added to a solution of 1 g. of I and 1 g. of the aldehyde in 50 cc. of ethanol, and the resulting solution stirred at room temperature for 2 hr. The product precipitated during this time, and was removed by filtration and washed with ethanol. Under these reaction conditions, benzaldehyde formed the quinolone, isomerization being too rapid to permit isolation of IIIa.

Isomerization of aralkylidene derivatives IIIa,b,c. One hundred mg. of the arylidene derivative was heated under reflux with 20 cc. of a *N* solution of potassium hydroxide in absolute ethanol, for 10 min. As the more soluble quinolone was formed, all of the solid went into solution. Concentration to 10 cc. and cooling gave the crystalline product in quantitative yield. It was recrystallized several times from methanol and dried at 60°/1 mm. for several hours. By this procedure the following were prepared:

4-Oxo-5-benzyl-4H-pyrido[3,2,1-jk]carbazole (IVa), m.p. 214–215° (reported[6] m.p. 215°). Ultraviolet spectrum: λ_{max} 218 mμ (ε 44,500), 236 (25,800), 253 (20,100), 294 (20,900), 384 (18,900). This compound was also formed when benzaldehyde was stirred with I at room temperature, with sodium hydroxide as the catalyst, under the conditions reported above.

4-Oxo-5-p-diethylaminobenzyl-4H-pyrido[3,2,1-jk]carbazole (IVb), m.p. 114.5–115°, unchanged on further recrystallization (reported[6] m.p. 144°). Ultraviolet spectrum, λ_{max} 218 mμ (ε 38,400), 237 (25,000), 243 (23,500), 250 (25,300), 293 (20,900), 384 (15,000).

Anal. Calcd. for $C_{36}H_{24}N_2O$: C, 82.1; H, 6.3; N, 7.4. Found: C, 82.5; H, 6.6; N, 7.4.

4-Oxo-5-furfuryl-4H-pyrido[3,2,1-jk]carbazole (IVc), m.p. 156–156.4°. Ultraviolet spectrum, λ_{max} 213 mμ (ε 40,700), 237 (26,600), 251 (20,600), 294 (18,700), 383 (15,300).

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.3; H, 4.4; N, 4.7. Found: C, 79.7; H, 4.6; N, 4.7.

4-Oxo-5-p-dimethylaminophenylimino-5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole (V). A solution of 0.3 g. of 4-oxo-5,6-dihydro[3,2,1-*jk*]carbazole (I) in 10 cc. of methanol containing 2 cc. of 10% sodium hydroxide solution (or 0.1 cc. of piperidine, or saturated with potassium carbonate) was boiled while a solution of 0.3 g. of *p*-dimethylaminonitrosobenzene in 10 cc. of methanol was added dropwise over 5 min. The solution was boiled for a few minutes longer, filtered, and allowed to cool. Very dark red needles formed, which were recrystallized three times from absolute ethanol and dried at 120°/5 mm., m.p. 180.5–181°. Ultraviolet spectrum: λ_{max} 225 mμ (ε 35,300), 294 (27,900).

Anal. Calcd. for $C_{23}H_{19}N_3O$: C, 78.2; H, 5.4; N, 11.9. Found: C, 78.4; H, 5.5; N, 12.1.

This compound was recovered unchanged when it was allowed to stand with alcoholic hydrochloric acid, or boiled with potassium hydroxide in ethanol, or boiled with potassium *t*-butoxide in *t*-butyl alcohol.

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[CONTRIBUTION FROM THE ENTOMOLOGY RESEARCH DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Syntheses of Compounds with the Methylenedioxyphenyl Group

