Conclusion

It has been observed by many workers that the lactic acid content of fresh silage declines rapidly with rising pH and it has been shown by Barnett (1951*b*) that this decline follows a smooth curve. In the present work using dried silage, however, while the relationship still holds, the curve is much flatter and approximates to a straight line throughout most of its length. In this connexion the relation between the D.M. content and the L.A. content is of importance because a ready explanation may be found for all these facts. It is obvious that ensiled material of high dry-matter content contains a larger amount of carbohydrate upon which the lactic acid organisms may act, producing lactic acid from the carbohydrate substrate with an accompanying fall in pH. It has been shown by Barnett (1950) that silage of high D.M. content is usually characterized by a low pH, a fact in accord with the foregoing reasoning. Although lactic acid is considered to be non-volatile, as is assumed in determinations of volatile fatty acids in silage, it is in fact volatile to some extent in water vapour ; during the drying process with a wet silage, greater proportional amounts of lactic acid will be lost than if the silage is relatively of a dry nature. Again, lactic acid is present partly as inorganic lactate, if not in ester form as well, and these materials react with the reagents used, as free lactic acid does. Lastly, even lactic acid itself is converted to lactide by heating at 120° c. but it is conceivable that such conversion takes place slowly and incompletely at 80° c. At any rate, in whatever form the lactic acid may be present in the dried silage, whether free or combined, it is soluble in ether and the present work has shown that the difference between the ether and light petroleum ' oil ' extraction figures is due largely to this residual lactic acid.

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PHOTO-DECOMPOSITION OF ROTENONE IN SPRAY DEPOSITS. III.—Kinetics of the Photo-Decomposition

By N. V. SUBBA RAO and A. G. POLLARD

Special artificial light sources have been designed and constructed to investigate the photo-decomposition of rotenone in controlled conditions. The various factors that affect the decomposition are investigated, and the rates of decomposition of rotenone and derris deposits on exposure to sunlight and the artificial light sources are determined. The rates of decomposition indicate the reaction to be of the first order. From the data obtained, the period over which the deposits are likely to remain active under field conditions is estimated.

Introduction

The use of rotenone in sprays requires the employment of rotenone-solvents, the reactions of a number of which have been examined by Davidson & Jones (1931). They observed that in certain solvents, such as pyridine, rotenone is decomposed with the formation of products of low insecticidal properties. The yellow colour of the decomposition products recalled the earlier observation of Tattersfield & Roach (1923) that such products were formed when alcoholic solutions of rotenone were exposed to light. This decomposition is of important practical significance, particularly when rotenone is employed as a protective insecticide, for the toxicity of the spray deposit on the leaf surface exposed to air and light should be retained as long as possible. Jones & Haller (1931) showed that the yellow decomposition products were dehydrorotenone and rotenonone. Both the substances are practically non-toxic to gold-fish and insects (Gersdorff, 1935).

Jones, Gersdorff, Gooden, Campbell & Sullivan (1933) applied rotenone, dihydrorotenone, rotenone hydrochloride, a rotenone-bentonite mixture, a rotenone–lampblack mixture, ground *Derris* root, and powdered *Derris* extractives in paste form to glass plates. Groups of the plates were exposed to direct sunlight for 10 days and 20 days and to arc light for an equivalent number of hours. After exposure the loss of toxicity was estimated by bio-assay employing gold-fish and mosquito larvae as test animals. All but the dihydrorotenone and the rotenone–lampblack mixtures lost more than half their toxicities during a ten-day exposure to sunlight ; the arc light practically destroyed their toxicities. Wheeler (1934) found that on exposing to sunlight thin layers of a dust containing crushed *Derris* root, barium fluosilicate and sulphur, the dust lost in 25 hours its characteristic odour and that the concentration of rotenone decreased by 40%. According to van der Laan (1935) derris powder is not so sensitive to light as is rotenone and could be preserved for years, if dry and protected from the sun. In the sun, however, the dry powder lost about 50% of its activity in 3 days.

A considerable amount of work has been done on the stability and keeping qualities of rotenone-containing solutions. The most important published data on this were those of Gunther (1943), who has shown clearly (i) that the decomposition of rotenone solutions is of the first order and (ii) that the decomposition could be considerably reduced by incorporating antioxidants such as hydroquinone. A number of patents (Christman & Jayne, 1939, 1943 ; Faloon, 1939) have been taken to protect and stabilize rotenone-containing preparations.

