Methylenedioxyphenyl Synergists for Pyrethrins

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Table IV. Residue of Ethylene Dibromide from 100 g of Wheat Fumigated for 3 Days with 16 mg/L of EDBr (1,2-^{14}C) and 8 Days of Aeration[a]

| aeration temp, °C | EDBr, ppm | | | | | |
| | 75-85% RH | | | zero humidity | | |
	A	B	C	A	B	C
3	50	10	4	204	228	170
10	62	10	6	230	283	216
25	20	11	8	182	244	265

[a] A, whole wheat; B, wheat ground before treatment; C, wheat ground after treatment.

similarly lower at 5 °C than at 25 °C. The residue extracted by the petroleum ether method was again lower from wheat held at the high temperature thus showing the same trend as previously demonstrated with this solvent.

Finally, the role of moisture and relative humidity in residue retention was investigated when wheat that had been fumigated with labeled ethylene dibromide was analyzed for labeled carbon. The lowest levels of residue were found in grain held at high humidity during the desorption period (Table IV). At 75-85% RH the level of residue remaining in whole wheat fumigated with 16 mg/L of EDBr-*1,2-^{14}C* for 3 days and aerated for 8 days was less than half that found in wheat retained over calcium chloride in a completely dry atmosphere at a temperature of 10 °C. At temperatures above and below this level at 25 and 3 °C appreciably less fumigant was found in wheat held at the high humidity. Similar results on residue levels from the fumigated wheat held at different humidities during the aeration period were found

using solvent extraction and GLC analysis.

When wheat was ground either before or after fumigation, residue levels remaining after 8 days of aeration were about three-ten times below that found in the whole wheat at 75-85% humidity. In the low humidity atmosphere the amounts of residue remaining in whole and ground wheat did not differ appreciably.

In conclusion it may be said that desorption of ethylene dibromide from fumigated wheat was influenced by temperature, relative humidity, and particle size of the treated product. Undoubtedly moisture content of the grain along with temperature would affect humidity in intergranular spaces of the grain mass along with other factors involved in desorption. Similarly moisture content, humidity, and temperature might be expected to affect sorption of fumigant by the grain during treatment. Humidity appeared to be the most important factor that governed rate of desorption of the fumigant from grain, particularly when the grain had been ground to a fine particle size. Other factors may be important in the sorption and desorption processes. Further investigation is needed to fully understand the mechanism of the processes involved.

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New Methylenedioxyphenyl Synergists for Pyrethrins

S. K. Mukerjee,* V. S. Saxena, and S. S. Tomar

Several new ester derivatives of alcohols derived from dillapiole have been prepared and evaluated for their synergistic efficacy toward pyrethrins against *T. castaneum* Herbst. A few of these compounds have shown comparable activity to piperonyl butoxide, a standard synergist. The relationship among the number of carbon atoms in the ester chain of these compounds, their lipophilicity, and synergistic potency is discussed.

The synergistic properties of dillapiole (2,3-dimethoxy-4,5-methylenedioxyallylbenzene, I), one of the major constituents of Indian dill (*Anethum sowa* Roxb.) seed oil, toward pyrethrins (Gulati and Parmar, 1969) and toward *N*-methylcarbamates (Tomar et al., 1978) have been described earlier. It has also been converted into a number of potent derivatives and their activities as pyrethrum synergists (Saxena et al., 1977; Tomar et al., 1979a,b) as well as toward *N*-methylcarbamates (Tomar et al., 1978; Saxena et al., 1978) have been reported. In this paper the preparation of a series of esters of two new alcohols derived from dillapiole and their synergistic properties toward pyrethrum are reported. Some of these have shown good
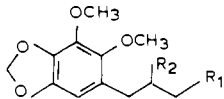
synergism for pyrethrins against the test insect *T. castaneum* Herbst.

METHODS AND MATERIALS

All compounds were finally purified by column chromatography on activated silica gel and purity was checked by TLC, spots being visualized by warming the dilute H$_2$SO$_4$. Infrared spectra were recorded in CHCl$_3$ on a Perkin-Elmer 457 grating spectrophotometer. NMR spectra were normally taken in CCl$_4$ solution, unless otherwise stated, on a Varian A-60 spectrometer using Me$_4$Si as internal reference; chemical shifts are given in δ values.

