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Chemical Constitution and Insecticidal Action

1. ORGANIC SULPHUR COMPOUNDS

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Until the discovery of the newer synthetic insecticides of the chlorinated hydrocarbon class, such as DDT and γ -benzene hexachloride, organic compounds of sulphur had attracted considerable attention, and this work led to the commercial introduction of the long-chain alkyl thiocyanates, to phenothiazine (originally as an insecticide but later developed as an anthelmintic) and more recently to tetraethylthiuram sulphide, an acaricide used in the treatment of scabies and mange. During the last ten years we have made an extensive investigation of the insecticidal action of organic sulphur compounds, in collaboration with the Hawthorndale Laboratory of Jealott's Hill Research Station (Imperial Chemical Industries Ltd.) where the entomological testing was carried out. Although these investigations did not result in the introduction of any new commercial insecticides, nevertheless, marked insecticidal activity was found in certain types, and the correlation of structure with activity presented points of considerable interest. It is the purpose of this communication to record some of our observations on this subject.

METHODS

All compounds were submitted to routine sorting tests, and from the results the more promising were selected for extended evaluation. The extended tests necessitated the preparation of a variety of types of emulsions and dispersions (Collie, Ellingworth & Robertson, 1939; Collie,

Davies & Sexton, 1939; Harland & Sexton, 1943) suitable for the practical application of the poisons. This aspect of the research is mentioned only so far as it provides data confirming the higher activities found by the sorting tests and illustrates the selective poisoning effect on insect species.

Contact insecticides. The sorting tests were carried out in the Tattersfield spraying apparatus using aphids (*Macrosiphum* spp. except where otherwise stated, the choice of species being governed by its availability at the time of the test), or adult blowflies (*Calliphora erythrocephala* Meig.) as the test insects. The compound to be tested was dissolved in ethanol, and poured into a 0.1% aqueous solution of a surface-active agent of the sulphonated hydrocarbon type, the concentrations being such that the final spray contained the substance dispersed in 50% ethanol. In certain instances it was necessary to use acetone instead of ethanol. As it was appreciated that the organic solvent might play a significant part in the apparent toxicities, controls were carried out with sprays of similar composition from which the poison had been omitted; the 'absolute mortality' due to the substance under test was calculated by the formula:

Percentage absolute mortality

$$= \frac{\begin{array}{l} \text{(number killed by poison spray)} \\ - \text{(number killed by control spray)} \end{array}}{\begin{array}{l} \text{(total number of insects)} \\ - \text{(number killed by control spray)} \end{array}} \times 100.$$

In spite of this adjustment, the ethanol may have played a part in altering penetration of the insect cuticle by the poison (Hurst, 1943) so that the figures of 'absolute mortality' obtained may have been, considered as absolute values, false. It is felt, however, that for closely related

Table 1. *Insecticidal activities of 2-alkylthiobenzthiazoles*

Alkyl group (R, formula I)	Percentage absolute mortality		
	Blowflies at 0.5%	Aphids (<i>Macrosiphum</i> spp.) at 0.2%	<i>Sitophilus granarius</i> (biscuit method)
H	13*	—	0
CH ₃	100	86	99.4
C ₂ H ₅	100*	21	100
C ₃ H ₇ †	100	30	23.3
C ₄ H ₉	96	17	2.7
C ₅ H ₁₁	41	3	0
C ₇ H ₁₅	37	0	7
C ₈ H ₁₇	—	9	0
C ₈ H ₁₇ (sec.)	—	17‡	0
C ₁₂ H ₂₅	4	45	0
C ₁₆ H ₃₃	0*	17	0
(CH ₃) ₂ CH	100*	24	50
(CH ₃) ₂ CHCH ₂	92*	86	7
C ₅ H ₁₁ (iso)	—	17	—
CH ₂ :CHCH ₂	99*	52	13.6
C ₆ H ₅ CH ₂	62*	6	10.5
HOCH ₂ H ₄	18*	—	83§
C ₂ H ₅ OC ₂ H ₄	86*	30‡	—
Standards: Rotenone	100*	100	—
Lead arsenate	—	—	58.1
C ₁₂ H ₂₅ SCN	100	100	—

* Sprays contained 25% acetone instead of 50% ethanol.

