SYNTHESIS AND PESTICIDAL ACTIVITY OF PHENAZINES

II.*—Alkyl, alkoxy, alkylthio and alkylsulphonyl phenazines

By B. CROSS, C. L. DUNN, D. H. PAYNE and J. D. TIPTON

The synthesis of forty-one phenazines, mono-substituted with alkyl, alkoxy, alkylthio and alkylsulphonyl groups is described.

Phytotoxicity was highest in the alkyl series and both 1- and 2-methylphenazines are highly effective herbicides.

Although several n-alkyl, branched alkyl and n-alkoxyphenazines were highly fungicidal and acaricidal, only 2-t-octylphenazine combined high dual activity with negligible phytotoxicity.

Introduction

In Part I,[1] the synthesis and pesticidal properties of halophenazines were reported and some conclusions were drawn concerning the inter-relationship of structure with these properties. Data on the influence of certain other substituents on the pesticidal properties of the phenazine nucleus are presented in this paper.

Experimental

Chemical synthesis

All melting points are uncorrected (see Table I).

2-iso-Propylphenazine (13) (Method A)

4-iso-Propylcatechol (15 g) and *o*-phenylenediamine (11 g) were heated together in a sealed tube at 240° for three days. The cooled contents of the tube were dissolved in toluene and stirred with mercuric oxide at 50° for 5 h. After filtration and removal of the solvent, the residue was chromatographed through a column of acidic alumina using toluene–light petroleum (40–60°) as eluant. Yellow needles of 2-iso-propylphenazine (13) were obtained after crystallisation from 40–60° light petroleum, 7·5 g (34%). (Analysis, Table I).

2-(1,1,3,3-Tetramethylbutyl)phenazine (15) (Method B)

A solution of *o*-phenylenediamine (108 g, 1 mole) and 4-(1,1,3,3-tetramethylbutyl)catechol (222 g, 1 mole) in benzene (2·5 l) was added slowly to a mixture of manganese dioxide and benzene which was vigorously stirred and cooled to 6°. The addition was completed in 30 min and the reaction mixture was stirred for a further 3 h at 20°. After filtration the filtrate was chromatographed through a neutral alumina column using benzene as eluant. Crystallisation from hexane gave 265 g of 2-(1,1,3,3-tetramethylbutyl)-phenazine (15), 90% yield, m.p. 99°. (Analysis, Table I.)

2-Ethoxyphenazine (26) (Method C)

Sodium ethoxide [from sodium (0·8 g) in absolute ethanol (100 ml)] and 2-chlorophenazine-5-oxide (5·7 g) were heated under reflux for 48 h. After cooling, a brown solid was filtered off and treated with sodium hydroxide (7·5 g) and sodium dithionite (7·5 g) in 300 ml of water–ethanol (1 : 1) at 50° for 1 h and then set aside for 16 h at 20°. Ether extraction, drying with anhydrous sodium sulphate and removal of the ether gave a solid which afforded yellow needles of 2-ethoxyphenazine (26) after crystallisation from 60–80° light petroleum, 3·4 g, (61%), m.p. 112·5–114°. (Analysis, Table I.)

2-Methylthiophenazine (33) (Method C)

To methylmercaptan (0·7 g) and sodium hydroxide (0·7 g) in ethanol (200 ml) was added 2-chlorophenazine-5-oxide (1·9 g). The mixture was heated under reflux for 16 h. Ethanol and unchanged mercaptan were removed by distillation under reduced pressure. The residue was dissolved in ethanol (150 ml) and added slowly with stirring to aqueous ethanolic dithionite (5 g) and sodium hydroxide (3 g), maintained at 40° for 30 min and then at 20° for 16 h. The reaction mixture was poured into water (500 ml) and ether-extracted, and the ether layer was shaken with sodium chloride, filtered and evaporated under reduced pressure to give an orange solid. Purification by alumina chromatography, using benzene as eluant, gave crude 2-chlorophenazine (m.p. 117–135°; 0·26 g), and then 2-methylthiophenazine (33) m.p. 157–158°, 1·65 g, (82%). (Analysis, Table II.)

