argument used was a sound one. He eliminated the possibility of two hydrogen atoms falling close to one another, on the ground that they repel. It appears likely here that he overlooked the possibility that the CH_3-$(CH_2)_7$- and the -$(CH_2)_7$-COOH groups might also repel, and overshadow the natural repelling action of the two hydrogens to such an extent as to actually reverse the process. The data of this paper supports such a view. In addition it is possible to reconcile the work of Bertram and Kiperman (10) if we recall that the acids, and possibly the potassium salts as well, associate in pairs (30). The resemblance between stearic and the cis isomer oleic, then becomes clear, a condition not existing were oleic the trans compound.

An examination of the Raman data on the a and β linoleates shows them to be identical, a conclusion reached by one of us (20) on purely chemical grounds and since supported by the work of Riemenschneider, Wheeler and Sando, (19) and by Kass and Burr (17).

The Raman lines for ethyl linoleate and ethyl linelaidate, Table 1, show a heavy intense polarised line at approximately 1,657 cm^{-1} in both compounds and a weaker depolarised line 15 units lower than the main frequency line for the linoleate and 12 units higher for the linelaidate. This symmetrical structure leads one to believe that the elaidic reaction reverses not one, but both bonds. From chemical considerations, it would be hard to conceive of only one bond being isomerized under the drastic conditons of the reaction, a point of view supported by the work of Hilditch and Jasperson (15). Therefore if lineoleic were cis-trans or trans-cis, the elaidic form would also be trans-cis or cis-trans. However, it can be demonstrated that all four of these compounds should exhibit infra red absorption at wave length 6.0 μ. From Fig. 2, it is seen that ethyl linoleate is strongly absorbing, while ethyl linelaidate does not absorb infra red radiation to any extent. It is concluded therefore that these compounds are not cis-trans or trans-cis isomers but must be cis-cis and trans-trans. From the strength of the infra red absorption in the two cases, it is concluded that ethyl linoleate is cis-cis while the linelaidate is trans-trans. The intensity of the Raman line at frequency 3,012 and 3,009 cm^{-1} lends additional support to the above conclusion.

Ethyl linolenate is strongly absorbing in the infra-red, Fig. 2, has a single strong polarised frequency at 1,656 cm^{-1} and an intense line at frequency 3,013 cm^{-1}. It is concluded therefore that this compound is undoubtedly cis-cis-cis. The fact that it has no dopolarised lines may be attributed to its symmetrical character.

Summary

Infra-Red and Raman spectroscopic examination of the unsaturated C_{18} fatty acids leads to the conclusion that the naturally occurring acids such as oleic, linoleic and linolenic contain only cis double bond linkages, while the artificial elaidic and linelaidic acids contain only the trans linkages.

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The Insecticidal Properties of Some Fatty Acid Derivatives

A. W. RALSTON, J. P. BARRETT and E. W. HOPKINS

RESEARCH LABORATORY, ARMOUR AND CO., CHICAGO, ILL.

Introduction

The high cost of pyrethrum, uncertainty of supplies, and unsuccessful attempts to grow the crop commercially in this country have given considerable impetus to the search for new insecticidal compounds. The fatty acid derivatives present a logical and promising field for such an investigation. The fats themselves, such as whale oil, fish oil, peanut oil, palm oil or cottonseed oil, have been employed for the control of scale insects on plants and have been used in a number of cases as fungicides. The latter use has been rather extensively investigated by Martin and Salmon (1). The soaps are frequently used as the emulsifying and spreading agents for insecticides and less generally as the toxic principle. The activity varies somewhat with the particular type of insect used in the test; however, it is generally found to be at a maximum with the soaps of capric, lauric, and myristic acids. Tattersfield and Gimingham (2) stated that the toxicity of soap is due to the free acid liberated by hydrolysis. Fleming and Baker (3) found potassium myristate to be effective against the Japanese beetle. Ginsburg and Hunt (4) observed that certain fatty acids are injurious to plant tissues. Soaps and oleic acid are generally more toxic to insects than those of stearic acid. Metallic soaps, such as copper oleate, have been frequently used for the control of various fungus diseases, and since the soaps of the heavy metals are oil soluble, they are generally applied in a hydrocarbon solvent.

While the simpler fatty derivatives, such as the soaps of fatty esters, have been extensively employed, either as the toxic agent or as the wetting and spreading agent, to increase the effectiveness of known toxic agents, such as nicotine, their use has been limited to plant insecticides. Because of obvious limitations, the soaps and fatty esters cannot be considered as indicated for the usual type of household insecticide. It is the purpose of this paper to study the insecticidal properties of representative fatty derivatives and to attempt to correlate toxic action to insects to the type of polar group or groups present in the compound. An attempt will also be made to determine the effect of the chain length upon toxicity in any series of compounds shown to possess appreciable insecticidal properties.