† C₃H₇, C₄H₉, C₅H₁₁, etc., indicate primary straight-chain alkyl radicals unless otherwise stated.

‡ Against *Doralis ruficis* L. (= *Aphis rumicis* L. (*fabae* Scop.)) in place of *Macrosiphum* spp.

§ Lead arsenate in this experiment gave 88.7% absolute mortality.

groups of compounds such as those examined the 'absolute mortality' figures give a reasonably adequate comparison of the toxicities of individual members of such groups. That the toxicities were genuine was later shown by the examination of special preparations of the more active compounds.

Stomach poisons. The sorting tests were carried out against *Sitophilus granarius* L. (grain weevils) by a technique known as the 'biscuit' method. One part of the poison was mixed with 50 parts of flour and the whole made into a dough with 30 parts of water; the dough was dried in thin layers and broken up to provide 'biscuits' on which the insects were allowed to feed. Lead arsenate, similarly compounded, was used as a standard of comparison.

RESULTS

Tests on *S*-alkylated derivatives of 2-thiolbenzthiazole and 2-thiolquinoline

The contact insecticidal activity of alkyl thiocyanates (Bousquet, Salzberg & Dietz, 1935) prompted the exploration of other compounds containing the sequence of atoms —S—C—N—, and derivatives of types (I) (Collie, Ellingworth & Robertson, 1939) and (II) (R = alkyl) were therefore investigated. Preparative methods for type (II) have been described elsewhere (Sexton, 1939; Reed, Robertson & Sexton, 1939). (The numbering of the benzthiazole ring is indicated in formula (I).) The results of the preliminary tests with the *S*-alkylated derivatives (I) are given in Tables 1 and 2. Against blowflies, toxicity is at a maximum at C₃ in the

normal series: for aphids, the methyl and *isobutyl* compounds were the most toxic, the normal C₅ to C₈ compounds being practically inactive. There was,

however, appreciable activity with the *isooctyl* and *dodecyl* derivatives, but the *hexadecyl* was again inactive. For the grain weevil there was a marked fall in toxicity after the methyl, ethyl and β -hydroxyethyl compounds.

Table 2. *Effect of concentration on toxicity to blowflies of aqueous acetone dispersions of homologous 2-alkylthiobenzthiazoles*

Alkyl group (R, formula I)	Percentage absolute mortality Concentration (%)				
	0.5	0.3	0.15	0.075	0.05
CH ₃	100	98	34	10	—
C ₂ H ₅	100	94	49	16	—
C ₃ H ₇	100	99	85	10	—
(CH ₃) ₂ CH	—	—	18	—	0
(CH ₃) ₂ CHCH ₂	—	—	13	—	0
CH ₂ :CHCH ₂	—	—	40	—	23
Rotenone	—	—	—	—	100

2-Ethylthiobenzthiazole, because of its toxicity to blowflies, was subjected to further evaluation. Its insecticidal effect was confirmed by the following findings in separate experiments: (a) a 40 % solution in odourless kerosene gave a 68 % kill when sprayed on houseflies (*Musca domestica* L.), (b) emulsified preparations gave kills of 64–98 % at the same strength, (c) a 2 % solution in kerosene gave a 81 % kill of mosquito larvae, and (d) there was moderate toxicity to bedbugs (*Cimex lectularius* L.).

The effect of substitution in the benzene ring was examined in the cases of the 2-alkylthio derivatives (C_1 to C_4) of 6-amino-, 6-nitro- and 5-chloro-benzthiazoles. The results will not be given in detail, but the general effect was a reduction in insecticidal activity, which was least marked in the case of the chloro compounds, against blowflies.