Biological evaluation

The methods used for the assessment of herbicidal, acaricidal and fungicidal activity were identical to those described previously.[1]

Pre- and post-emergence herbicidal activity was measured on maize, oat, ryegrass, pea, linseed, mustard and sugar-beet.

Acaricide screening was carried out against adult glasshouse red spider mites (*Tetranychus telarius*) on leaf discs of French bean. Compounds were tested for fungicidal activity against powdery mildew (*Erysiphe cichoracearum*) on cucumber seedlings.

Results

Chemical synthesis

Method A (Table I)

Many of the alkylphenazines (**IV**) were prepared by the thermal condensation of the appropriate alkylcatechol (**I**) with *o*-phenylenediamine (**II**) in a sealed tube at 220–240° for 48–72 h. The resulting product, a dihydrophenazine (**III**), was readily oxidised by a metal oxide, e.g. silver oxide, mercuric oxide or manganese dioxide in an aprotic solvent (e.g. benzene or toluene) to the corresponding phenazine (**IV**).

* Part I: *J. Sci. Fd Agric.*, 1969, **20**, 8

TABLE I

Preparation and biological activity of alkylphenazines

	Phenazine	Yield, % (Method)	M.p., °C	Analysis, %	Phytotoxicity ratings[a] Post-emergence, kg/ha 10	Post-emergence, kg/ha 1	Pre-emergence, kg/ha 10	Pre-emergence, kg/ha 1	Acaricidal[b] activity TI	Fungitoxicity[c] category
1	[d]	54 (A) < 5 (B)	175–176	Found C 79·5 H 4·5 N 15·6 Req. C 80·0 H 4·5 N 15·6	8	5	7	1	50	C
2	1-CH_3	40 (A) < 5 (B)	107–108	Found C 80·4 H 5·5 N 14·7 Req. C 80·3 H 5·2 N 14·4	9	7	8	2	100	A
3	1-C_3H_7[i]	8 (A)	141–142	Found C 81·1 H 6·4 N 12·6 Req. C 81·1 H 6·4 N 12·6	7	2	6	0	300	—
4	2-CH_3	80 (A) 10 (B)	117	Found C 80·4 H 5·2 N 14·1 Req. C 80·3 H 5·2 N 14·4	9	7	7	1	75	A
5	2-C_2H_5	12 (A)	59–60	Found C 80·5 H 5·8 N 13·8 Req. C 80·7 H 5·8 N 13·8	8	6	6	0	100	B
6	2-C_4H_9[n]	16 (A)	49–51	Found C 81·1 H 7·0 N 11·8 Req. C 81·3 H 6·8 N 11·9	8	6	4	1	100	B
7	2-C_5H_{11}[n]	21 (A)	45–46·5	Found C 81·5 H 7·5 N 10·8 Req. C 81·6 H 7·3 N 11·2	7	5	2	0	300	C
8	2-C_6H_{13}[n]	27 (A)	65·5–66·5	Found C 81·7 H 7·1 N 10·3 Req. C 81·9 H 7·6 N 10·6	5	4	1	0	150	C
9	2-C_7H_{15}[n]	35 (A)	45–46	Found C 82·1 H 7·9 N 9·8 Req. C 82·0 H 8·0 N 10·0	6	5	1	0	80	D
10	2-C_8H_{17}[n]	7 (A)	56–57	Found C 81·8 H 8·6 N 9·3 Req. C 82·1 H 8·3 N 9·6	3	2	0	0	C	D
11	2-$C_{12}H_{25}$[n]	35 (A)	68–69	Found C 82·6 H 9·3 N 8·3 Req. C 82·7 H 9·3 N 8·0	0	0	0	0	B	D
12	2-$C_{18}H_{37}$[n]	44 (A)	78–80	Found C 83·3 H 10·2 N 6·6 Req. C 83·3 H 10·2 N 6·5	0	0	0	0	C	E
13	2-C_3H_7[i]	34 (A) 59 (B)	91–92	Found C 81·4 H 6·6 N 12·8 Req. C 81·1 H 6·4 N 12·6	8	6	5	1	150	A
14	2-C_4H_9[t]	54 (A)	85	Found C 81·6 H 6·4 N 11·8 Req. C 81·3 H 6·8 N 11·9	7	5	6	0	300	A
15	2-C_8H_{17}[t]	67 (A) 90 (B)	98–99	Found C 82·4 H 8·6 N 9·7 Req. C 82·1 H 8·3 N 9·6	1	0	0	0	200	A
16	5-O[d]	35[e]	220–221	Found C 73·4 H 4·0 N 14·3 Req. C 73·7 H 4·1 N 14·2	7	5	6	0	< 15	—
17	5,10-di-O[d]	61 (D)[f]	182	Found C 67·7 H 4·0 N 13·2 Req. C 67·9 H 3·8 N 13·2	3	0	6	0	< 10	D
18	2-CH_3 5-O	— [b]	—	—	8	7	3	0	100	D
19	2-CH_3 5,10-di-O	2 (D)	157·5–158·5	Found C 39·1 H 4·6 Req. C 69·0 H 4·4	3	1	1	0	—	B
20	2-C_8H_{17}[t] 5-O	25[b]	161–162	Found C 77·9 H 8·0 N 8·8 Req. C 77·9 H 7·8 N 9·1	1	0	1	0	C	E
21	2-C_8H_{17}[t] 5,10-di-O	60 (D)[c]	156–157	Found C 73·9 H 7·6 N 8·4 Req. C 74·1 H 7·4 N 8·6	1	0	0	0	C	E