There seems to be considerable divergence of opinion as to the period over which derris deposits on the foliage remain effective. Japanese workers have stated that rotenone decomposes within two days after application to foliage (Shepard, 1946). Wisecup & Reed (1938) found that a considerable proportion of the effectiveness of cubé remained after 5 days' exposure of treated cabbage to varied weather conditions in the field. Todd (1938) showed that bean plants, treated with derris either by dusting or spraying, retain the effectiveness of the treatment much longer when kept in the shade than when exposed to the sun. In the sun a 0·75 rotenone-dust was ineffective in a little over a week, whereas in the shade the effectiveness was still high at the end of two weeks.

The only quantitative work carried out on the photo-decomposition of rotenone was that of Gunther (1943), but this was on rotenone in solution. No quantitative work has so far been presented on the rate of decomposition of rotenone in spray deposits. The work of Jones *et al.* (1933) was mainly on thick deposits which are not normally met with and, further, their methods of assay were toxicity methods. Although the ultimate criterion is the toxicity of the deposits, and in this sense bio-assay methods may be the final deciding factors, chemical methods are relatively simple to employ and accurate enough for following the mechanism of the processes taking place.

The present investigation has, therefore, been undertaken with a view to present quantitative data on the photochemical decomposition of rotenone and derris deposits and to improve the permanence of these deposits either by incorporating antioxidants or by using suitable covers to protect from light. Chemical methods described in an earlier publication (Subba Rao & Pollard, 1950) have been employed to estimate rotenone in deposits and in the residues obtained after exposure to light. Further, the deposits produced by spraying technique (Tattersfield, 1932) were subjected to more or less standardized conditions of exposure.

Sources of light

Insecticides used as protective agents are generally applied either in early or late spring ; occasionally they are applied in summer as well. Depending on the locality, time of the day, time of the year and climatic conditions, the intensity and spectral composition of sunlight varies. Therefore, a certain amount of deposit might undergo decomposition to varying extents depending on all these factors and it is possible for apparently contradictory statements to be made on the retention of toxicity of deposits. Hence, the need for investigating the loss of toxicity under more or less standardized conditions.

Previous investigators of the loss of toxicity of rotenone (Jones *et al.*, 1933) and pyrethrum (Tattersfield, 1932; Tattersfield & Martin, 1934) made use of either sunlight, light from a carbon arc or from a 1000-w. tungsten-filament lamp. In the present investigation artificial illumination from two sources of light constructed for this purpose have been used besides sunlight.

Sunlight.—In sunlight, maximum energy is radiated in the green of the visible spectrum, with an appreciable amount of ultra-violet on the one side and the infra-red on the other. A considerable proportion of solar radiation is absorbed by the earth's atmosphere, particularly in the short-wave region. Most of the photochemical reactions are caused by the near ultra-violet and the violet end of the spectrum, this region having comparatively higher quantum energy.

The average variations in daylight illumination at different times of the day and in different months of the year have been recorded (National Physical Laboratory). These values were obtained as a result of observations extending over ten years. The variation in the illumination arising from even small changes in atmospheric or cloud conditions are often surprisingly great and take place with extreme rapidity.

In view of these observations, most of the experiments with sunlight were conducted on clear days and the period of investigation extended from February to September 1948. The deposits were exposed in the open on the roof of the laboratory at South Kensington and the records of illumination for those days of exposure were obtained from the Meteorological Observatory at Richmond. These values were considered to be applicable since exposures were made on clear days. (The daylight illumination values considered here were measured on a horizontal plane in the open without any obstruction.)

Daylight fluorescent lamp.—The special feature of this source of light is that it provides a natural white light and is closely similar to daylight in spectral composition. Apart from the advantages of greater efficiency in light output and minimum amount of heat radiation, it is the nearest approach to daylight in the visible region. The ultra-violet radiation from this source is very small. The characteristics of light from this source, shown in comparison with noon sunlight in June, have been published (Electric Lamp Manufacturers' Association).

The illumination from a 2-ft. fluorescent lamp operating at 25-w. is very low and therefore a special light source consisting of two such fluorescent lamps under one reflector was constructed. The reflector was designed to give uniform illumination at a distance of about 1 ft. over a region of at least 6 in. width. Details of the dimensions of the reflector and the lamps are shown in Fig. 1.

