sugar-containing foods (jams, syrups, candies, etc.), based on selective extraction at different pH, followed by identification by paper chromatography. (10 references.)　　　　　C. A. FINCH.

Carotenoid preparations suitable for colouring foodstuffs and animal feeds. F. Hoffmann-La Roche & Co. A.-G.(B.P. 803,077, 28.9.56. Switz., 30.9.55).—The prep. comprises a solidified solution of a carotenoid colouring material (≮3, e.g., 15%) such as β-carotene, and a solid edible solvent (alkanol, aliphatic acid or ester, e.g., cetyl alcohol, palmitic acid, cetyl palmitate or glyceryl monostearate).

F. R. BASFORD

Preservatives

Combined effects of preservatives. II. Effects of simple mixtures on Escherichia coli. H.-J. Rehm (*Z. LebensmittUntersuch.*, 1959, **110**, 356—363).—Graphs are presented showing the mutual effects

of preservatives in binary mixtures with respect to their threshold concn. for the complete inhibition of *E. coli.* In combination with other preservatives, benzoic acid and the Et and Pr esters of *p*-hydroxybenzoic acid show additive or slightly antagonistic effects. Within limited ranges of concn. sorbic and boric acids and Na formate are antagonistic to other preservatives, whilst Na_2SO_3 is generally synergistic.   P. S. ARUP.

Filter-paper method for rapid testing of preservatives against moulds. H.-J. Rehm (*Z. LebensmittUntersuch.*, 1959, **110**, 375—381).—The test can be made with various nutrient media and moulds. The results obtained for sorbic acid and the Et and Pr esters of *p*-hydroxybenzoic acid are generally in fair agreement with those obtained by the liquid culture method. As regards the effects of mixed preservatives, the test will only detect very pronounced syneigistic or antagonistic effects. The Raible technique is recommended for use in preliminary tests on account of its convenience and economy in material.   P. S. ARUP.

Food Processing, Refrigeration

The action of radiations on foodstuffs. IV. Influence on potatoes, fresh vegetables, vegetable preserves, fruit, jam, wine and fruit juices. H. Lück and R. Kohn (*Dtsch. LebensmittRdsch.*, 1959, **55**, 219—227).—Present knowledge of preservation by radiation applied to the foregoing foodstuffs is reviewed. Rats fed vegetables irradiated at from $3—6 \times 10^6$ rep showed no toxic symptoms. Germination but not rotting is prevented in stored potatoes by γ-irradiation at 10^4 rep, and there is loss of vitamin C and change in sugar content. Preservative radiation doses to fruit and vegetables normally produce tissue damage, colour changes, etc., but doses $<10^5$ rep may be used to supplement other preservative measures. Mould growth on the surface of jam is prevented by irradiation of 5×10^4 rep but the colouring matters of the product may be sensitive. In wine, irradiation can under some circumstances improve the organoleptic properties. (72 references.)   E. C. APLING.

Chemical effect of ethylene during storage of peas. F. A. Lee (*Nature, Lond.*, 1959, **184**, 462).—Peas were stored in jars in atm. of (*a*) 5% CO_2, 3% O_2 and 92% N_2 and (*b*) 5% CO_2, 3% O_2, 91·98% N_2 and 0·02% ethylene. Controls of peas stored in pods were examined with the peas stored in gas after a period of 7 months. The peas stored in gas (*a*) were found to give lipid fractions with much lower peroxide values than either of the other two, confirming that ethylene does have an effect on the lipid of peas stored in its presence.   C. A. SLATER.

Practical experience with deep freezing. A. Schulerud (*Brot u. Gebäck*, 1959, **13**, 177—179).—Several years' experience of deep freezing of baked goods in Norwegian bakeries is summarised. Experience shows that only freshly baked goods (within <6 hr.) should be frozen. Freezing must be rapid, and thawed goods must not be re-frozen. The process is more successful with sweet or fatty goods than with bread, but almost all goods can be frozen when the correct technique is used. Bread-crumb freezes at $-5°$ to $-7°$, temp. of the freezing room should therefore be $-12°$ to $-15°$, preferably $-18°$ to $-20°$. The tendency for the goods to dry out requires packing in boxes, cartons of polyethylene film. For storage of dough, the scaled and moulded dough is ½ to ¾ proved and then quickly frozen. Fermentation ceases and the dough may be kept for up to one week if protected from drying and skin-formation. The frozen dough is then thawed overnight in a cool-room and baked the following day. Deep freezing of baked goods or partly-finished doughs is not economic for total production, but is useful for coping with fluctuations in demand.   E. C. APLING.