[a] Mean phytotoxicity scores for all seven test species, rated on a 0–9 scale (0 = no effect, 9 = killed)

[b] TI (toxicity index) = $\frac{LC_{50} \text{ of methyl parathion}}{LC_{50} \text{ of phenazine}} \times 100$ (B = incomplete kill and C = no appreciable kill in preliminary screen)

[c] Inhibition of cucumber powdery mildew
A = 90–100% inhibition at 50 ppm, or equal to Karathane in the same test
B = 90–100% inhibition at 100 ppm, or half as active as Karathane in the same test
C = 90–100% inhibition at 300 ppm
D = 90–100% inhibition at 1000 ppm, or > 50% inhibition at 300 ppm
E = inactive at the highest concentration tested (300 or 1000 ppm)

[d] Non-alkylated phenazine
[e] Prepared by the Wohl-Aue procedure[1]
[f] Oxidation carried out with hydrogen peroxide at 50–55°C
— = Data not available
[i] Iso
[n] Normal
[t] Tertiary

Yields of 2-substituted phenazines were generally greater than those of the corresponding 1-isomer. This procedure, a modification of Morley's synthesis,[2] was particularly useful in the preparation of phenazine from those catechols which do not generate stable *o*-benzoquinones (V).

Method B

The preparation of phenazines from *o*-benzoquinones (V) has been known for at least eighty years[3] but a one-step synthesis has now been developed in which an alkylcatechol (I) and *o*-phenylenediamine (II) are treated with an oxidising agent, which selectively converts the catechol (I) to its corresponding *o*-benzoquinone (V) which in turn condenses with the diamine (II). Manganese dioxide in benzene was found to be the most suitable system. This procedure was particularly effective with higher alkylcatechols, but less successful with lower alkyl substituents owing to rapid self-condensation of the generated *o*-benzoquinone (V). Thus 2-(1,1,3,3-tetramethylbutyl)phenazine (15) (hereafter referred to as 2-t-octylphenazine) was prepared in 90% yield by running the oxidation–condensation reaction in benzene at 10–20° in the presence of an excess of manganese dioxide.