Tests with S-alkylated derivatives of 2-thiolquinoline and of 2-thiolbenzoxazole

The chemical similarity between thiazole and the corresponding pyridine derivatives suggested that this might also extend to their biological action. Accordingly several quinoline derivatives, analogous to the benzthiazole derivatives already examined, were tested against the standard insects. The results, which are not given in detail, showed that the general order of toxicity was lower than for the isosteric thiazole compounds. A notable feature was that, whereas alkylation of the thiol group in the 2-thiol-benzthiazole series raised the toxicity to the grain weevil, a reduction occurred with the quinoline compounds. The results with the other isosteric series, the benzoxazoles, showed, among the limited number

Table 3. *Insecticidal activity of alkylated benzthioazole derivatives*

Compound	Percentage absolute mortality						<i>Sitophilus granarius</i> *
	Blowflies		<i>Doralis rumicis</i>		<i>Doralis pomi</i>		
	(0.5 %)	(0.2 %)	(0.2 %)	(0.1 %)	(0.2 %)	(0.1 %)
100	73	11	8	32	—	99.4 (58.1)
0	13	73	55	100	73	11.5 (82.3)
„ (R = C ₂ H ₅)	12	—	70	—	—	—	27.1 (82.3)
„ (R = C ₃ H ₇)	7	—	0	—	—	—	16.7 (67.7)
„ (R = C ₅ H ₁₁)	0	—	10	—	—	—	8.3 (67.7)
25	—	20	—	—	—	90.5 (82.3)
„ (R = C ₂ H ₅)	12	—	70	—	—	—	—

The following had very low toxicities both as contact insecticides and stomach poisons:

* The figures in brackets in this column give the percentage absolute mortality with a lead arsenate bait.

of compounds examined, results parallel to those obtained with the benzthiazole derivatives in that blowflies and grain weevils were more susceptible than aphids.

*Tests with N-alkylated derivatives
of 2-thiolbenzthiazole*

The tests in this series were confined to the lower *N*-alkylated derivatives of type (II) which were readily obtainable by methods already mentioned. An important difference in the relative susceptibility of different insects to the isomeric *S*- and *N*-alkylated pairs was revealed, for whereas the *S*-alkyl derivatives had low toxicity to aphids and high toxicity to blowflies, the *N*-methyl compound, which received the most study, was highly toxic to aphids and relatively non-toxic to blowflies. The results with these and related compounds are summarized in Table 3. In the *N*-alkyl series, the lowest member was the most active aphicide. It will be seen from Table 3 that replacement or interchange of >S, >O and >NH groups could exert marked effects, and the *S* derivative was not always the most toxic.

The aphicidal properties of the *N*-methyl compound, 2-thio-3-methylbenzthiazolone, were investigated thoroughly, and clear evidence was obtained that the activity was not due to the ethanol in the spray; indeed this may even have lowered the aphicidal activity. A concentrated emulsion was prepared by dissolving 10 parts of 2-thio-3-methylbenzthiazolone in 55 parts of cottonseed oil and emulsifying with 25 parts of water with the aid of 10 parts of a sulphonated cod oil. This emulsion, diluted with 0.1% 'Agral' Liquid Wetter, was sprayed on plants infested with several species of aphids. High kills of the insects were obtained, sometimes even at spray concentrations of less than 0.025% active ingredient. Other emulsions gave similar results. The aphicidal activity was, however, generally lower than that of dodecyl thiocyanate, and the practical utilization of this compound was limited by occasional damage to plants.

Tests on carbamates and thiocarbamates

An obvious extension of the types of compound containing adjacent S, C and N atoms was to derivatives of dithiocarbamic acid. Since, moreover, interchange of sulphur and oxygen in this class had not led to marked alterations in fungistatic activity (Davies & Sexton, 1946), or even to a more limited extent in selective herbicidal activity (Templeman & Sexton, 1946), a comparison of the insecticidal activity of carbamates and thiocarbamates was necessary. The results of contact tests are given in Table 4. As stomach poisons against *Sitophilus granarius* nearly all were less toxic than lead arsenate.