Resazurin reduction test as an index of the bacteriological quality of frozen foods. K. Kereluk and M. F. Gunderson (*J. Milk Tech.*, 1959, **22**, 299—303).—Frozen food samples (123) were examined bacteriologically by plate methods and by the above test and the method of Stokes and Straker was found to be satisfactory for screening some groups; however the present authors use four groups instead of three ; (*a*) a bacterial count of 0—10,000 per g. showed reduction in >8 hr., (*b*) 10,000—100,000 in 6—8 hr., (*c*) 100,000—1,000,000 in 3—4 hr. while greater no. gave a positive result in <3 hr.   C. V.

Pasteurisation [of liquid egg] and freezing plant in Suffolk. Anon. (*Mod. Refrig.*, 1959, **62**, 856—858).—A fully automatic plant is described. Eggs are broken by hand and examined for imperfections. If there is any delay in production, they are chilled but normally they are immediately homogenised. This enables slightly higher pasteurisation temp. to be used ; the liquid egg is then held for 2·5 min. in a series of holding plates and rapidly cooled to 38°F, being then automatically filled into cans for freezing. It was found that after a few hours running, a film of partially denatured

protein built up on the heating section plates and the hot water temp. had to be raised to compensate. The freezing plant is also described.   C. V.

Cold storage capacity of foods as a function of temperature. R. Plank (*Kältetechnik*, 1959, **11**, 306—310).—The temp. ratio Q_{10} for the speed of chemical reactions was supplemented (Kuprianoff) by Q'_{10} for the permissible duration of cold storage of foods up to a definite quality-loss. Where duration of storage is merely a function of temp., these ratios have the same numerical value, but variations occur when the dependence is on the amount of reaction products causing deterioration. It is recommended that these ratios be replaced by Q_1 and Q'_1 ($1°$ interval) ; the relationship between Q_{10} and Q_1 is shown to be a simple one. (11 references.)   W. H. KEMP.

Storage conditions for frozen chicken. J. Gutschmidt (*Kältetechnik*, 1959, **11**, 310—317).—The max. storage periods for satisfactory, packaged fowls were : 7—8 months at $-24°$, 5—6 months at $-18°$ and 3—4 months at $-12°$, and for unpackaged birds 3—6 weeks on account of unfavourable changes in appearance. (27 references.)   W. H. KEMP.

Frozen sardines. M. Boury (*Rev. gén. Froid*, 1958, **35**, 845—849).—With quick freezing optimum results were obtained and when maintained at $-20°$ were entirely satisfactory for periods up to 3 months. The method of thawing appeared to be immaterial.   C. V.

Packaging

New polyester film. P. J. Vaughan (*Packag. Engng*, 1958, **3**, No. 11, 27—31).—A non-plasticised extruded polyester possessing good abrasive, scratch-resistance, strength and optical properties is discussed. Available in two forms, Videne A (**I**) and TC (**II**), **I** is an amorphous unoriented film capable of adhering permanently to Al foil and many other substances but not to polyethylene, polystyrene or silicones. **II** is an oriented product, a self-supported, heat sealing, heat shrinkable film, sealing without shrinking. **I** and **II** can be used for meat, fresh vegetables and fruit, being impervious to odour and imparting no taste. Both may be used for refrigeration and frozen products, they burn with difficulty and are self-extinguishing.   C. V.

Wrappings used in the refrigeration of fruit. P. Marcellin (*Rev. gén. Froid*, 1958, **35**, 715—719).—The ripening times in gas storage as reported by eight workers are discussed. The O_2, CO_2, N_2 mixture must be applied in ratios suitable to the physiological development and temp. but on removal from storage ripening is still retarded. Varieties should not be mixed nor should they be oil wrapped ; CO_2 (10%) can be responsible for core flush. Use of Pliofilm, polyethylene and waterproofed Cellophane markedly reduce loss of wt. and these are compared with the use of waxes, paraffin or liquid oils.   C. V.