This light source was fitted in a box (36 in. × 24 in. × 24 in.), lined in the interior with blotting paper, to exclude extraneous light. Peep-holes were provided in the box for ventilation and also for observation of the readings with a light meter. In the initial stages there was a considerable drop in the intensity of illumination as measured by a foot-candle meter, but later the intensity remained practically steady over the periods of exposure. The intensity of illumination at the place of exposure, 14 in. from the lamp, was measured twice a day during the period of exposure. The initial value of the illumination provided by this light source was 220 ft.-candles, and after a few hours' use it remained steady for a quite long period at about 165 ft.-candles. After considerable use, this value was found to decrease gradually.

Artificial source of light comprising mercury-vapour discharge lamps and tungsten-filament lamps.—Sunlight, which reaches the earth after absorption by the atmosphere, consists of light of wavelengths from 2900 A. to 7500 A. As regards spectral composition, the nearest likely sources of such illumination were Mazda S.1 lamps and Osram U.V.1 lamps. Even these sources of light give strong emission lines characteristic of the mercury-vapour discharge and hence light emitted by them is not identical in all respects with sunlight.

At that time it was not possible to obtain the Mazda S.1 lamp or the Osram U.V.1 lamp. A combination of two Osira mercury-vapour discharge lamps (125-w.) and two tungsten-filament lamps (100-w.) was, however, used to produce radiation from 3000 A. upwards. Although Osira lamps of higher wattage were available, the 125-w. lamp was preferred because of its higher percentage of transmission between 3000 and 4000 A. (General Electric Co. Research Laboratories). The relative positions of these bulbs shown in Fig. 2 have been adjusted so that they give, at a distance of about 2 ft., uniform illumination in which the ultra-violet proportion is nearly equal to that in daylight. The measurements were made using an Osram UNG7 photocell behind a Chance's OX1 filter and the variation between the two sources measured at nearly equal intensities was not more than 10%. (These measurements were made with the help of the General Electric Co. Research Laboratories.)

The four bulbs were fixed in an aluminium reflector, which was held about 4 in. from the top of a box (14½ in. × 13 in. × 33 in.) by means of nuts and bolts. The interior of the box had double linings, the first being asbestos board in contact with the wood and the second, blotting paper, fastened to the asbestos board. The asbestos lining was used to protect the box from the heat generated by the lamps and the blotting paper served to provide an intense and even illumination. The box was fitted with a hinged door so that deposits could be placed in and taken out without inconvenience and in order to prevent outside light affecting the intensity of illumination inside.

One of the problems which became quite serious was the dissipation of the enormous heat evolved by the lamps. Apart from the risk of the box catching fire, against which the asbestos lining was provided, the temperature to which the deposits were exposed was far higher than those normally met with in outdoor conditions. To avoid these complications, attempts were made to abstract the heat either by suction of air through the box or by blowing air across the bulbs. The latter method proved satisfactory. A blower (70 cu. ft. per min. capacity) was mounted on the right-hand side of the box and a large opening was made on the opposite side to allow the air to pass freely. The draught created by the bottom peep-holes was not sufficient to create any turbulence in the box, and further, as the holes were 3 in. above the surface of the deposits exposed in the box, the draught did not in any way affect the deposits. The temperature at the bottom of the box, where the plates were exposed, did not exceed 10° c. above the external temperature, and usually varied between 20° and 32° c., which agreed admirably with the limits of temperature met with in exposures to sunlight. As for variation in intensity of illumination at the place of exposure, an area of about 8 in. × 8 in., with a variation of not more than 10%, could be secured at a distance of about 2 ft. from the centres of the bulbs. Hence, a maximum of four plates (4 in. × 4 in.) could be exposed simultaneously without introducing appreciable error. The initial illumination inside the box at a distance of 23 in. from the centre of the bulbs was 1400 ft.-candles, but the value gradually dropped to a final value of about 1100 ft.-candles. For each exposure, the illumination was measured with the light meter.