Table 4. *Contact insecticidal activity of derivatives of carbamic acid*

Compound	Percentage absolute mortality	
	Blowflies (0.5%)	Aphids (0.2%)
$C_6H_5NH.COOCCH_3$	58	4 (a)
$C_6H_5NH.COOC_2H_5$	87	0 (a)
$C_6H_5NH.CSOCH_3$	96	23 (a)
$C_6H_5NH.COSCH_3$	81	0 (a)
$C_6H_5NH.COSC_2H_5$	100	4 (a)
$C_6H_5NH.CSOC_2H_5$	92	86 (b)
$C_6H_5NH.CSOC_4H_9$	55	11 (b)
$C_6H_5NH.CSSCH_3$	31	0 (a)
$C_6H_5NH.CSSC_2H_5$	76	28 (a)
$C_6H_5NH.CSSC_4H_9$	84	45 (a)
$C_6H_5NH.CSSCH_2C_6H_5$	57	0 (a)
$C_6H_5(CH_3)N.COOCCH_3$	2	0 (b)
$C_6H_5(CH_3)N.COOC_2H_5$	40	6 (b)
$C_6H_5(CH_3)N.CSSCH_3$	9	17 (b)
$C_6H_5(CH_3)N.CSSC_2H_5$	0	56 (b)
$C_6H_5(C_2H_5)N.COOCCH_3$	16	23 (b)
$C_6H_5(C_2H_5)N.COOC_2H_5$	59	0 (b)
$C_6H_5(C_2H_5)N.CSSCH_3$	28	27 (b)
$C_6H_5(C_2H_5)N.CSSC_2H_5$	6	24 (b)
$(CH_3)_2N.COOCCH_3$	0	6 (b)
$(CH_3)_2N.COOC_2H_5$	0	3 (b)
$(CH_3)_2N.CSSCH_3$	—	3 (b)

(a) *Macrosiphum* spp. (b) *Doralis rucicis* L.

Tests on thiocarbimide (isothiocyanate) derivatives

The insecticidal activity of thiocyanates differs from that of the corresponding thiocarbimides (*isothiocyanates*), just as does the fungistatic activity. Though dodecyl thiocyanate is a powerful contact insecticide, the corresponding *isothiocyanate* is much less active: experiments with bedbugs and houseflies have shown that it is almost without action on these insects.

In the aromatic series, the thiocarbimides are powerful insecticides (Goldschmidt & Martin, 1937), and the α -naphthyl compound has been developed commercially as a fly spray. The starting point for the results recorded here was phenylthiocarbimide. During a search for new compounds having a high toxicity to locusts, it was observed that this substance was highly toxic when used in a poison bait, but its volatile nature precluded its practical application. Attention was, therefore, directed to less volatile derivatives which might be expected to break down to phenylthiocarbimide *in vivo*, and the reaction products of phenyldithiocarbamic acid with formaldehyde and ammonia or primary amines, the so-called 'carbothialdines', were studied in some detail. During the course of this work their constitution as reduced thiadiazines (III) was established (Ainley, Davies, Gudgeon, Harland & Sexton, 1944). The first substance examined was 'phenylmethylene carbothialdine' ($R=H$, $R'=C_6H_5$), which was obtained as an amorphous powder by treating ammonium phenyldithiocarbamate with formaldehyde under controlled conditions. The crude pro-

duct, which could not be purified because of its instability, proved highly toxic to locusts. More stable, crystalline compounds of the same type were obtained by using primary amines in place of ammonia, thus giving 'carbothialdines' in which R = alkyl: the preparation and properties of these compounds are described elsewhere (Ainley *et al.* 1944; Gudgeon, Harland & Sexton, 1943). In testing as locust poisons, the substances were ground with

an equal weight of talc, and the resulting 50 % dusts were made into baits by mixing with bran, molasses and water in the proportions 1 : 56 : 2 : 84. Locusts (*Locusta migratoria migratorioides* R & F. 3rd instar hoppers) were allowed to feed on the mixtures, and the mean mortality determined after 20 hr.: a similarly compounded sodium arsenite bait was used as a standard. The results with a series of compounds (Table 5) showed that substitution in the phenyl