Chemical dips for control of decay in packaged carrots. R. B. Marlatt, H. Tucker and J. K. Stewart (*Plant Dis. Reptr*, 1959, **43**, 741—744).—Dipping washed, topped carrots in NaClO (0·01% Cl_2) for 1—3 min. prior to storage was usually effective in reducing all forms of decay during packaged storage at 21·1—26·7° for 21 days. In one of 5 tests the treatment was sufficiently phytotoxic to increase the incidence of bacterial and *Penicillium* decays during storage. Dipping carrots in 0·05—0·20% sorbic acid prior to storage decreased *Alternaria* decay in only one test and had no effect on *Mucor* or *Penicillium* decays.   A. H. CORNFIELD.

Bacterial state of fresh meat package in transparent films. J. Verge, J. Pantaleon, M. G. Brevot and C. Collignon (*Rev. gén. Froid*, 1958, **35**, 767, 775).—Chopped and cut meat samples were examined for *Escherichia coli*, faecal streptococci and S-reducing clostridia (**I**). 92% contained none in 0·05 g., 76% had 10^6 mesophiles or facultative psychrophiles per g. and in 95% **I** were absent. (15 references.)   C. V.

Transportation and storage of prepared foods. Mealpack Corp. (Inventor : H. W. Clarke) (B.P. 803,387, 11.7.56).—A method for packing a hot individual meal for storage and transport is described.   F. R. BASFORD.

Miscellaneous

Nutrition, proteins, amino-acids, vitamins

Nutritive value of commercial breads. R. J. Block, H. W. Howard, W. J. Monson and C. D. Bauer (*J. Amer. dict. Ass.*, 1959, **35**, March, Reprint).—It was previously calculated that the amount

of " complete protein " consumed by an animal should be a better index of nutritional value than the amount of crude or total protein. Calculations for different types of bread were confirmed by experiments with weanling rats, receiving the bread as the main constituent of a diet also containing maize oil, salts and vitamins. Average weekly gains of wt. were closely correlated with " complete protein " contents of the breads. For the four types of bread : white, whole wheat, special-formula cracked wheat, and white enriched with lactalbumin, milk and soya-bean flour, the crude protein contents were 13·6, 14·2, 14·9 and 18·1%, and the " complete protein " contents 7·1, 8·6, 10·4 and 14·4%.   M. D. ANDERSON.

Oxalate content of plant tissues. S. K. Srivastava and P. S. Krishnan (*J. sci. industr. Res.*, 1959, **18C**, 146—148).—Several plant tissues are analysed for sol. and total oxalates. Some of the leaves used in the diet contain high concn. of sol. oxalates and may, therefore, lead to Ca deficiency and oxaluria. Tubers in general contain less oxalate than the leaves.   I. JONES.

Nutritional values of Indian vegetables. I. (N.O. Cucurbitacae). M. D. Dhargalkar and S. K. Guha (*J. Instn Chem. India*, 1959, **31**, 109—112).—There are five cucurbitaceous plants common and cheap in India. Chemical and chromatographic methods have been used to estimate their nutritional value. All were found to contain mineral salts and a number of essential amino-acids, carbohydrates and fats.   C. A. SLATER.

Shelf-life of sweets containing Indian multipurpose food. K. Krishnamurthy, K. Indira, R. Rajagopalan, M. Swaminathan and V. Subrahmanyan (*Food Sci., Mysore*, 1959, **8**, 312—314).—Four types of sweets containing Indian multipurpose food were prepared. Their shelf-life at 37° after periods of heat treatment for 1 and 2 hr. was investigated ; the sweets were free from microbial spoilage during the storage period of 6 months.   S. G. AYERST.

Chemical composition and nutritive value of sesame seed (*Sesamum indicum*) **and its products.** K. Krishnamurthy, T. N. Ramakrishnan, R. Rajagopalan. M. Swaminathan and V. Subrahmanyan (*Food Sci., Mysore*, 1959, **8**, 316—320).—The literature on the composition, nutritive value and uses of sesame seed, oil and cake is reviewed. Sesame cake is rich in methionine and contains Ca and is of value as a supplement to poor Indian diets. (46 references.)   S. G. AYERST.

Basic fat for feeding experiments. Fractionation of cocoa butter with acetone. A. Jart (*Fette Seif. Anstrichm.*, 1959, **61**, 1084—1086).—In feeding experiments it is preferred to feed control animals with a food containing basic fat in place of the normal fat-free diet, and cocoa butter is selected as the basic fat in place of synthetic glycerides. The cocoa butter is rendered free from the glycerides of linoleic acid and other essential fatty acids by fractionation with acetone (4 kg. dissolved in 40 l. acetone at 50°) at 15° for 2—3 days.   G. R. WHALLEY.