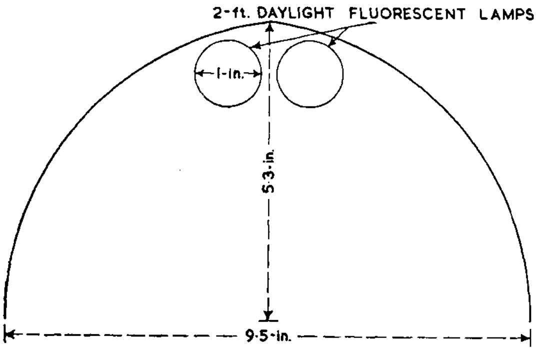

FIG. 1.—*Relative position of daylight fluorescent lamps and reflector*

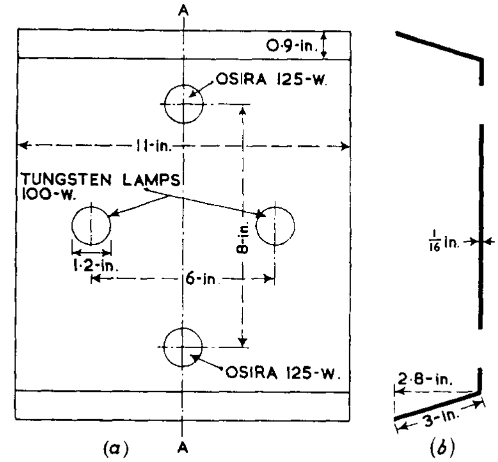

FIG. 2.—*Mercury-tungsten light source*
(a) reflector showing relative position of lamps
(b) section at AA

Energy-distribution data for this source of light (M–T represents mercury–tungsten) in comparison with sunlight were kindly supplied by the G.E.C. Research Laboratories and are shown in Fig. 3 (spectral lines are represented by an arbitrary width of 200 A.). The sunlight curve is based on summer conditions at a latitude of 51·1°, corresponding to that of London.

Experimental

The deposits used in these experiments were made by employing the spraying technique described in an earlier publication (Subba Rao & Pollard, 1951). The amount of deposit varied between 0·3 and 1·8 mg. (area of deposit being 61 sq. cm.). Solutions of either pure rotenone or derris resin (rotenone content, 25% ; supplied by Stafford Allen & Sons Ltd.) in acetone were used for spraying. Procedures for the determination of rotenone in spray deposits and residues already described in a previous publication (Subba Rao & Pollard, 1950) were adopted. In the examination of derris deposits, the rotenone equivalent was calculated from the tintometer red values.

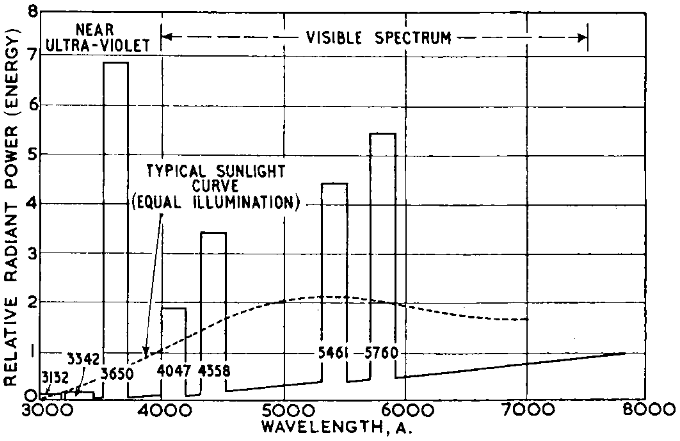

FIG. 3.—*Energy-distribution data for mercury–tungsten light in comparison with sunlight in summer conditions*

Effect of storage of deposits in darkness

Out of six plates sprayed in one lot, four plates were taken at regular intervals and the mean deposit on them, together with the coefficient of variation, was determined as described in Part II of this series of papers (Subba Rao & Pollard, 1951). The other two plates were kept in the dark for a week and later rotenone in the deposits was estimated. The results obtained at two different thicknesses of deposit are shown in Tables I(*a*) and I(*b*)

Table I(*a*)

Total no. of plates sprayed : 6
Mean deposit (4 plates) : 0·61 mg.
Coeff. of variation : 2·2%

Series no.	Description of treatment	Rotenone, mg.	Deviation
1	Kept in dark at room temp.	0·606	— 0·004
2	(15–20° C.) for one week	0·618	+ 0·008

Table I(*b*)

Total no. of plates sprayed : 6
Mean deposit (4 plates) : 0·96 mg.
Coeff. of variation : 3·2%

Series no.	Description of treatment	Rotenone, mg.	Deviation
1	Kept in dark at room temp.	0·94	— 0·02
2	(15–20° C.) for one week	0·96	0·00

The results given in Tables I(*a*) and (*b*) show that the variation from the original deposit is well within the limits of the coefficient of variation and it may, therefore, be concluded that there was no decomposition on storage in darkness.