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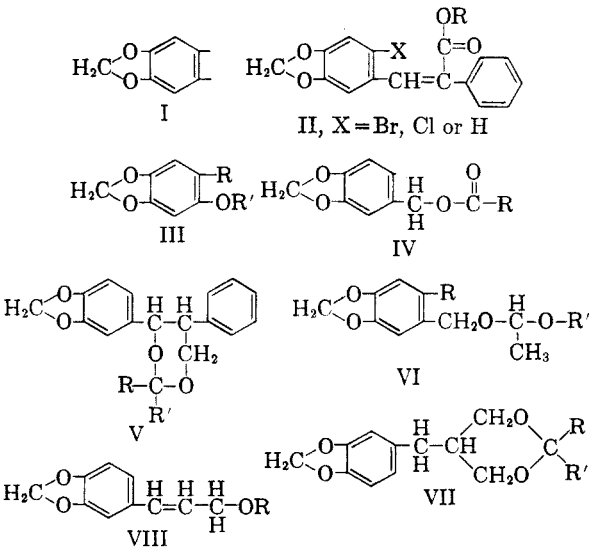
Since the development of several insecticidal substances with the methylenedioxyphenyl group, a variety of new compounds embodying this group has been prepared for insecticidal study. The preparation of these compounds as well as their intermediates is described.

Since a number of compounds with the methylenedioxyphenyl structure I have shown insecticidal or synergistic (with pyrethrins) activity,[1] several other compounds containing this group were prepared for similar testing. Such compounds include types II and III that had not previously been described. The synthesis of the other new methylenedioxyphenyl compounds (IV–VIII) was also undertaken to determine the effect of lengthening the side chain or the inclusion of ring compounds (*m*-dioxanes) on insecticidal activity.



Most of the preparations proceeded smoothly and in good yields to give the expected products. The high yield of 6-nitrosesamol (III, R = NO_2, R′ = H) obtained from the hydrolysis of its acetate

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(III, R = NO_2, R′ = $COCH_3$) was unanticipated, since we had previously shown that the saponification of the corresponding acetate of 6-bromosesamol (III, R = Br, R′ = $COCH_3$) yielded only polymeric substances.[2] The excellent yield of the 6-nitrosesamol is understandable when it is noted that hydrogen bonding of the hydroxyl group is possible with the nitro but not with the bromo group.

The ease of preparing II (X = H)[3] made possible the preparation of similar compounds (II, X = halogen). This substitution in position 6 was suggested by the considerable insecticidal activity of the 6-halopiperonyl chrysanthemumates[4] in contrast to the unsubstituted piperonyl chrysanthemumate which was far less active. Introducing the halogen atom into the 6-position of the methylenedioxyphenyl compounds generally increased the activity. The new acetals (VI) were prepared essentially as described by Beroza.[1]

Attempts to isolate the diol intermediate necessary for the preparation of V often resulted in partial dehydration due to the instability of the diol in the acidic medium whence it came.

EXPERIMENTAL

3,4-Methylenedioxyphenyl-1-piperidinecarboxylate [III, R = H, R′ = $CON(CH_2)_4CH_2$] was prepared in the usual way by refluxing a mixture of sesamol (20.7 g.), benzene (100 ml.), pyridine (15 ml.), and 1-piperidinecarbonyl chloride (22.2 g.) for 1 hr.; m.p. 89° (95% alcohol); b.p. 144°/0.1 mm.; yield 32%.

Anal. Calcd. for $C_{14}H_{17}NO_3$: N, 5.67%. Found: N, 5.69%.

4,5-Methylenedioxy-2-nitrophenyl acetate (III, R = NO_2, R′ = $COCH_3$) was prepared by the nitration of 3,4-methylenedioxyphenyl acetate, the preparation of which was reported by Beroza.[1] A solution of 3,4-methylenedioxyphenyl acetate (388 g.) in glacial acetic acid (335 ml.) was added dropwise, with stirring, over a period of 3 hr. to a solution of concentrated nitric acid (255 ml.) and glacial acetic acid (500 ml.) maintained below 5°. The mixture was then poured into a mixture of ice (500 g.) and 10% sodium hydroxide (800 ml.). Precipitation occurred and the mixture was filtered. The yellow crystals were washed free of solvent with cold water and then dried; yield 67%, m.p. 104–105° (alcohol).

Anal. Calcd. for $C_9H_7NO_6$: N, 6.22%. Found: N, 6.24%.

4,5-Methylenedioxy-2-nitrophenol (III, R = NO_2, R′ = H) was obtained by the sodium methylate saponification of the acetate in the usual way,[4] with this exception: After treatment with sodium methylate the mixture contained the phenol and its sodium salt. It was poured into water and, while it was stirred, concentrated hydrochloric acid was added to a *p*H of 2. After standing overnight at 25°, the desired product was filtered off; crude yield 99%; m.p. 93–94° (alcohol).