Separation of protein from potato liquors by ion-exchange. K. Siebert (*Ernährungsforschung*, 1959, **4**, 253—268).—Experiments with four different cation exchangers are reported. Exchange capacity was heavily reduced with successive regenerations, and it is concluded that the process would be uneconomical for the starch industry.   E. C. APLING.

Changes in protein-containing food arising from heat treatment. I. Ross (*Milchwissenschaft*, 1959, **14**, 579—580).—In skim milk powder, lysine (I), histidine, arginine, cystine, methionine, asparagine, glutamine and tyrosine are the most heat labile ; the conditions of inactivation are studied. With I, the ε-amino group (which is not bound by the reactive groups in the normal protein) readily reacts when heated with carbohydrate and fats, etc. Heating for 3 hr. at 150° results in an 80% inactivation or 40% for a shorter period. In evaporated milk 20% of I is inactivated and with boiled milk, 5%.   C. V.

Amino-acid composition of egg protein under different conditions of poultry-keeping. S. K. Karapetyan and N. G. Mikaelyan (*Dokl. Akad. Nauk SSSR*, 1959, **126**, 200—202).—The amino-acid contents of the eggs laid by the free range and battery kept hens fed the same diet for 1 year were investigated by the paper chromatography methods. The egg yolk and white were separated, each dried, defatted, powdered and hydrolysed with HCl. n-Butyl alcohol, acetic acid and water in the 4 : 1 : 5 ratio were used for all determinations. Qual. and quant. amino-acid composition of the respective egg yolks and egg whites was identical. (10 references.)   A. L. GROCHOWSKI.

Amino-acid co-polymerisates. G. Krampitz (*Naturwissenschaften*, 1959, **46**, 558).—The thermally copolymerised amino-acids of the albumin complex were examined, after treatment with water, for chemico-physical properties, e.g., solubility and reactions with the usual reagents. On the electropherogram the polymerisates migrate towards the cathode. Paper chromatograms showed that there was no cleavage when dissolved in conc. HCl, but after 36 hr. at room temp., partial hydrolysis occurred. After 24 hr. hydrolysis (Dustin method), the customary picture of a protein hydrolysate was obtained. Proteolytic ferments acted progressively in the degradation of co-polymerisates, this being quant. followed by the ninhydrin reaction.   W. H. KEMP.

Unclassified

1958 summary of disease outbreaks [in foods]. C. C. Dauer and D. J. Davids (*J. Milk Tech.*, 1959, **22**, 335—339).—Water- and milk-borne typhoid, salmonellosis, shigellosis, trichinosis, botulism, staphylococcal food poisoning, gastroenteritis of unknown origin and chemical food poisoning (insecticides, metal contamination, etc.) are discussed and the incidence and causative nature is tabulated.   C. V.

An antifungal antibiotic AYF produced by a strain of *Streptomyces aureofaciens*. M. A. Kaplan, B. Heinemann, I. Mydlinski, F. H. Buchwalter, J. Lein and I. R. Hooper (*Antibiotics & Chemotherapy*, 1958, **8**, 491—495).—Isolation and characteristics are described. It is shown to be composed of at least two closely related antibiotics. The antiyeast factor (AYF) is particularly effective against *Candida albicans* and *Trichophyton schoenleinii* and in low concn. it is active against a variety of yeasts.   C. V.

Oxidation-reduction potential, a determining factor in microbiological changes in foodstuffs. M. Lubieniecka-von Schelhorn (*Dtsch. LebensmittRdsch.*, 1959, **55**, 213—216).—The rH requirements of the various groups of micro-organisms and the rH values normally encountered in various fresh and processed foods are summarised and their significance in relation to the control of microbiological growth in foodstuffs, particularly vac.-packed goods, is discussed. (16 references.)   E. C. APLING.

Influence of moisture on course of enzymic reactions in foods containing little moisture. II. L. Acker and H. Kaiser (*Z. LebensmittUntersuch.*, 1959, **110**, 349—356).—Previous observations (cf. J.S.F.A. Abstr., 1959, i, 232) that enzymic hydrolysis reaches increasing max. values with increasing R.H. at constant temp. are confirmed for mixtures of barley-malt and lecithin. Experiments are described which rule out the possibility of enzymic inactivation on exposure to low R.H. (25—60%) during 48 days. The increased phospholipase (B and D) activity is probably due to increases in the condensation of moisture in the capillary cavities of the samples. At R.H. >85% a steep increase in the production of choline is observed. The existence of an enzyme capable of hydrolysing choline glycerophosphate at high R.H. is confirmed by experiments with this ester. (17 references.)   P. S. ARUP.