Effect of heat on the deposits

Since the preceding experiments have shown that deposits kept in darkness at 15–20° C. were unaffected, it was considered desirable to investigate the effect of heat alone on the deposits. The deposits of pure rotenone were kept in an incubator operating at 40° ± 1° C. for a week and examined for rotenone content. This temperature was chosen because deposits exposed to sunlight or artificial illumination rarely attained temperatures above 40° C. At higher temperatures the complication of loss by volatilization might arise. The results of investigation are presented in Table II.

Table II

Total no. of plates sprayed : 6
Mean deposit (4 plates) : 0·87 mg.
Coeff. of variation : 4·4%

Series no.	Description of treatment	Rotenone, mg.	Deviation
1	Kept in dark at 40° ± 1° C. for one week	0·864	− 0·006
2		0·882	+ 0·012

These results indicate that there is no appreciable change in the deposits by raising the temperature to 40° C.

Influence of source of light

Three sources of light with different emission characteristics, described in the previous pages, were used to investigate the effect of spectral composition of an illumination on the photo-decomposition. For comparison, deposits containing nearly the same amount of rotenone were exposed under each source to approximately equal quantities of light energy measured in foot-candle-hours. The percentage decomposition in each case was determined by subtracting the rotenone estimated in the residue from the mean deposit and expressing it as percentage. The results are shown in Table III.

Table III

Description of light source	Quantity of light energy, ft.-candle-hr.	Mean deposit, mg.	Coeff. of variation	Rotenone, mg.	Decomp., %
Daylight fluorescent lamp	40,000	0·597	1·0	0·414	31
Sunlight on 10 March, 1948	29,000	0·597	1·0	0·291	51
Mercury–tungsten combination	40,000	0·413	4·3	0·035	90
Daylight fluorescent lamp	80,000	0·510	3·4	0·246	52
Sunlight on 23 to 25 March	81,000	0·510	3·4	0·162	68
Mercury–tungsten combination	80,000	0·413	4·3	< 0·035	> 90

The results indicate that the spectral composition of an illumination plays an important part in the photo-decomposition studies and, therefore, great care should be taken in the selection of the light source. For the same amount of light energy (foot-candle-hours), the mercury–tungsten combination seems to be more powerful than sunlight in causing this decomposition. This observation is confirmed in subsequent experiments. The results further show that the near ultra-violet and violet end of the spectrum are the main regions responsible for the decomposition. To examine this aspect more thoroughly, the experiments described in the next section were conducted.

Spectral region responsible for the decomposition

Out of the large list of Chance filters, the three filters OX1, OB10, and OY4 were selected for the purpose of these experiments. OX1 transmits light of wavelengths between 3000 A. and 4000 A., with a maximum transmission of 70% at 3650 A.; OB10 transmits light between 3300 A. and 5100 A., with a maximum of 58% at 4250 A.; OY4 transmits light beyond 5000 A., with a maximum of 84% from 5500 A. onwards. There is, no doubt, overlapping between the two filters OX1 and OB10, but OB10 was selected as it covers the entire violet and blue regions.

Four deposits from one batch of spraying were taken and they were exposed to sunlight for one day. One of the plates was exposed without any filter and each of the other three was exposed behind one of the three filters. The percentages of decomposition caused by sunlight and by each one of the light regions transmitted by the filters were estimated. The experiments were repeated under the mercury–tungsten combination. Results obtained with sunlight are presented in Table IV(*a*) and those with the artificial light source in Table IV(*b*).

Table IV(*a*)

Total no. of plates sprayed: 8
Mean deposits (3 plates): 0·429 mg.
Coeff. of variation: 1·6%
Exposure: sunlight on 31 Aug., 1948; 48,000 ft.-candle-hr.

Description of filter	Maximum transmission, %	Rotenone in residue, mg.	Decomposition, %	Relative decomposition, %
No filter	—	0·140	67·4	100
OX1	70	0·234	45·5	67
OB10	58	0·374	13·0	19
OY4	84	0·419	2·5	4

Table IV(*b*)

Total no. of plates sprayed: 10
Mean deposit (3 plates): 0·45 mg.
Coeff. of variation: 2·7%
Exposure: mercury–tungsten combination; 7200 ft.-candle-hr.