3-(2,3-Dimethoxy-4,5-methylenedioxyphenyl)-propan-1-ol (II). Dillapiole (I, 22.2 g) in dry dioxane (150 mL) was hydroborated and the product was oxidized with alkaline hydrogen peroxide (30%, 15 mL) in aqueous NaOH (10%, 15 mL) (Brown and SubbaRao, 1957). The

Division of Agricultural Chemicals, (S.K.M., S.S.T.) and the Division of Entomology (V.S.S.), Indian Agricultural Research Institute, New Delhi, India.

Table I. R_M Values and Factors of Synergism for
Various Dillapiole-Derived Esters[a]

| struct. no.	R_1	R_2	R_M	factor of syn- ergism
II	OH	H	−0.48	1.5
III	H	OH	−0.46	1.6
IV	$OCOCH_3$	H	−0.35	2.1
V	$OCOC_2H_5$	H	−0.27	2.4
VI	$OCOC_3H_7$	H	−0.21	2.6
VII	$OCOC_4H_9$	H	−0.17	3.2
VIII	$OCOC_5H_{11}$	H	−0.13	3.7
IX	$OCOC_6H_{13}$	H	−0.07	3.6
X	$OCOC_7H_{15}$	H	+0.05	3.1
XI	$OCOC_8H_{17}$	H	+0.14	2.5
XII	$OCOC_9H_{19}$	H	+0.18	2.0
XIII	$OCOCH_2Cl$	H	−0.43	1.6
XIV	$OCOC_6H_5$	H	−0.38	1.7
XV	H	$OCOCH_3$	−0.27	3.3
XVI	H	$OCOC_2H_5$	−0.17	3.7
XVII	H	$OCOC_3H_7$	−0.13	3.8
XVIII	H	$OCOC_4H_9$	−0.10	4.0
XIX	H	$OCOC_5H_{11}$	−0.05	4.1
XX	H	$OCOC_6H_{13}$	+0.00	4.2
XXI	H	$OCOC_7H_{15}$	+0.09	4.1
XXII	H	$OCOC_8H_{17}$	+0.18	3.7
XXIII	H	$OCOC_9H_{19}$	+0.27	3.4
XXIV	H	$OCOCH_2Cl$	−0.38	1.8
XXV	H	$OCOC_6H_5$	−0.27	1.0
	piperonyl butoxide			2.0

[a] Alkyl groups from C_3H_7 to C_9H_{19} have straight-chain structures.

resulting mixture was diluted with water (300 mL) and extracted with ether (3 × 150 mL). The ether extract was dried over Na_2SO_4 and the solvent was removed. The product on purification afforded II as colorless viscous oil, 22 g. ν_{max} (CHCl$_3$) 3440 cm^{-1} (OH); NMR (CCl$_4$) 1.73 (m, 2 H, CH_2CH_2OH), 2.62 (t, J = 7.5 Hz, ArCH$_2$), 3.58 (t, J = 6.5 Hz, $-CH_2OH$), 3.83 (s, 3 H, OCH$_3$), 3.92 (s, 1 H, CH_2OH, exchanged with D$_2$O), 4.05 (s, 3 H, OCH$_3$), 5.96 (s, 2 H, OCH$_2$O), 6.43 (s, 1 H, aromatic proton). Anal. Calcd for $C_{12}H_{16}O_5$: C, 60.0; H, 6.7. Found: C, 59.9; H, 6.9.

3-(2,3-Dimethoxy-4,5-methylenedioxyphenyl)-propan-2-ol (III). III was prepared following the method of Brown and Geoghegan (1967). Dillapiole (22.2 g) in THF (200 mL) was added dropwise to a well-stirred suspension of mercuric acetate (32 g) in THF (200 mL) and water (50 mL) over a period of 1 h. The mixture was stirred for 3 h and the product was demercurated by the addition of NaBH$_4$ (5 g) in aqueous KOH (10 g, 50 mL) in an ice bath. The precipitated mercury was filtered and from the filtrate, and the solvent was distilled off under vacuum. The product was taken in ether (3 × 150 mL), washed free of alkali, and worked up as above to give III
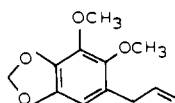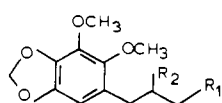
as a colorless viscous oil (18 g). ν_{max} (CHCl$_3$) 3440 cm^{-1} (OH); NMR 1.15 (3 H, d, J = 6.5 Hz, CHCH$_3$), 2.66 (2 H, d, J = 6.5 Hz, ArCH$_2$), 3.04 (s, 1 H, OH; exchanged with