Method C (Table II)

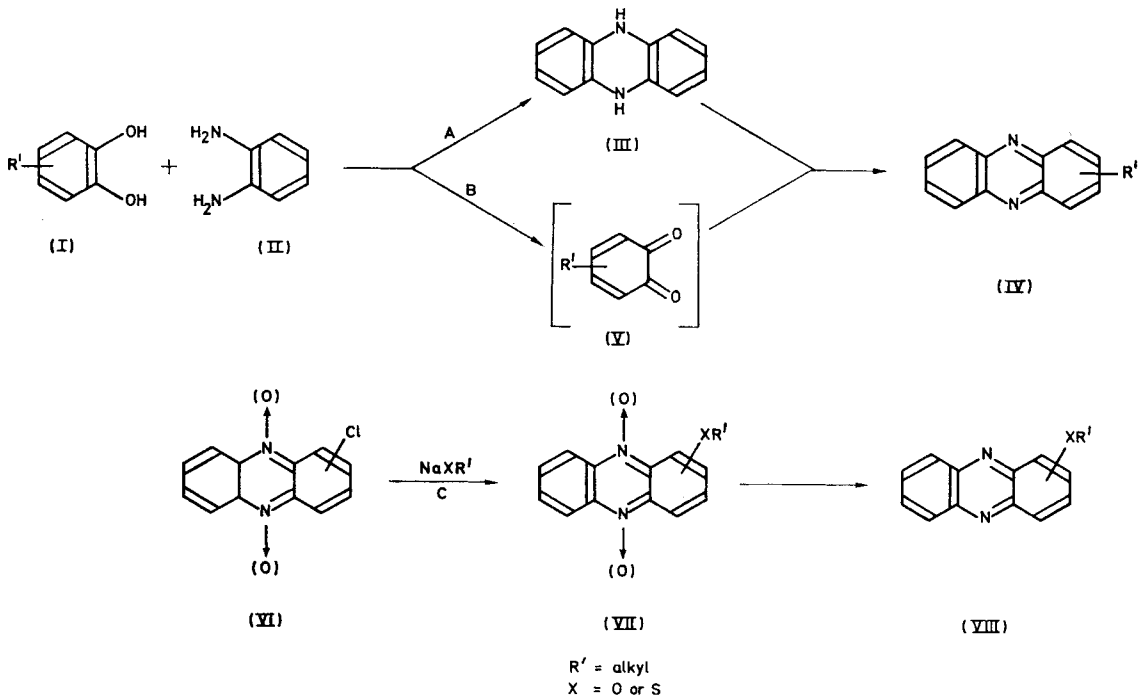
The nucleophilic displacement of halide by alkoxide or mercaptide from a halophenazine (VI), its mono-oxide or its dioxide was the route most generally applicable to the alkoxy and alkylthiophenazines. The ease of halide displacement decreased in the order dioxide > mono-oxide > parent. Most of the displacement reactions were carried out at the reflux temperature of the appropriate alcohol in the presence of alkoxide or mercaptide. If a mono- or di-oxide product (VIII) resulted, de-oxygenation was accomplished in almost quantitative yields with alkaline sodium dithionite.

TABLE II

Preparation and biological activity of alkoxy, alkylthio and alkylsulphonylphenazines