Phosphates and organic compounds of phosphorus in foods. V. Separation of phosphopeptides by continuous electrophoresis. J. Schormüller and K. Lehmann (*Z. LebensmittUntersuch.*, 1959, **110**, 363—366).—The technique is applied with the use of the Grassmann apparatus to the resolution of the phosphopeptides in a " pure peptone" fraction obtained from ripe Harz cheese, in N-AcOH solution. Four fractions are obtained which are well-differentiated by their ratios of amino-acids to P. (16 references.)   P. S. ARUP.

Determination of fat in mayonnaise. W. Diemar and M. Salvisberg (*Z. LebensmittUntersuch.*, 1959, **110**, 366—371).—The results by seven standard methods are compared. Preference is given to the Hadorn and Jungkunz method with C_6H_6–EtOH (1 : 1) as extracting solvent. This method shows a standard deviation of ±0·170% (for 6 results) and ensures complete extraction of the lecithin with the fat. (13 references.)   P. S. ARUP.

Determination of DDT residues in foodstuffs. G. A. Sergeant and R. Wood (*Analyst*, 1959, **84**, 423—426).—The solution of the fat components in hexane is treated gradually with H_2SO_4 and the hexane layer is applied to a column of acidified Celite. The conc. eluate is washed on to a silica gel column with hexane and the column is washed with hexane. The DDT is eluted with ether, the eluate is evaporated to dryness at 40°, the residue is nitrated with HNO_3–H_2SO_4, the deriv. is extracted with light petroleum–benzene and the extract is washed with alkali and evaporated to dryness at low temp. The residue is dissolved in benzene, ethanolic KOH is added and the extinction of the coloured liquid is measured at 600 mμ and referred to a calibration graph prepared with pp'-DDT nitrated similarly. Recovery ranges from 86 to 95%.   A. O. JONES.

Food, fallout and the isotopes of strontium. J. Hawthorn (*Chem. & Ind.*, 1959, 1294—1298).—Transfer of ^{89}Sr and ^{90}Sr to human bone via rainwater, soil and plant and animal food is discussed from quant. data. Levels of ^{90}Sr in human bone are minimised by (i) the cow acting as intermediate biological filter, (ii) the much

slower rise of level in milk as the concn. of ^{90}Sr on the earth's surface rises steadily, and (iii) human discrimination against Sr in favour of Ca between diet and bone. Further systematic data to explain fully the movement of ^{90}Sr through food chains and a simpler procedure for determining radio-Sr in food are needed. ^{89}Sr can still be a danger if nuclear tests continue. The higher intake of Sr by plants in hilly regions is discussed briefly in relation to food and water supplies. Risks associated with ingestion of Sr isotopes cannot at present be evaluated accurately.   W. J. BAKER.

Prevention of growth of micro-organisms on perishable substances. Best Foods Inc. (B.P. 803,947, 27.5.55. U.S., 28.5.54).—Growth of fungi, moulds and other micro-organisms on perishable goods (foodstuffs) is minimised by coating with or wrapping in a coating material containing aq. dispersion, η 20—60 sec. (G-3 cup of a Zahn viscometer) of a colloidally-sol. hydrophilic gum (Na salt of carboxymethylcellulose) and edible, non-toxic fungistatic agent or propionic acid, dehydroacetic acid, or a compound $CRR';CR''·CO_2H$ (R is H when R' and R'' are H or with C form a cyclic radical ; or R is alkyl when R' and R'' are H), e.g., sorbic acid.   .   F. R. BASFORD.