D$_2$O), 3.9 (s, 3 H, OCH$_3$), 3.97 (m, 1 H, CHCH$_3$), 4.13 (s, 3 H, OCH_3), 6.06 (s, 2 H, OCH$_2$O), 6.59 (s, 1 H, aromatic proton). Anal. Calcd for $C_{12}H_{16}O_5$: C, 60.0, H, 6.7. Found: C, 59.8; H, 7.1.

Esters IV–XXV (Table I) were prepared by reacting the appropriate alcohol (II or III) with the appropriate acyl chloride in dry benzene in equimolecular proportions at room temperature, in the presence of triethylamine as an acid scavenger. Slight warming (50 °C) was required in the case of acyl chlorides higher than hexanoic acid. After 24 h the product was extracted with ether. The extract was washed free of acid and dried over sodium sulfate, and the solvent was removed and the product purified. Yields of the esters were good and ranged between 70 and 80%. All these esters gave a characteristic carbonyl peak at 1710–1730 cm^{-1} in their IR spectra, and their NMR spectra agreed fully with the proposed structures.

Formulation and Bioassay. Purified pyrethrum extract (20%) was used for making a stock solution (4%) in benzene for biological screening. The synergistic activity of all the test compounds was assessed as pyrethrum-based emulsions at insecticide to synergist ratio of 1:5 (ww) Benzene solvent (10%) and Tween-80 emulsifier (0.2%) were maintained throughout in the spray emulsions. The tests were conducted against 2–3-week-old red flour beetles (*T. castaneum* Herbst.) reared on wheat flour (free from pesticides), in three replications of ten insects each, as reported by Mukerjee et al. (1973). The data were subjected to probit analysis (Finney, 1971), and factors of synergism were calculated from LC$_{50}$ values (Chadwick, 1963).

Lipophilicity of the Synergists. Lipophilicity of the test compounds was determined from the R_M values of these chemicals on reversed-phase chromatography using the method of Boyce and Milborrow (1965). Silica gel plates of 400 μm thickness after activation for 2 h at 100 °C were coated with liquid paraffin (10% in hexane, 24 h). The coated plates were spotted and developed in acetone/water mixture (80:20) and visualized, and R_f values were measured. The mean of three R_f values of each compound was used for calculating its R_M value.

RESULTS AND DISCUSSION

The test chemicals are two series of esters derived from alcohols II and III, both prepared from dillapiole (I). The propan-1-ol (II) was obtained from dillapiole by hydroboration, followed by hydrogen peroxide oxidation. The propan-2-ol (III), on the other hand, was prepared from this source by mercuration, followed by reductive de-
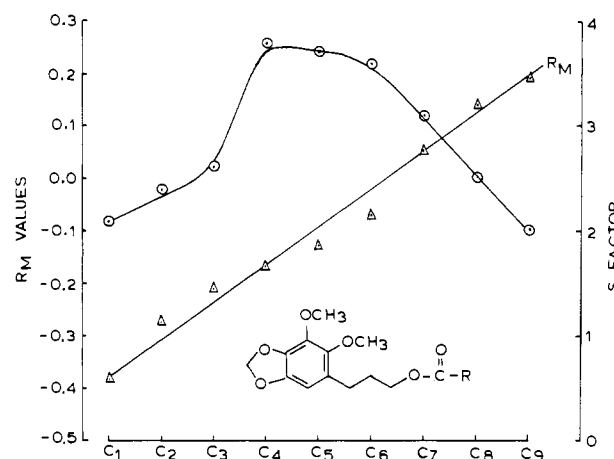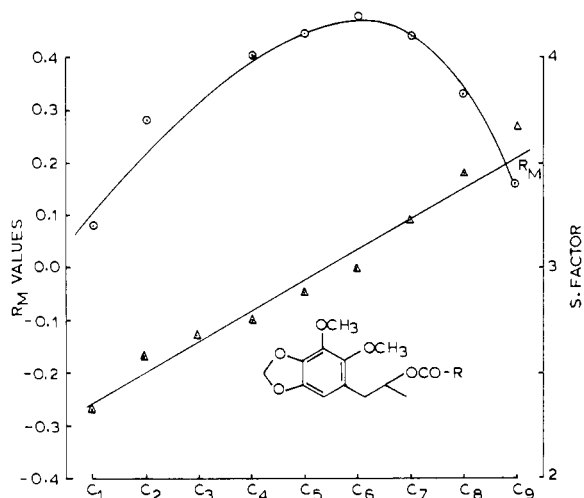