Anal. Calcd. for $C_7H_5NO_5$: C, 45.92%; H, 2.75%; N, 7.65%. Found: C, 46.18%; H, 2.99%; N, 7.75%.

4,5-Methylenedioxy-2-nitrophenyl propionate (III, R = NO_2, R′ = COC_2H_5) was prepared in the usual manner by reacting propionyl chloride with the phenol in the presence of pyridine and benzene; yield 86%; m.p. 94–95° (benzene–petroleum ether, 60–70°).

Anal. Calcd. for $C_{10}H_9NO_6$: N, 5.87%. Found: N, 5.80%.

4,5-Methylenedioxy-2-nitrophenyl chrysanthemumate (III, R = NO_2, R′ = COC_9H_{15}) was prepared in the same manner as the propionate from synthetic chrysanthemumoyl chloride; yield 85%; m.p. 85–86° (alcohol).

Anal. Calcd. for $C_{17}H_{19}NO_2$: N, 4.20%. Found: N, 4.48%.

4,5-Methylenedioxy-2-nitrophenyl benzoate (III, R = NO_2, R′ = COC_6H_5) was made in the same manner as the other esters; yield 78%; m.p. 141–142° (alcohol).

Anal. Calcd. for $C_{14}H_9NO_6$: N, 4.88%. Found: N, 5.24%.

4,5-Methylenedioxy-2-nitrophenyl-1-naphthoate (III, R = NO_2, R′ = $COC_{10}H_7$) was prepared in the same manner as the other esters; yield 28%; m.p. 129–130° (alcohol).

Anal. Calcd. for $C_{18}H_{11}NO_6$: N, 4.15%. Found: N, 3.86%.

3-(3,4-Methylenedioxyphenyl)-2-propen-1-yl chrysanthemumate (VIII, R = COC_9H_{15}) was prepared as above from 3-(3,4-methylenedioxyphenyl)propanol and synthetic chrysanthemumoyl chloride; yield 94%; b.p. 185–190°/0.1 mm.; $n_D^{25°}$ 1.5528.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14%; H, 7.37%. Found: C, 73.39%; H, 7.26%.

3-(3,4-Methylenedioxyphenyl)propyl chrysanthemumate [VIII (*dihydro*), R = COC_9H_{15}] was prepared as above; yield 89%; b.p. 170–173°/0.3 mm.; $n_D^{25°}$ 1.5210.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 73.00%; H, 7.93%. Found: C, 73.29%; H, 8.08%.

3-(3,4-Methylenedioxyphenyl)-2-propen-1-yl 3,5-dinitrobenzoate [VIII, R = $COC_6H_3(NO_2)_2$] was prepared as above; yield nearly quantitative, m.p. 148–149° (alcohol).

Anal. Calcd. for $C_{17}H_{12}N_2O_8$: C, 54.84%; H, 3.25%; N, 7.53%. Found: C, 55.06%; H, 3.27%; N, 7.73%.

3-(3,4-Methylenedioxyphenyl)propyl 3,5-dinitrobenzoate [VIII (*dihydro*), R = $COC_6H_3(NO_2)_2$] was prepared as above; yield nearly quantitative; m.p. 125–126° (alcohol).

Anal. Calcd. for $C_{17}H_{14}N_2O_8$: C, 54.55%; H, 3.77%; N, 7.49%. Found: C, 54.79%; H, 3.88%; N, 7.35%.

2,2-Dimethyl-5-piperonyl-m-dioxane (VII, R = R′ = CH_3) was prepared from 2-piperonyl-1,3-propanediol and acetone by the procedure of Prill, Hartzell, and Arthur,[5] except that 85% phosphoric acid was used as catalyst instead of *p*-toluenesulfonic acid. The intermediate diol was made by the lithium aluminum hydride reduction of piperonylmalonic ester and melted at 92–93° (benzene); yield of *m*-dioxane 66%; m.p. 81–82° (alcohol).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18%; H, 7.25%. Found: C, 66.73%; H, 6.92%.