Description of filter	Maximum transmission, %	Rotenone in residue, mg.	Decomposition, %	Relative decomposition, %
No filter	—	0·203	55·0	100
OX1	70	0·293	35·0	64
OB10	58	0·367	18·5	34
OY4	84	0·428	5·0	9

The figures in the last columns of Tables IV(*a*) and IV(*b*) represent values expressed as a per cent. of the decomposition produced with no filter. With both the sources of light, when allowance is made for the percentage transmission of the filters, the corrected values indicate over 90% decomposition by light transmitted by filter OX1, i.e. light between 3000 and 4000 A. The decomposition caused by filter OB10 may be mostly due to light transmitted between 3300 and 4000 A.; a small proportion of decomposition by radiation between 4000 and 4500 A. is not ruled out. Light beyond 5000 A., however, has no appreciable effect on rotenone deposits.

Effect of thickness of deposit

The results presented in earlier sections, together with some new data, are assembled in Table V to indicate the extent of decomposition in deposits of different thicknesses exposed to the same light source and to nearly the same quantity of light energy.

Table V

Description of light source	Quantity of light, ft.-candle-hr.	Mean deposit, mg.	Coeff. of variation, %	Rotenone in residue, mg.	Decomposition, %
(*a*) Sunlight					
23–24 Mar., 1948	35,000	0·330	1·0	0·141	57
10 Mar.	29,000	0·597	1·0	0·291	51
10 Mar.	29,000	1·390	2·6	0·917	34
23–25 Mar.	81,000	0·330	1·0	< 0·030	> 90
,, ,,	81,000	0·510	3·4	0·162	68
(*b*) Daylight fluorescent lamp	80,000	0·330	1·0	0·090	72
	80,000	0·510	3·4	0·246	52
(*c*) Mercury–tungsten combination	40,000	0·413	4·3	0·035	90
Mercury–tungsten combination	37,000	0·878	5·6	0·153	82

As would be expected from theoretical considerations, the results given in Table V show that in similar conditions of exposure thicker deposits undergo decomposition to a lesser degree than do thinner deposits. Data presented in Tables VI(*b*) and VI(*c*) supply further evidence in support of this.

Kinetics of decomposition of rotenone and derris deposits

Rotenone deposits.—With a view to finding the relation between light energy and the extent of decomposition, data obtained by exposure of deposits of pure rotenone of nearly the same thickness to sunlight on clear days are shown in Table VI(*a*).

These results show that the extent of decomposition is not directly proportional to the quantity of light energy, but has a logarithmic relationship as indicated by Fig. 4.

A set of carefully controlled experiments were made using the mercury–tungsten combination. From one lot of spraying, four deposits were picked and the mean deposit on the plates was estimated in the usual way. Seven or five of the rest were exposed to mercury–tungsten light for different periods to follow the rate of decomposition. Each of these plates was then analysed by the procedure adopted for spray residues. Deposits of different thicknesses were used in these experiments and the results obtained are given in Tables VI(*b*) and VI(*c*).

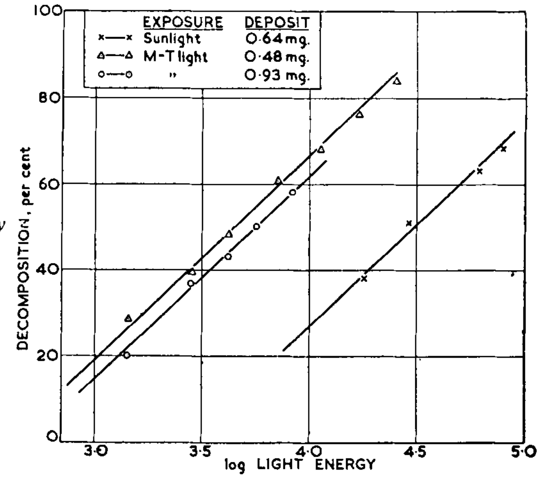

FIG. 4.—*Relation between the quantity of light energy and the extent of decomposition*

Table VI(*a*)

Date of exposure	Quantity of light, ft.-candle-hr.	Mean deposit, mg.	Coeff. of variation, %	Rotenone in residue, mg.	Decomposition, %
9 Feb., 1948 ..	18,000	0·612	2·2	0·375	38
10 Mar., 1948 ..	29,000	0·597	1·0	0·291	51
11 and 12 Mar., 1948	61,500	0·597	1·0	0·222	63
23–25 Mar. ..	81,000	0·510	3·4	0·162	68

Table VI(*b*)

Total no. of plates sprayed : 12
Mean deposit (4 plates) : 0·479 mg.
Coeff. of variation : 4·4%
Exposure : mercury–tungsten light source