Figure 1. Relationship among the length of acyl moiety of esters from propan-1-ol (II), R_M values, and factors of synergism. (△–△) R_M value; (O–O) factor of synergism.

Figure 2. Relationship among the length of acyl moiety of esters from propan-2-ol (III), R_M values, and factors of synergism. (△–△) R_M value; (○–○) factor of synergism.

Higher molecular weight esters in both the series, although more lipophilic, are less potent synergists. Similar results have been observed earlier in a series of substituted cinnamic esters (Vaidyanathaswami et al., 1977) and alkoxy derivatives from dillapiole (Tomar et al., 1979a), but these showed a maximum of synergistic activity with only two or three carbon atoms in the side chain.

As seen from Table I, other esters like benzoates and chloroacetates of these alcohols show poor synergism.

Supplementary Material Available: A listing of data from IR and NMR spectra and elemental analysis of esters IV–XXV (8 pages). Ordering information is given on any current masthead page.

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mercuration with sodium borohydride. Both these alcohols as well as the esters derived from them showed no significant toxicity up to 1% concentration against the test insect *T. castaneum*.

In studies on synergistic activity, all of them showed different degrees of synergism. The factors of synergism ranged from 1.5 to 4.2 as compared to 2.0 for the standard reference synergist, piperonyl butoxide. A perusal of the data given in Table I shows that the esters XV–XXV derived from propan-2-ol (III) are more active than the corresponding esters IV–XIV, derived from propan-1-ol (II). Further, a comparison of synergistic activity of these compounds and their lipophilicity shows that the latter alone is not the criterion for better synergism. Thus in both the homologous series in compounds IV to XII (Figure 1) and XV to XXIII (Figure 2), the synergistic factor increases with increasing lipophilicity only up to a maximum of six or seven carbon atoms in the ester chain.

Determination of (Z)-9-Tetradecen-1-ol Formate, a *Heliothis* spp. Mating Disruptant, in Air by Electron-Capture Gas Chromatography following Photolytic Cleanup

Joseph H. Caro,* Horatio P. Freeman, and Barbara A. Bierl-Leonhardt

A sensitive method for determination of (Z)-9-tetradecen-1-ol formate (Z-9-tdf) in air has been developed. The compound is trapped on a bed of Chromosorb 102, eluted from the bed with hexane, and reacted with bromine to form the *vic*-dibromide. The latter is subjected to two clean-up procedures—silica gel microcolumn chromatography, followed by thin-film ultraviolet light irradiation—and is then determined by electron-capture gas chromatography. Recovery through the method after correction for a consistent 40% loss of dibromide during UV cleanup is about 89%, and the quantitative limit in unpolluted air is less than 3 ng/m^3. Identity of the Z-9-tdf-dibromide may be confirmed at levels of 40 ng/m^3 and above by saponification and reaction with acetyl chloride to form the corresponding acetate.

The principle of insect control by air permeation with synthetic sex attractants or mating disruptants is now

Soil Nitrogen and Environmental Chemistry Laboratory, Agricultural Environmental Quality Institute, Beltsville Agricultural Research Center, U.S. Department of Agriculture, Beltsville, Maryland 20705.

firmly established. Although not a component of the natural sex attractant emitted by the female moths, (Z)-9-tetradecen-1-ol formate (Z-9-tdf), when vaporized into the atmosphere, effectively disrupts mating of several species of Lepidoptera, principally in the *Heliothis* genus—*H. zea*, the corn earworm or cotton bollworm, and *H. virescens*, the tobacco budworm (Mitchell et al., 1975; Gothilf et al., 1978). For emission into the air in the field,