	Phenazine	Yield, % (Method)	M.p., °C	Analysis, %	Phytotoxicity ratings[a] Post-emergence, kg/ha 10	Post-emergence, kg/ha 1	Pre-emergence, kg/ha 10	Pre-emergence, kg/ha 1	Acaricidal[b] activity TI	Fungitoxicity[c] category
22	1-OCH_3	29 (C) 10 (B)	171–174	Found C 74·7 H 5·0 N 13·3 Req. C 74·3 H 4·8 N 13·3	5	3	0	0	200	C
23	1-OC_2H_5	60 (C)	129–130[g]	—	7	3	0	0	C	—
24	1-$OC_3H_7^n$	60 (C)	103·5–104	Found C 75·7 H 6·2 N 11·8 Req. C 75·6 H 5·9 N 11·8	6	1	3	0	C	—
25	2-OCH_3	22 (C)	127–127·5	Found C 74·5 H 4·7 N 13·6 Req. C 74·3 H 4·8 N 13·3	8	7	6	2	200	C
26	2-OC_2H_5	61 (C)	114–115	Found C 74·7 H 5·2 N 12·4 Req. C 75·0 H 5·4 N 12·5	8	7	4	1	300	B
27	2:$OC_3H_7^n$	56 (C)	92–92·5	Found C 75·5 H 6·2 Req. C 75·6 H 5·9	8	7	3	1	400	B
28	2-$OC_4H_9^n$	32 (C)	51–52, 76	Found C 76·2 H 6·4 Req. C 76·0 H 6·4	7	6	1	0	400	B
29	2-$OC_5H_{11}^n$	17 (C)	75·5–76·5	Found C 76·7 H 7·2 Req. C 76·5 H 6·8	6	4	0	0	C	C
30	2-$OC_8H_{17}^n$	30 (C)	63·5–64	Found C 77·9 H 7·9 Req. C 78·0 H 7·9	3	2	0	0	C	E
31	1-SCH_3	70 (C)	166–167	Found C 69·0 H 4·2 N 12·3 S 14·2 Req. C 69·0 H 4·5 N 12·4 S 14·2	5	4	1	0	C	B
32	1-SC_6H_5	47 C)	141–142	Found C 69·9 H 5·1 N 11·4 S 13·6 Req. C 70·2 H 5·0 N 11·7 S 13·4	6	4	1	0	< 7	C
33	2-SCH_3	82 (C)	158–158·5	Found C 69·2 H 4·5 N 12·3 S 14·0 Req. C 69·0 H 4·5 N 12·4 S 14·2	8	6	2	0	15	C
34	2-SC_6H_5	70 (C)	121–122	Found C 70·2 H 4·9 N 11·7 S 13·6 Req. C 70·2 H 5·0 N 11·7 S 13·4	8	6	3	1	80	B
35	2-$SC_3H_7^n$	48 (C)	72–73	Found C 70·8 H 5·6 N 11·2 S 12·4 Req. C 70·8 H 5·6 N 11·0 S 12·6	8	6	3	0	80	B
36	2-$SC_4H_9^n$	80 (C)	74–75	Found C 71·4 H 5·8 Req. C 71·6 H 6·0	7	5	1	0	40	D
37	2-$SC_3H_7^i$	78 (C)	58·5–59·5	Found C 70·6 H 5·5 N 10·8 S 12·5 Req. C 70·8 H 5·6 H 11·0 S 12·6	8	6	3	0	80	B
38	2-$SC_5H_{11}^i$	67 (C)	55·5–56	Found C 72·4 H 6·4 N 9·5 S 11·7 Req. C 72·3 H 6·4 N 9·9 S 11·4	8	6	1	0	60	C
39	2-$SC_8H_{17}^t$	25 (C)	49–50	Found C 73·9 H 7·5 N 8·7 Req. C 74·1 H 7·4 N 8·6	6	2	0	0	15	D
40	2-SO_2CH_3	39 (D)	228–229	Found C 61·2 H 4·1 N 10·9 S 12·4 Req. C 61·0 H 3·9 N 10·9 S 12·4	2	1	6	1	C	E
41	2-$SO_2C_3H_7^i$	49 (D)	159–160	Found C 62·7 H 4·7 N 9·6 Req. C 62·9 H 4·9 N 9·8	2	1	2	0	C	—

[a–c] Abbreviations at foot of Table I
[g] Ref.[4] m.p. 130°C



Method D

The oxidation of 2-alkylthiophenazines at 20° with permanganate in acetic acid or 30% hydrogen peroxide in acetic acid gave 2-alkylsulphonyl phenazines.

Phytotoxicity

The alkyl, alkoxy and alkylthiophenazines were similar to halophenazines in being more active when applied as foliar sprays than as pre-emergence soil sprays. In the alkyl series activity generally decreased with increase in the carbon content of the substituent so that 1-methyl and 2-methylphenazine were the most active. The ratio of pre- to post-emergence activity, however, varied between positional isomers and although 2-methylphenazine proved to be the most active post-emergence, 1-methylphenazine was the most active pre-emergence. *N*-oxidation, particularly 5,10-dioxidation, resulted in lower levels of phytotoxicity than those of the parent phenazines (18–21).