The insect toxicity experiments reported in this paper are confined to the common house fly, Musca domestica, although considerable preliminary work was done upon two common species of roach, Blattela germanica and Periplaneta americana, as well as the black carpet beetle, Attagenus piceus. The flies used were reared in the laboratory under carefully controlled conditions of temperature and relative humidity.

Test Procedure

A modified Peet-Grady chamber was used in all of the tests. The chamber (30″, 30″, 30″ inside dimensions) was of wooden construction lined throughout with tin and was practically air tight. The insecticide was introduced into the chamber by a De Vilbiss No. 16 atomizer operating under four pounds air pressure. The spray chamber was maintained at 85° F. and 64% relative humidity.

One cage containing approximately five hundred three- to five-day old flies was placed in the center of the spray chamber, the door clamped into place, the atomizer inserted into the door, and the air pressure applied. In order to effect an even distribution of the spray throughout the chamber, the nozzle of the atomizer was swung horizontally during the run-out of the liquid. Since the spray has access to the confined flies only through the two screened sides of the cage, it was necessary to determine the quantity of Official Test Insecticide required to obtain a fifty per cent kill in twenty-four hours. By a series of tests, it was found that this kill with O. T. I. was obtained with 38 cc., and this amount was used in all of the tests.

The 38 cc. of test solution required about five minutes for the run-out when four pounds air pressure was used, after which time the atomizer was removed and the aperture stoppered. The chamber was opened after ten minutes and the cage containing the flies removed and the number of flies knocked down determined. All of the flies were then transferred to a clean cage which contained a ball of cotton soaked in a dilute sugar solution, and the cage was removed to the culture room to await the twenty-four hour kill count.

At the end of twenty-four hours the dead flies were removed from the cage and counted. Only flies which showed no signs of life upon being touched were counted as dead. The live flies were killed by placing the cage in the freezer at —20° F. for two minutes and were then counted. The number of paralyzed flies, dead flies and live flies gave the total number of flies in the test unit. The twenty-four hour kill counts are adjusted on the basis of a fifty per cent kill with the Official Test Insecticide in order to take into account the variability of fly resistance, and also the fact that the proportionality of per cent kill to concentration of insecticide decreases as the percentage of kill approaches one hundred.

Insecticidal Value of Fatty Acid Derivatives

With the exception of the esters the most common fatty acid derivatives are the ketones, aldehydes, nitriles, amides, alcohols and amines. Our work was initiated by a study of the insecticidal value of at least one representative member of each of these series in order to correlate insecticidal activity with the particular functional group present in the molecule. Five per cent solutions of the various fatty acid derivatives in a highly refined kerosene, Deobase, were prepared and tested as previously described. Table 1 shows the toxicity of some fatty acid derivatives to Musca domestica.

TABLE 1

Toxicity of Some Fatty Acid Derivatives to Musca domestica (5% solutions in Deobase)

Compound	% Knockdown (10 min.)	% Kill (24 hrs.)
Dodecyl Alcohol	3	51
Lauronitrile	17	60
Lauraldehyde	0	5
Caprylaldehyde	0	24
Caprone (Dihexyl Ketone)	0	27
Lauramide 1%	0	7
Octyl Amine	100	97
Dodecyl Amine	50	81

The results shown in Table 1 indicate that the fatty alcohols, nitriles, aldehydes, ketones and amides are not sufficiently toxic to flies to warrant further consideration. The toxicity of octyl and dodecyl amines shows that the amino group exerts a very definite lethal effect. In view of these results a rather complete study was made of the insecticidal value of various high molecular weight amines and their simple derivatives.

The aliphatic amines can be considered as alkyl substituted ammonias and are classed as primary, RNH_2; secondary, R_2NH, and tertiary amines, R_3N, depending upon whether one, two or three hydrogen atoms are replaced by alkyl groups. The secondary amines have much higher boiling points and somewhat higher melting points than the primary amines. The toxicity of a number of primary, secondary and tertiary amines and also of some amine salts is shown in Table 2. The solvent used in all cases was Deobase and the test solution contained five per cent of amine by weight unless otherwise indicated. The amount of solution used was 38 cc. and the manner of conducting the test and the tabulation of the results were as previously described.

