material in the zones were eluted with ethanol, crystallized from ethanol, and identified[3,11] by melting point, mixed melting point ultraviolet and infrared analyses. On several occasions the purity of the zone was checked by a high vacuum sublimation.

(11) J. D. Roberts and Charlotte Green, *J. Am. Chem. Soc.*, **68**, 214 (1946); E. H. Brande and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

INDIAN HEAD, MD.

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

Preparation of Some Substituted Derivatives of Sesamol. I. Synthesis of Halogenated Sesamol Esters

B. H. ALEXANDER, T. A. ODA, R. T. BROWN, AND S. I. GERTLER

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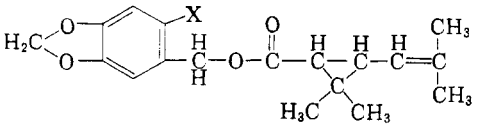
Following studies on two exceptionally active insecticidal substances, 6-chloropiperonyl chrysanthemumate and its bromo analog, a series of new halogenated sesamol (3,4-methylenedioxyphenol) esters having a structural resemblance to them have been synthesized. A method for the bromination of sesamol is described. Simultaneous addition of halogen to a double bond and substitution in the ring was obtained in the bromination of sesamyl chrysanthemumate.

6-Chloro- and 6-bromopiperonyl chrysanthemumates (I)[1] have shown marked insecticidal proper-



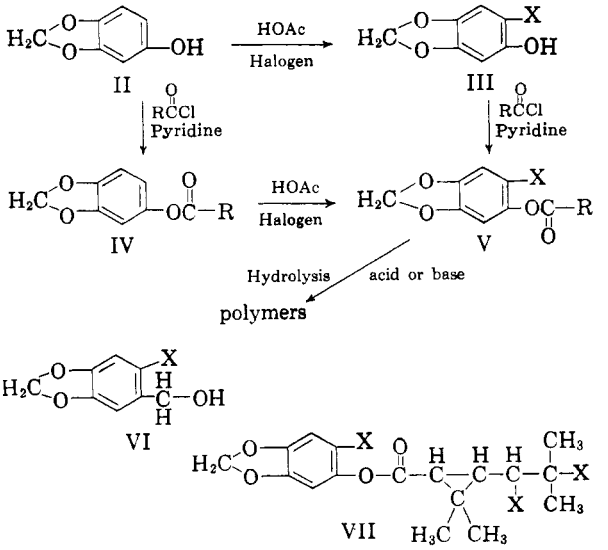
I, X = Br or Cl

ties in preliminary tests against a wide variety of insects. In view of the considerable interest in these chrysanthemumates, the preparation of similar compounds was undertaken. VII, a halogenated sesamol derivative, was synthesized and found to be insecticidal. Since the literature discloses no previous syntheses of halogenated sesamol compounds, many such derivatives were prepared and tested, and those more closely related to the active esters (I) are reported here.

Very little has been reported also on the chemistry of sesamol derivatives, although several methods of synthesizing the parent compound (II) have been described.[2,3] Haslam and Haworth presented the synthesis of sesamol *p*-toluenesulfonate[4] in 1955. A year later Beroza[3] reported the preparation of 66 sesamol ethers, esters, acetals, sulfonates, and urethans, some of which have outstanding properties as pyrethrin synergists.

The 6-halopiperonyl alcohols (VI) were made by halogenation of piperonyl alcohol to give 6-halopiperonyl halide, acetylation of the halide, and then hydrolysis of the resultant acetate.[1,5] A similar halogenation of sesamol acetate (IV) gave V, but attempts to saponify it to give III yielded only polymeric substances. Polymer formation was avoided and the product (III) obtained in 90% yield by adding halogen to sesamol in glacial acetic acid below 10° and working up the mixture immediately.

The chrysanthemumoyl ester (IV, R = C_9H_{15}) was made from synthetic chrysanthemumoyl chloride which is a DL-*cis-trans* compound. The preparation of VII from IV (R = C_9H_{15}) involves the simultaneous addition of halogen to a double bond and substitution in the ring.



II III IV V VI VII

EXPERIMENTAL

3,4-Methylenedioxyphenyl acetate (IV, R = CH_3) was prepared as previously reported;[3] b.p. 144–145°/14 mm., $n_D^{25°}$ 1.5265; yield quantitative.

3,4-Methylenedioxyphenyl chyrsanthemumate (IV, R =

(1) W. F. Barthel and B. H. Alexander, *J. Org. Chem.*, **23**, 1012–14 (1958).

(2) J. Boeseken, W. D. Cohen, and C. J. Kip, *Rec. trav. chim.*, **55**, 815 (1936).

(3) M. Beroza, *J. Agr. Food Chem.*, **4**, 49 (1956).

(4) E. Haslam and R. D. Haworth, *J. Chem. Soc.*, 827 (1955).

(5) R. G. Naik and T. S. Wheeler, *J. Chem. Soc.*, 1780 (1938).

C_9H_{15}) was prepared from synthetic chrysanthemumoyl chloride according to the method of Beroza,[3] b.p. 140–141°/0.25 mm., $n_D^{25°}$ 1.5302; when the supersaturated liquid was seeded with crystals (m.p. 66–67°) obtained from Beroza, a crystalline mass was obtained which was purified by crystallization from petroleum ether; crude yield 92%.