Series no.	Time of exposure, hr.	Quantity of light energy ft.-candle-hr.	Rotenone in residue, mg.	Decomposition, %
1	1	1400	0·338	29
2	2	2800	0·288	40
3	3	4200	0·245	49
4	5	7000	0·185	61
5	8	11,200	0·155	69
6	12	16,800	0·113	76
7	17·75	24,850	0·070	84

Table VI(*c*)

Total no. of plates sprayed : 8
Mean deposit (3 plates) : 0·93 mg.
Coeff. of variation : 1·0%
Exposure : mercury–tungsten light course

Series no.	Time of exposure, hr.	Quantity of light energy, ft.-candle-hr.	Rotenone in residue, mg.	Decomposition, %
1	1	1400	0·74	20
2	2	2800	0·58	37
3	3	4200	0·53	43
4	4	5600	0·46	50
5	6	8400	0·39	58

These results confirm the observation made in the sunlight experiments that the rate of decomposition of rotenone in deposits bears a logarithmic relationship to the quantity of light energy received. Further, when these results are plotted along with those obtained in sunlight on the same graph (see Fig. 4), a very striking relationship is noticeable. The mercury–tungsten light source is five to six times more powerful than sunlight in causing the decomposition ; this ratio is maintained throughout the range of observations.

Derris deposits.—To determine the rate of decomposition of rotenone in derris deposits, similar experiments were conducted with derris deposits of two different thicknesses using the mercury–tungsten light source and the data obtained are shown in Tables VII(*a*) and VII(*b*).

Table VII(*a*)

Total no. of plates sprayed : 8
Mean weight of rotenone in deposit (3 plates) : 0·299 mg.
Coeff. of variation : 4·5%
Exposure : mercury–tungsten light source

Series no.	Time of exposure, hr.	Quantity of light energy, ft.-candle-hr.	Rotenone in residue, mg.	Decomposition, %
1	2	2600	0·234	22
2	3	3900	0·210	30
3	4	5200	0·198	34
4	6	7800	1·180	40

Table VII(*b*)

Total no. of plates sprayed : 9
Mean weight of rotenone in deposit (4 plates) : 0·773 mg.
Coeff. of variation : 2·2%
Exposure : mercury–tungsten light source

Series no.	Time of exposure, hr.	Quantity of light energy, ft.-candle-hr.	Rotenone in residue, mg.	Decomposition, %
1	2	2400	0·652	16
2	4	4800	0·584	25
3	6	7200	0·496	36
4	9	10,800	0·472	39

These results indicate that in derris deposits also the logarithmic relationship holds good. However, one thing noticeable from the results is that for equal exposures, decomposition in derris deposits is less than that in pure rotenone deposits. This aspect has been more carefully investigated by comparing both deposits under identical conditions, and the results will be reported in a subsequent communication.

Discussion

Deposits used in the present investigation were produced by the spray technique described previously (Subba Rao & Pollard, 1951) and the amount of rotenone varied between 0·3 and 1·4 mg. (area 61 sq. cm.). For most of the experiments deposits between 0·5 and 1·0 mg. were used. Although thinner deposits, whose rotenone content would probably correspond with those under field conditions, could be produced, limitations imposed by the analytical procedures prevented such a course being adopted. For a satisfactory leaching of the deposit, at least 10 c.c. of acetone is required and unless each c.c. contains 0·025 mg. the initial rotenone values would be so low that error in the analysis of residues would be rather high. The alternative is to concentrate the leachates to a smaller value before estimation of rotenone. It was considered that, unless complete information is available as to the changes that would be likely to take place on concentration of rotenone solutions, it would be undesirable to work with deposits containing less than 0·3 mg. rotenone.

Before subjecting a deposit from a batch of spraying to any treatment, the mean deposit obtained on any single plate during the spraying was determined. Plates for this purpose were selected at regular intervals to cover the entire range of spraying, so that the plates used for decomposition studies lie in between a set of plates whose deposits had been determined. This method of sampling of plates both for initial estimations and for exposure would eliminate to a large extent avoidable errors.

In the examination of derris deposits which contain, besides rotenone, rotenoids (which also give red colour in the Goodhue test), their rotenone equivalent was calculated from the red values obtained in the test, and all the calculations were based on this. Since toxicities of derris extracts were found by Jones, Campbell & Sullivan (1935) to be closely related to the red values obtained in the test, the extent of decomposition as measured by the decrease in red colour should represent the loss of toxicity.

By keeping the deposits in darkness either at ordinary temperatures (15–20° C.) or at slightly higher temperature (40° C.) no perceptible change was noticed. The effect of temperatures higher than 40° C. was not examined.