Table 5. Toxicity of compounds of formula (III) to locusts

Constitution		Mean percentage mortality after 20 hr. (sodium arsenite = 8 %)
R'	R	
C_6H_5	CH_3	100
	C_2H_5	7
	C_3H_7	100
	C_4H_9	53
	$(\text{CH}_2)_5\text{CHCH}_3$	68
	cyclohexyl	<10
	$\text{C}_2\text{H}_4\text{OH}$	100
	$-\text{CH}_2\text{CH}_2-$ *	98
$(p)\text{CH}_2\text{C}_6\text{H}_4$	$-(\text{CH}_2)_6-$ *	<10
	CH_3	88
	CH_3	62
	CH_3	<10
CH_3	CH_3	88
	C_2H_5	74
	$-\text{CH}_2\text{CH}_2-$ *	<10
	C_2H_5	74

* These are double molecules comprising two heterocyclic nuclei united by the divalent group R .

group reduced the toxicity, and that the nature of the group R also had a marked effect. The result with the second compound in Table 5 appears anomalous. Further tests, in which the amount of poison in the bait was reduced showed that no compound was more toxic than (III) ($R = \text{CH}_3$, $R' = \text{C}_6\text{H}_5$). This was next evaluated against different insects, when it was observed to be highly toxic to crickets and to the large white cabbage butterfly caterpillar (*Pieris brassicae* L.). It was of low toxicity to winter

moth larvae (*Operophtera brumata* L.), and non-toxic to the diamond back moth (*Plutella maculipennis* Curt.) and to aphids. This compound, therefore, provides another outstanding example of selective insecticidal action.

The relative susceptibility of different insect species

The previous tables show that individual compounds have considerable selective insecticidal action against aphids or blowflies. This is characteristic of organic compounds, not only when employed as contact insecticides, but also, as can be seen from the rapidly growing literature on the subject, in their antibacterial, antiprotozoal, fungicidal and herbicidal activities. It is further illustrated in the case of insecticidal action by the figures in Table 6 where stomach poison tests are considered. The first three columns refer to tests by the 'biscuit' method, and the last five columns to tests in which various insect larvae were allowed to feed on foliage sprayed with dispersions of the insecticides. In these tests the mortality by lead arsenate, which was used as a standard of comparison, was 100 % unless otherwise indicated by a figure in brackets. An outstanding example of this selective toxicity is the first compound in the list, 2-methylthiobenzthiazole, which was very toxic to *Sitophilus granarius*, *Ephestia kühniella*, vanessids and *Hypocrita jacobaeae*, but relatively non-toxic to *Corcyra cephalonica* and *Operophtera brumata*.

DISCUSSION

Läuger, Martin & Müller (1944) have put forward the hypothesis regarding contact insecticidal action that the molecule should contain a grouping responsible for its toxic action, and a 'carrier' grouping conferring lipid solubility enabling the compound to pass through the fatty and lipoprotein layers of the insect cuticle. It is of interest to examine this hypothesis further, particularly in the light of the results now recorded. As Läuger *et al.* (1944) point out it is difficult to decide in complicated molecules such, for example, as the pyrethrins, which part represents the toxic grouping and which the lipophilic carrier. We would prefer to speak of (a) the chemically functioning group or groups of the molecule, and (b) the physico-chemical properties, for example, of lipid and water solubility, surface activity, etc. of the molecule as a whole. By chemically functioning group is meant the group which is responsible for attachment to cell constituents. The force of attachment may not be strong in absolute terms, but if the union is of sufficient stability to disturb a delicate balance of dynamic biochemical processes then biological activity may result. This conception of the dual contribution towards biological activity should not be applied too rigidly for the two factors may, to

Table 6. *Percentage absolute mortality (stomach poison tests) by several compounds against different insect larvae*

Compound	Tests by 'biscuit' method			Tests on foliage			
	Flour moth (<i>Ephestia</i> <i>kühniella</i> Zell.)	Rice moth (<i>Coryra</i> <i>cephalonica</i> Staint.)	Grain weevil (<i>Sitophilus</i> <i>granarius</i> L.)	Winter moth (<i>Operophtera</i> <i>brumata</i> L.)	Small tortoise- shell (<i>Aglais</i> <i>urticae</i> L.)	Peacock (<i>Nymphalis</i> <i>io</i> L.)	Diamond back moth (<i>Plutella</i> <i>maculipennis</i> Curt.)
	100 (25.1)*	26.5 (38.7)	99.4 (58.1)	13.8	100	100	—
	81 (25.1)	—	100 (58.1)	19.5	100	91	74.7
	23.1 (20.6)	—	83 (38.7)	—	—	0	7.1 (27.1)
	—	—	95.2 (13)	—	—	0	—
	—	—	0.7 (66.6)	—	—	—	9.3 (27.1)
	—	—	—	44.5	—	2.2	—