2-Methyl-5-piperonyl-m-dioxane (VII, R = H, R′ = CH_3) was prepared from 2-piperonyl-1,3-propanediol and acetaldehyde; yield 54%; b.p. 137–146°/1 mm.; m.p. 76–78° (alcohol).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08%; H, 6.83%. Found: C, 66.24%; H, 6.85%.

2-Ethyl-5-piperonyl-m-dioxane (VII, R = H, R′ = C_2H_5) was prepared from 2-piperonyl-1,3-propanediol and propionaldehyde; yield 64%; b.p. 140–153°/0.8 mm.; m.p. 66–67° (alcohol).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18%; H, 7.25%. Found: C, 67.01%; H, 7.28%.

2-Ethyl-2-methyl-5-piperonyl-m-dioxane (VII, R = CH_3, R′ = C_2H_5) was prepared from 2-piperonyl-1,3-propanediol and 2-butanone; yield 40%; b.p. 151–158°/0.8 mm.; $n_D^{25°}$ 1.5251.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16%; H, 7.63%. Found: C, 67.91%; H, 7.74%.

2-Methyl-4-(3,4-methylenedioxyphenyl)-5-phenyl-m-dioxane (V, R = H, R′ = CH_3) was prepared from 1-(3,4-methylene-

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(4) W. F. Barthel and B. H. Alexander, *J. Org. Chem.*, **23**, 1012 (1958).

(5) E. A. Prill, A. Hartzell, and J. M. Arthur, *Contrib. Boyce Thompson Inst.*, **14**, 397 (1947).

dioxyphenyl)-2-phenyl-1,3-propanediol and acetaldehyde. This diol was prepared by the lithium aluminum hydride reduction of the methyl ester of the acetate of *beta*-(3,4-methylenedioxyphenyl)tropic acid, the preparation of which has been reported by Alexander and Barthel.[3] The procedure for making the *m*-dioxane is the same as described above; yield 60%; b.p. 200–225°/0.8 mm.; m.p. 109–111° (alcohol).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47%; H, 6.08%. Found: C, 71.60%; H, 6.18%.

2,2-Dimethyl-4-(3,4-methylenedioxyphenyl)-5-phenyl-m-dioxane (V, $R = R' = CH_3$) was prepared as described above from 1-(3,4-methylenedioxyphenyl)-2-phenyl-1,3-propanediol and acetone; yield 80%; m.p. 137–139° (alcohol).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06%; H, 6.45%. Found: C, 73.00%; H, 6.31%.

4-[1-(2-Ethylhexyloxy)ethoxy]methyl-1,2-methylenedioxybenzene [VI, $R = H$, $R' = CH_2CH(C_2H_5)C_4H_9$] and the other acetals, described below, were prepared from piperonyl alcohol and the vinyl ether of R′ according to the procedure reported by Beroza.[1] Because these acetals were somewhat unstable at high temperatures, they were distilled rapidly. Rapid distillation necessitated superheating, so that wide boiling ranges were obtained; yield 60%; b.p. 143–154°/0.8 mm.; $n_D^{25°}$ 1.4891.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10%; H, 9.15%. Found: C, 69.37%; H, 8.88%.

4-(1-Ethoxyethoxy)methyl-1,2-methylenedioxybenzene (VI, $R = H$, $R' = C_2H_5$); yield 79%; b.p. 112–116°/1.1 mm.; $n_D^{25°}$ 1.5021.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27%; H, 7.19%. Found: C, 63.85%; H, 7.38%.

4-[1-(2-Chloroethoxy)ethoxy]methyl-1,2-methylenedioxybenzene (VI, $R = H$, $R' = CH_2CH_2Cl$); yield 83%; b.p. 137–156°/0.7 mm.; $n_D^{25°}$ 1.5202.

Anal. Calcd. for $C_{12}H_{15}ClO_4$: Cl, 13.71%. Found: Cl, 13.67%.

4-(1-Butoxyethoxy)methyl-1,2-methylenedioxybenzene (VI, $R = H$, $R' = C_4H_9$); yield 71%; b.p. 123–132°/0.6 mm.; $n_D^{25°}$ 1.4954.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64%; H, 7.99%. Found: C, 66.66%; H, 7.83%.