TABLE 2

Toxicity of Amines and Amine Salts to Musca domestica

Amine	% Knockdown	% Kill
Primary		
Hexyl	99	90
Octyl	100	97
Decyl	99	98
Dodecyl	50	81
Octadecenyl	0	41
Secondary		
Dipropyl	96	67
Dibutyl	100	83
Dihexyl	100	89
Dioctyl	100	98
Didecyl	76	81
Didodecyl	0	40
Methyldodecyl	0	2
Methyl 2-ethylhexyl	100	60
Tertiary		
Trioctyl	0	33
Amine Salts 1%		
Aniline Caproate	0	4
Pyridine Caproate	0	4
Pyridine Laurate	0	4
Hexylamine Caproate	0	2
Hexylamine Laurate	0	6
Dihexylamine Caproate	0	33

Table 2 shows that the highest per cent knockdown and kill with the primary amines is obtained with octyl and decyl amine. Hexyl amine gives a high knockdown but is less lethal to flies than either octyl or decyl amine. The two higher molecular weight primary amines examined, dodecyl and octadecenyl amine, are much less active. Since the primary amine solutions are irritating to the nose and throat, their use would be limited to agricultural or cattle spray.

The insecticidal properties of the secondary amines, as shown in Table 2, are of interest. The percentage kill increases from dipropyl to dioctyl amine and then decreases rapidly. Methyldodecyl amine is essentially without activity. The high knockdown and killing power of dioctyl amine indicates that this compound has a possible commercial application in view of the fact that solutions of the secondary amines above dihexyl amine are not irritating when sprayed and are free of objectional odors.

Trioctyl amine, the only tertiary amine examined, possessed no paralyzing effect and a low kill which indicate that the higher molecular weight tertiary amines are not comparable with either the primary or secondary amines as insecticides. The amine salts which were investigated showed no paralyzing action and low kills, indicating the superiority of the free amines over the salts when used for this purpose. Other work has shown, however, that water solutions of some of the amine salts are quite effective against certain insects.

Evaluation of Dioctyl Amine as a Contact Insecticide

A series of solutions of dioctyl amine in Deobase was prepared, the concentration of dioctyl amine varying from one per cent in the most dilute solution to five per cent in the most concentrated. These were then compared against the Official Test Insecticide for the killing of flies by the method previously described. The results obtained are summarized in Table 3. The figures shown represent averages of approximately thirty tests of from five to six hundred flies each.

The results tabulated in Table 3 show that dioctyl amine in concentrations of four per cent or higher in Deobase is a highly effective insecticide. Tests performed upon other insects, such as roaches, carpet beetles and mosquitoes, have verified these conclusions.

TABLE 3

Toxicity of Dioctyl Amine to Musca domestica

38 cc. Official Test Insecticide			38 cc. $(C_8H_{17})_2NH$ in Deobase		
% Knockdown (10 Min.)	% Kill (24 hrs.)	% $(C_8H_{17})_2NH$ in Deobase	% Knockdown (10 Min.)	% Kill (24 hrs.)	Adjustment to 50% O.T.I. Kill
95	54	1.0	61	35	31
94	52	2.0	77	49	47
94	54	2.5	84	60	56
95	54	3.0	91	75	72
95	58	3.5	95	85	80
97	56	4.0	96	93	91
96	56	4.5	99	96	95
95	58	5.0	99	98	97

Toxicity of Dioctyl Amine to Warm Blooded Animals

A series of inhalation toxicity studies was made with rabbits in which a 5% solution of dioctyl amine in Deobase was compared with the Official Test Insecticide. These inhalation tests demonstrated that neither 5% dioctyl amine in Deobase or pyrethrum (Official Test Insecticide—5% pyrethrum extract—0.125% pyrethrins in Deobase) cause any toxic effects when the animals are subjected to spray mists in excessive concentration as high as ten times the usual spray mists applied in commercial insecticide applications. While slight skin irritation was found in rabbits thus treated, the same irritation was produced in rabbits exposed to mists of the Deobase alone.

Summary

The insecticidal properties of a number of fatty acid derivatives have been investigated, and it was found that certain primary and secondary amines were highly lethal to the common house fly, Musca domestica.

Of the primary amines examined, octyl and decyl amine possessed the highest insecticidal activity; however, they were considered to be somewhat irritating for general use. Dioctyl amine was found to be the most active of the secondary amines examined. In view of its exceptionally high paralyzing and killing power for insects and its comparatively non-irritating properties to humans, together with its absence of toxicity to domestic animals, it can be considered as a possible substitute for pyrethrum.

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