The post-emergence activity of analogues in the 2-n-alkoxy and 2-n-alkylthio series was similar. There was a general decrease in activity with increasing carbon content of the substituent but in each series the same level of activity was recorded for the methyl, ethyl and propyl members (25–27, 33–35). In the 1-n-alkoxy and 1-n-alkylthio series the methyl compounds were less active than the ethyl but the activity peak was difficult to define with so few examples (22–24, 31 and 32). This pattern was not followed by the pre-emergence activity, at least in the 2-n-alkoxy series where methoxyphenazine was the most active and there was a rapid fall in activity to an insignificant level at butoxyphenazine. The 1-n-alkoxy and alkylthio compounds were much less active pre-emergence and no trend was obvious. By contrast, the alkylsulphonyl derivatives, particularly methylsulphonylphenazine (40), had a high ratio of pre-emergence to post-emergence activity.

Acaricidal activity

The activity of the 2 n-alkylphenazines against adult mites increased with increasing chain length to give peak activity with 2-n-pentylphenazine (7). Thereafter activity decreased until, at 2-n-octyl (10), no acaricidal effect was detected. In contrast to the inactivity of 2-n-octylphenazine, 2-t-octylphenazine (15) was twice as active as methyl parathion with negligible phytotoxicity in the herbicide screen. Oxidation of one or both nitrogens in unsubstituted phenazine resulted in a product with reduced acaricidal activity, and 2-t-octylphenazine was completely inactive after oxidation.

Activity in the 1-n-alkoxy- series was restricted to the methoxy compound. The most effective members of the 2-n-alkoxy series possessed chain lengths of three or four carbons; 2-n-butoxyphenazine was four times as active as methyl parathion, but the next member in the series (2-n-pentyloxy-) was inactive. None of the 2-n-thioalkylphenazines exceeded methyl parathion in acaricidal activity. The most active members of this series with alkyl chains of two or three carbons were, in common with the most effective members of the n-alkyl series, too phytotoxic for further consideration as agricultural acaricides. The alkylsulphonylphenazines were non-acaricidal. Only 2-t-octylphenazine combined good acaricidal effect with low phytotoxicity.

Fungitoxicity

The most active powdery mildew fungicides in the 2-n-alkylphenazines occurred where the alkyl chain was short (e.g. 4–6), and activity decreased rapidly with increasing chain length. Thus fungitoxicity paralleled phytotoxicity and no compound of this series was specific enough to warrant further evaluation as a foliage fungicide. Where, however, a t-octyl group was substituted in the 2-position (15), high fungicidal activity was retained with negligible phytotoxicity.

The fungitoxicity of the 2-n-alkoxy and 2-alkylthiophenazines generally followed the acaricidal activity, but active members were always too phytotoxic for further consideration.

In contrast to 2-t-octylphenazine (15), 2-t-octylthiophenazine (39) was only slightly fungicidal and was still significantly phytotoxic. No fungicidal activity was observed with 2-methylsulphonylphenazine (40).

Discussion

In a previous paper[1] the halophenazines were shown to include compounds with strong acaricidal, fungicidal and herbicidal properties. Sometimes these three properties were present in a single compound (e.g. 1-chlorophenazine) which was therefore potentially useful only as a herbicide. More often one or two of these activities were better developed than the third; thus 1,4-dichlorophenazine was sufficiently non-phytotoxic to be of interest as a potential fungicide/acaricide.

The four classes of phenazines considered here also show various combinations of the three biological activities. In the halophenazine series variations in biological properties were considered in relation to the number and position of chlorine atoms around the nucleus. In the alkyl and alkyl ether substituted phenazines, however, interest has been centred on the biological response to the nature of the substituent groups, and the majority of compounds synthesised contain a single substituent in the 2-position. Thus, although phenazines substituted in the 1-position are of some interest as herbicides, the remainder of this discussion will be largely concerned with structure/activity relations in 2-substituted phenazines.

Fungitoxicity and phytotoxicity decrease consistently with increase in carbon number in the 2-n-alkyl series, but the acaricidal activity reaches a maximum at C_5 and then decreases (Table I). When biological activity responds to structure as decisively as this, it is useful to relate trends in biological effectiveness to one or more physico-chemical parameters of the molecules. Six members of the n-alkyl series were therefore subjected to reverse phase thin-layer chromatography with silica gel impregnated with silicone oil as the stationary phase and 30% (by vol.) aqueous methanol as the mobile phase. The R_f values obtained are inversely proportional to the partition coefficient and decrease with increase in carbon number (Table III). They thus have a similar trend to the fungitoxicity and post-emergence phytotoxicity. This relationship could be the result of the greater penetration into plant and fungal cells of homologues of higher R_f; Hansch *et al.*[5] have demonstrated that, in certain homologous series, cell penetration can be correlated with partitioning into an aqueous phase.