4-(1-Isobutoxyethoxy)methyl-1,2-methylenedioxybenzene [VI, $R = H$, $R' = CH_2CH(CH_3)_2$]; yield 63%; b.p. 116–129°/0.8 mm.; n_D^{25} 1.4938.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64%; H, 7.99%. Found: C, 66.05%; H, 7.67%.

4-{1-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}methyl-1,2-methylenedioxy-5-propylbenzene [VI, $R = C_3H_7$, $R' = (C_2H_4O)_2C_2H_5$] was prepared from 6-propylpiperonyl alcohol which was made by the chloromethylation of safrole[6] and then hydrogenation; yield 50%; b.p. 169–195°/0.5 mm.; n_D^{25} 1.4950.

Anal. Calcd. for $C_{19}H_{30}O_6$: C, 64.38%; H, 8.53%. Found: C, 64.54%; H, 8.53%.

4-{1-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}methyl-1,2-methylenedioxy-5-propenylbenzene [VI, $R = CH{:}CHCH_3$, $R' = (C_2H_4O)_2C_2H_5$]; yield 60%; b.p. 186–209°/0.3 mm.; n_D^{25} 1.5136.

Anal. Calcd. for $C_{19}H_{28}O_6$: C, 64.75%; H, 8.01%. Found: C, 64.61%; H, 8.01%.

4-{1-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}methyl-1,2-methylenedioxybenzene [VI, $R = H$, $R' = (C_2H_4O)_2C_2H_5$]; yield 70%; b.p. 172–180°/0.3 mm.; n_D^{25} 1.4941.

Anal. Calcd. for $C_{16}H_{24}O_6$: C, 61.52%; H, 7.75%. Found: C, 61.30%; H, 7.40%.

Ethyl-3-(2-chloro-4,5-methylenedioxyphenyl)-2-phenylacrylate (II, $R = C_2H_5$, X = *Cl*) was prepared from 6-chloropiperonal according to reported directions;[7] over-all yield 37%; m.p. 61–63° (alcohol).

Anal. Calcd. for $C_{18}H_{15}ClO_4$: C, 65.36%; H, 4.57%; Cl, 10.72%. Found: C, 64.93%; H, 4.53%; Cl, 10.20%.

Ethyl-3-(2-bromo-4,5-methylenedioxyphenyl)-2-phenylacrylate (II, $R = C_2H_5$, X = *Br*) was prepared as above; over-all yield 45%; m.p. 76–78° (alcohol).

Anal. Calcd. for $C_{18}H_{15}BrO_4$: C, 57.61%; H, 4.03%; Br, 21.30%. Found: C, 58.12%; H, 3.90%; Br, 21.84%.

Piperonyl octanoate [IV, $R = (CH_2)_6CH_3$] was made in the usual manner from the alcohol and acid chloride; yield 90%; b.p. 130°/0.3 mm.; n_D^{25} 1.4977.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.06%; H, 7.91%. Found: C, 68.97%; H, 8.20%.

Piperonyl chloroacetate (IV, $R = CH_2Cl$) was prepared as above; yield 90%; b.p. 126–127°/0.4 mm.; n_D^{25} 1.5440.

Anal. Calcd. for $C_{10}H_9ClO_4$: C, 52.51%; H, 3.94%. Found: C, 53.24%; H, 4.15%.

Piperonyl isobutyrate [IV, $R = CH(CH_3)_2$] was prepared as the above; yield 90%; b.p. 99°/0.07 mm.; n_D^{25} 1.5068.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85%; H, 6.35%. Found: C, 64.40%; H, 6.64%.

Piperonyl p-anisate (IV, $R = p\text{-}CH_3OC_6H_4$) was prepared as the above; yield 82%; b.p. 200°/0.1 mm.; m.p. 61° (benzene–petroleum ether, 60–70°).

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13%; H, 4.90%. Found: C, 67.27%; H, 5.17%.

Piperonyl 1-naphthoate (IV, $R = alpha\text{-}C_{10}H_7$) was prepared as the above; yield 84%; m.p. 86–87° (alcohol).

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.51; H, 4.58%. Found: C, 74.27%; H, 4.61%.

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