For the same total light energy, the three kinds of illumination used in the investigation decomposed the deposits to different degrees. The artificial light source built by combining two mercury-vapour discharge lamps and two tungsten gas-filled lamps was found to be more powerful than sunlight in causing decomposition; this may in all probability be due to the strong emission by the mercury lamp–tungsten lamp combination at 3650 A. (see Fig. 3). The The data obtained with the three Chance filters OX1, OB10, and OY4 indicate that light of wavelength beyond 5000 A. does not cause any decomposition and that light between 3000 and 4000 A. is mainly responsible for the decomposition. However, this requires confirmation by experiments conducted with light sources transmitting high percentage of radiation between 2800 and 3200 A. and with the aid of suitable filters; this range is suggested because rotenone exhibits maximum absorption at 2950 A. Our results do not agree with the report of Jones *et al.* (1933) that the ultra-violet region does not appear to be as effective as the visible violet.

Experiments conducted both in sunlight and in artificial illumination revealed that the extent of decomposition is dependent on the thickness of a deposit, decomposition being greater in thinner deposits. The data are not sufficient to allow any mathematical relationship to be deduced between the thickness of a deposit and its decomposition.

The rate of decomposition of rotenone and derris deposits bears a logarithmic relationship to the quantity of light energy (Fig. 4); this shows that the reaction is of the first order. Theoretically, photochemical reactions ought to be of zero order. Deviation from this had been reported by Gunther (1943) in his study of the decomposition of rotenone solutions. He, too, found that the decomposition was of the first order. A similar relationship is noticeable in the photochemical studies on alkali halides by Smakula (1930) and on silver halides by Hilsch & Pohl (1930). This decrease in the rate of decomposition with increase in light energy may be due either to decrease in the concentration of the reactants or to the dehydrorotenone formed, which is yellow in colour, preventing absorption of light of shorter wavelengths that cause the decomposition. The latter explanation seems to be more probable.

From the data obtained in sunlight experiments, it appears that a pure rotenone deposit loses almost all of its toxicity in five to six average spring days (total daylight illumination, 25,000 ft.-candle-hr.) or in two to three summer days (total daylight illumination, 50,000 ft.-candle-hr.). Deposits thinner than those used in these experiments (0·01 mg./sq. cm.) lose their toxicity more rapidly; but at the same time one has to take into consideration the fact that in field spraying or dusting, either pure rotenone or derris resin is not used as such. They are usually diluted with some inert material and applied as a suspension or as a dust. In such instances rotenone is not exposed direct to sunlight but is covered more or less by the diluent. Results of investigation on such dilute dusts will be reported later.

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THE INFLUENCE OF ENVIRONMENT UPON THE COMPOSITION OF SUNFLOWER SEED OILS. III.—Oils from Sunflower Seeds grown in Different Regions of Australia

By R. E. BRIDGE, A. CROSSLEY and T. P. HILDITCH

Seeds grown in field trials of several varieties of sunflowers in diverse regions of the Australian Commonwealth have been examined in regard to the composition of their fatty oils. The results have shown close parallelism with similar studies (Barker & Hilditch, 1950*a*) of African sunflower seeds in that there is great variation in the proportions of linoleic and oleic acids in the oils from different localities. Seed grown in the Northern Territory gave oils of quite low linoleic content (31–36%) which would be exceptionally suitable in the edible fat industries. Those from the most southerly latitudes, on the other hand, contained 65% or more of linoleic acid and would be of interest to the paint trade. Seeds from intermediate latitudes, such as New South Wales and Queensland, contained oils of the more usual type with 50–60% of linoleic acid in their component acids.

Introductory

In Part I of this series (Barker & Hilditch, 1950*a*) the wide variations in the composition of sunflower seed oils from sunflowers grown in different parts of the African continent were reviewed. It became clear that varietal differences in the seed from which the plants were grown had little to do with the nature of the oil in the seed produced. On the contrary, the same strain of seed when grown, for example, in Southern Rhodesia, Tanganyika and Zanzibar produced seeds the oil in which was completely different in its contents of oleic and linoleic acids, the latter ranging from 72% to as low as 20% of the total fatty acids. The main influence which affected the composition of the oils appeared to be the rate of development of the ripening seed: slow development (relatively cool climatic conditions) favoured high proportions of linoleic glycerides in the seed oil, and conversely. This conclusion was reinforced by the result of growing five of the types of African-grown sunflower seeds of widely differing composition