Proteolytic enzyme. American Cyanamid Co. (B.P. 804,608, 5.10.55. U.S., 25.10.54).—The prep. of a new proteolytic enzyme is claimed. Aq. nutrient medium is subjected to fermentation in presence of a fungus of a species of the order *Entomophthorales* during 24—90 hr. at 20 (25)—30°, pH 5—9 (6—8), then the fermentation liquor is treated with an adsorbent (especially purified diatomaceous earth). The latter is then eluted with aq. alkali, and the eluate is diluted with an org. solvent, e.g., acetone, to precipitate the proteolytic enzyme. The latter is characterised by mol. wt. ~30,000 ; isoelectric point 10·2, optimal proteolytic activity at pH ~9. It is stable over a pH range of 4—11, and may be used in the leather industry, in the chill-proofing of beer, tenderising of meat, dry cleaning industry, etc.   F. R. BASFORD.

3.—SANITATION

Determination of dichlorodifluoromethane in fumigation mixtures with ethylene oxide by measurement of thermal conductivity. W. A. Affens, E. O. Haenni and R. A. Fulton (*Analyt. Chem.*, 1959, **31**, 1565—1568).—The thermal-conductivity method can be applied to the determination of CCl_2F_2 after removal of water vapour and ethylene oxide, which interfere. Moisture is removed with anhyd. $CaSO_4$ and the ethylene oxide is removed and determined by passing the gas sample through traps containing standard H_2SO_4 saturated with MgBr ; the ethylene oxide reacts with the acid, the excess of which is titrated with standard alkali. The accuracy for the ethylene oxide is $\pm2\%$ and that for the CCl_2F_2 is $\sim\pm8\%$.   G. P. COOK.

Evaluation of some space sprays for the control of house flies. H. G. Wilson and G. C. LaBrecque (*J. econ. Ent.*, 1959, **52**, 704—706). —After wind tunnel and space spray tests diazinon, Ronnel, malathion, allethrin and four chrysanthemumates were tested in dairy barns. All gave 90% knockdown in 10 min., but none gave good control after 24 hr.   C. M. HARDWICK.

Biochemical purification of industrial wastes. I. Microbiological specification of activated sludges for purification of industrial wastes. Ts. I. Rogovskaya and M. F. Lazareva (*Mikrobiologiya*, 1959, **28**, 565—573).—The action of activated sludge was studied in aq. wastes from rubber reclaiming, gasification of brown coal and slate, fatty-acid industry, and a synthetic mixture containing phenol and resorcinol. Biochemical purification characteristics are tabulated for 40 strains of bacteria from activated sludge. No great diversity in species was found. The mixture of cultures is more effective than any single strain. 45—90% of the studied bacteria are capable of oxidising phenol.   A. L. GROCHOWSKI.

Purification of sewage and other waste liquor. H. J. N. H. Kessener and Whitehead & Poole Ltd. (B.P. 804,249, 10.11.55).— A mixture of the sewage and/or other waste liquor is aerated and subsequently allowed to undergo main settling. Some of the sludge is allowed to settle from a down-stream portion of the mixture, as it undergoes progressive purification, while flowing in a stream, before the main settling takes place and is returned to an up-stream portion of the mixture undergoing treatment which has received less or no aeration.   J. M. JACOBS.

Fumigating compositions. Murphy Chemical Co. Ltd. and J. L. Walpole (B.P. 801,659, 17.7.53).—Melamine or dicyanodiamide is compounded (1) with a highly oxygenated compound capable of

yielding O_2, e.g., $KClO_3$ (0·9—6·5 pt.), to provide a self-combustible composition, suitable for use with a vaporisable pesticide (of flash point $\not<180°$, e.g., DDT, Gammexane or $PhSO_3·C_6H_4Cl-p$) ; to give a fumigating composition. A typical formulation is : DDT (56), melamine (8), china clay (10), $KClO_3$ (24) and ZnO (2 pt.). The melamine serves to moderate the burning rate of the ignited composition.   F. R. BASFORD.

4.—APPARATUS AND UNCLASSIFIED

Application of atomic science in agriculture and food. O.E.E.C. Project No. 376 July, 1958, 2, 250 pp. **Use of radio isotopes for soil analysis control.** A. Van den Hende, 79—84.—In studying the nutritive value and " plant-available " fractions of a soil, radioactive tracers are the best means of assessing the value of the extraction methods and of indicating the equilibrium and exchange mechanisms involved. (20 references.)

Developments of methods and principles of plant breeding resulting from the application of atomic science. A Gustafsson, 85—88.— Traditional methods based on selection and hybridisation and new principles of chromosome doubling and mutation are reviewed. Mutations do not arise at random ; the mutation spectrum varies with the type of species and mutagenic agent used.