R_f values were also determined for three branched-chain alkyl phenazines. A correlation still exists between phytotoxicity and R_f, but there is evidence that other factors operate in the fungitoxic response to structure. Proceeding from 2-methyl, through 2-iso-propyl and 2-t-butyl, to 2-t-octylphenazine, the R_f values fall steadily until the R_f of 2-t-octylphenazine is about equal to that of 2-n-hexylphenazine,

TABLE III

R_f values of some monoalkyl phenazines

System: silicone oil/30% (by vol.) aqueous methanol

Phenazine ring substituent	R_f value (mean of 6 results)
1-methyl	0·51
2-methyl	0·57
2-ethyl	0·53
2-isopropyl	0·49
2-t-butyl	0·44
2-n-hexyl	0·29
2-n-heptyl	0·23
2-t-octyl	0·28
2-n-lauryl	0·062
2-n-stearyl	0·00

yet the fungitoxicities of the branched chain compounds are similar and very high.

The 2-n-alkyl series has a peak of acaricidal activity at C_5. This may reflect an optimum solubility for the compound to penetrate into the plant but still be available to the mites walking over the surface and feeding on the contents of the epidermal cells. However, the solubility requirements are not narrowly defined and, as with the fungicidal activity, branched chain compounds show good acaricidal activity despite having lower R_f values than some inactive straight chain compounds. Certainly the high fungicidal and acaricidal activities of 2-t-octylphenazine, coupled with a negligible phytotoxicity, make it one of the most interesting potential pesticides among the phenazines.

Oxidation of one, then both nitrogen atoms of 2-methylphenazine is accompanied by progressive reduction of the herbicidal activity. Similarly oxidation of one or both nitrogens of 2-tertiary octylphenazine results in complete loss of acaricidal and fungicidal properties.

The herbicidal activity of the 2-n-alkoxy series is generally high and shows a decrease in activity with increasing carbon number similar to the 2-n-alkylphenazines. Acaricidal activity is higher than in the 2-n-alkyl series but the maximum is reached at C_3–C_4 and not at C_5.

The 2-n-thioalkyl compounds have enhanced post-emergence herbicidal activity but reduced pre-emergence activity when compared with the other two series. Acaricidal activity is reduced and, as with the alkoxy series, fungicidal activity parallels the acaricidal response to carbon number. The activity spectrum of 2-t-thio-octylphenazine contrasts with that of the 2-t-octyl analogue in having high post-emergence phytotoxicity but little acaricidal or fungicidal effect.

The lower biological activity of the 2-alkylsulphonylphenazines compared with the 2-alkylthiophenazines indicates that biological oxidation of the sulphur atom is not responsible for activation, but is possibly a detoxifying process.

Acknowledgments

The authors would like to thank Dr. S. Pietra of Pavia University who supplied some of the compounds, Mr. R. E. Woodall and Mr. P. J. Williams who assisted in the synthesis of the remainder, and Mr. C. A. Proctor who carried out the R_f value determinations.

Shell Research Ltd.,
Woodstock Agricultural Research Centre,
Sittingbourne, Kent

Received 9 December, 1968

References

1. Cross, B., Dunn, C. L., Payne, D. H., & Tipton, J. D., *J. Sci. Fd Agric.*, 1969, **20**, 8
2. Morley, J. S., *J. chem. Soc.*, 1952, p. 4008
3. Hinsberg, O., *Ber. dt. chem. Ges.*, 1885, **18**, 1228
4. Serebryanyi, S. B., *Zh. obshch. Khim.*, 1950, **20**, 1629; *Chem. Abstr.*, 1951, **45**, 2009 g
5. Hansch, C., Kiehs, K., & Lawrence, G. L., *J. Am. chem. Soc.*, 1965, **87**, 5770