* Mortality with lead arsenate (see text).

some extent, be interdependent. The chemically functioning groups may have their contribution to make towards physical properties, particularly when the lesser interatomic forces such as those of the hydrogen bond are concerned. Physical causes may predominate in insecticidal action, and in these instances certain characteristic effects can be observed. These have been considered in relation to biological activity generally on a thermodynamic basis by Ferguson (1939), and they include the effects on variation in homologous series, including the peak effect noted in the aphicidal properties of alkyl thiocyanates, and in several instances reported in this paper. Another characteristic manifestation of physical mechanisms is the varying response of different biological species (cf. Ferguson, 1939) to the same compound. Marked specificity of insecticidal action is recorded in this paper. This is probably a more general effect of organic insecticides than has been realized, for the more potent contact insecticides are usually used at such high strengths relative to their absolute potency that selective effects may be obscured. The chemically functioning groups in the compounds reported here are not identical, although the compounds nearly all contain the sequence of atoms —S—C—N— . In the powerfully insecticidal aliphatic thiocyanates, the critical feature of the molecule is probably the ability of the carbon atom of the —SCN group to accept electrons (Hoggarth & Sexton, 1947). In the 2-alkylthiobenzthiazoles and the isomeric *N*-alkyl compounds, on the contrary, donation of electrons would appear to be the characteristic function leading to chemical reactivity, for they readily give addition compounds with bromine and with copper salts. Much more drastic experimental conditions are required for other types of reactions, for example, hydrolysis, requiring electron accession to the carbon atom. As already mentioned, the cyclic type of compound (III) is believed to act through conversion to the aryl thiocarbimide which in turn reacts with a cell constituent. Although there is no conclusive evidence for this breakdown *in vivo*, the conception is supported by the finding (hitherto un-

published) that the fungistatic activity of compounds of type (III), in which substituents in the aryl nucleus are varied, exactly parallels that of the corresponding thiocarbimides (Davies & Sexton, 1946).

It is to be noted that the interchange of oxygen and sulphur in the carbamates (Table 5) has minor effects which might well be ascribed to no more than the differences in physical properties. The same absence of major effect on substitution of oxygen for sulphur was observed in the fungistatic activities of these substances (Davies & Sexton, 1946).

SUMMARY

1. The toxicities by contact and by stomach action of organic sulphur compounds of the following classes to various insects are recorded: benzthiazole derivatives and related quinoline and oxazole compounds, thio- and dithio-carbamates, substituted thiadiazines ('carbothialdines').

2. There is a marked selectivity in the action of the various substances against different insect species. Marked contact aphicidal activity is shown by 2-thio-3-methylbenzthiazolone (II, $R = \text{CH}_3$) and high toxicity to locusts (stomach poison) by the thiadiazine (III) ($R = \text{CH}_3$, $R' = \text{C}_6\text{H}_5$).

3. The results as a whole are discussed in relation to the hypothesis of Luger, Martin & Muller (1944) which relates contact insecticidal action to the presence in the molecule of a 'toxic' group and a 'carrier' group, and it is concluded that the physical properties of the molecules concerned play a dominating part in deciding their insecticidal activity.

We are indebted to Prof. A. Robertson of Liverpool University and Dr F. P. Reed for the original preparations of 2-alkylthiobenzthiazoles and the preparation of the quinoline derivatives. Certain other compounds were prepared as described in papers referred to in the text by Dr A. D. Ainley, Dr H. Gudgeon and Dr J. C. Harland. The emulsions were prepared by Dr B. Collie. We wish to make acknowledgement also to the entomologists at Hawthornedale Laboratories, Jealott's Hill Research Station, where the biological testing methods were devised and the routine evaluations carried out, and particularly to Messrs M. D. Price and F. J. D. Thomas who were associated with this work from its commencement.

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