Safeguarding agricultural interests from possible discharges of radioactive materials from Atomic Energy Establishments. I. Administrative aspects. J. G. Carnochan. **II. Technical aspects.** H. G. Wortley, 89—91, 92—96.—I. Measures to safeguard the purity of drinking water, and milk with reference to possible accidental release of radioactivity by atomic plant are discussed. This concerns mainly large atomic factories etc., the producers of nuclear energy, but problems attendant on the use of radioactive isotopes, and radioactive fall-out are surveyed. The need for scientists and legislators to work together very closely is stressed.

II. The limiting amount of radiation exposure recommended by the International Commission on Radiological Protection (I.C.R.P.) (1954) viz., 0·3 r/week for occupational workers, and the possible intake of food, water or milk with concn. of certain radioisotopes depending on their place of origin, are discussed. In the U.K. situations resulting from intentional discharges of radioactive materials are under control ; with regard to accidental discharges, plans should be able to contain any known possibility. In case of new I.C.R.P. levels demanding modifications in control, the question becomes, how to ensure public safety without unnecessary economic burden on the atomic energy industry.

Agricultural aspects of contamination arising from use of atomic energy. R. Scott Russell, 97—101.—The contamination of agricultural land which could result from accidents in nuclear reactors or fires in chemical plants containing large quantities of radioactive material is considered, particularly in regard to ^{131}I and ^{89}Sr or ^{90}Sr. Depending on the nature of the vegetation and the particle size of fall-out, milk, then leaf vegetables are the foods liable to be most seriously affected. Milk is likely to show most widespread contamination at an early stage and the probable time course of the transfer of fission products is known. By appropriate monitoring procedures, more complete protection is possible.

Use of radioactive isotopes in study of mineral nutrition of animals. J. Moustgaard, 192—206.—In this survey mention is made of the more recent applications of the isotopes ^{131}I, ^{59}Fe and ^{32}P in the study of theoretical and practical physiological problems. Thyroid secretion rates in cattle, pigs, lactating cows and growing pigs, the fate of intramuscularly administered Fe and the " turnover " of phospholipids in cattle are discussed. (14 references.)

Use of radioactive carbon in study of rôle of vitamins in animal metabolism. A. Wacker, 207—213.—The properties of biopterin, folic acid, vitamin B_{12}, inositol and xanthopterin and the importance of these substances in metabolism are discussed. (14 references.)   E. M. J.

Infestation control. A service to agriculture and food storage. (*Minist. Agric., Fish., Fd*, 1959, 32 pp. 12 plates).—The following are described : fumigation and other modern methods of dealing with stored products insects, new methods for controlling rats and mice, the measures now in operation for the control of land pests, with particular reference to rabbits, harmful birds and the history of pest control during the last 45 years. (149 references.)   E. M. J.

Characterisation and determination of traces of N-trichloromethyl-thiotetrahydrophthalimide (captan). J. Roubert (*Chim. anal.*, 1959, **41**, 333—334).—Captan is detected by a bright yellow fluorescence which is produced when the sample solution is evaporated with resorcinol in alcohol. The method can be made quantitative in the range 10 to 50 μg. by the prep. of suitable standards.   W. T. CARTER.

All Clear in Ceylon

Ceylon delights the eye with its shoreline fringe of dreamily-waving coconut palms—palms that are more than decorative. These slender graceful trees provide food and drink, coir fibre, copra, acetic acid, oils, timber and thatch for building. But they are also the target for rhinoceros beetles *(Oryctes rhinoceros)*, winged pests which, from refuse-dump breeding grounds, fly into the plantations and there bore into the crowns of the palms, attacking the young leaf shoots and growing points. Other organisms may enter into the bore holes and cause still further damage. Keeping the plantation areas clear of decaying vegetable

matter helps—but is not enough. An effective pesticide is also needed—one able to kill the beetle weeks after application. Dieldrin has proved ideally suited to this task. Applied to the crown of the tree as a dilute emulsion it runs down and collects in the leaf axils, there protecting the palm's most vulnerable part from its flying marauders. For the coconut growers of Ceylon, dieldrin has sounded the "all clear".

dieldrin

Issued by Shell International Chemical Company Limited. For further information consult your Shell Company (in U.K., apply to Shell Chemical Company Limited)

JOURNAL
OF THE SCIENCE OF FOOD
AND AGRICULTURE

CONTENTS

SOCIETY OF CHEMICAL INDUSTRY