2-Bromo-4,5-methylenedioxyphenol (III) was prepared by cooling to 0° a stirred solution of sesamol (II) (207 g.) and glacial acetic acid (450 ml.), and then slowly adding bromine (60 ml.) in glacial acetic acid (225 ml.) while holding the temperature below 10°. Immediately after the addition of bromine, the mixture was poured into ice and water, filtered quickly, and the crystals (III) washed with cold water until free of solvent; yield 90%. Although crude III is affected by light and air, when free of the acid solvent and kept in a dark bottle it was stable and could be used for further syntheses. The light green compound melted at 84° (dec.), and was very difficult to recrystallize. A small amount of III was purified by distillation under high vacuum and recrystallization from benzene; it melted at 88° (dec.); the yield from this distillation was low. III gave a positive phenol test with 2% ferric chloride solution.

Anal. Calcd. for $C_7H_5BrO_3$: C, 38.72; H, 2.32; Br, 36.8. Found: C, 39.50; H, 2.62; Br, 36.15.

2-Bromo-4,5-methylenedioxyphenyl acetate (V, R = CH_3) was prepared from III by treatment with acetyl chloride and pyridine and from IV by treatment with glacial acetic acid and halogen at 0°; recrystallized from ethanol; m.p. 84–86°; crude yield quantitative.

Anal. Calcd. for $C_9H_7BrO_4$: Br, 30.85. Found: Br, 30.65.

2-Bromo-4,5-methylenedioxyphenyl propionate (V, R = C_2H_5) was prepared *via* the acid chloride in the same way as was the acetate; b.p. 108°/0.2 mm., solidified; recrystallized from ethanol; m.p. 60–61°; yield 80%.

Anal. Calcd. for $C_{10}H_9BrO_4$: Br, 29.27. Found: Br, 28.92.

2-Bromo-4,5-methylenedioxyphenyl 1-naphthoate (V, R = $C_{10}H_7$) was prepared as described above; recrystallized from ethanol; m.p. 109–110°; crude yield quantitative.

Anal. Calcd. for $C_{18}H_{11}BrO_4$: Br, 21.53. Found: Br, 21.52.

2-Bromo-4,5-methylenedioxyphenyl benzoate (V, R = C_6H_5) was prepared as above described; recrystallized from ethanol; m.p. 131°; yield 80%.

Anal. Calcd. for $C_{14}H_9BrO_4$: Br, 24.89. Found: Br, 24.15.

2-Bromo-4,5-methylenedioxyphenyl ester of 3-(1,2-dibromo-2-methylpropyl)-2,2-dimethylcyclopropanecarboxylic acid (VII) was prepared by the bromination of 3,4-methylenedioxyphenyl chrysanthemumate (IV, R = C_9H_{15}). IV (28.8 g.) was placed in a 600-ml. beaker containing pyridine (8 g.) and glacial acetic acid (100 ml.) at 0° and bromine (32 g.) in glacial acetic acid (50 ml.) was added dropwise with continuous stirring. The whole was then poured into ice and water whereupon a yellow precipitate formed. The mixture was extracted with ether and the layers were separated. The ether layer was washed with dilute sodium bicarbonate, then water. After removal of the ether, crystallization occurred. Alcohol was added to the crystalline mass and triturated while being warmed to about 50°. The mixture was filtered and the crystals of VII were washed with alcohol; crude yield 96%; recrystallized once from a mixture of benzene and alcohol, m.p. 130–141°; and then twice from benzene alone; the product was rather soluble in benzene so that the purified yield was less than 30%; m.p. 140–142°.

Anal. Calcd. for $C_{17}H_{19}Br_3O_4$: C, 38.74; H, 3.66; Br, 45.49. Found: C, 39.16; H, 3.63; Br, 45.05.

2-Bromo-4,5-methylenedioxyphenyl chrysanthemumate (V, R = C_9H_{15}) was prepared from synthetic chrysanthemumoyl chloride in the same manner as were the halopiperonyl chrysanthemumates[1]; b.p. 163–171°/0.11 mm., $n_D^{25°}$ 1.5483; yield 67%.

Anal. Calcd. for $C_{17}H_{19}BrO_4$: C, 55.60; H, 5.21; Br, 21.76. Found: C, 55.27; H, 5.18; Br, 21.70.

The chloro derivative (V, R = C_9H_{15}), prepared in the same manner, boiled at 142–157°/0.2 mm. and had $n_D^{25°}$ 1.5355.

BELTSVILLE, MD.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DAINIPPON PHARMACEUTICAL CO.]

Palladium Dehydrogenation of Methyl Reserpate and Yohimbine in Cymene[1]

HIDEHIKO KANEKO

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On dehydrogenation with palladium-carbon in boiling cymene, methyl reserpate yielded 7-methoxyyobyrine and *Py*-tetradehydroreserpic acid lactone and yohimbine gave *Py*-tetradehydroyohimbic acid or *Py*-tetradehydroyohimbine.

The selenium dehydrogenation procedure has been widely employed for elucidation of the structure of indole alkaloids, for example yohimbine,[2] corynantheine,[3] reserpine,[4] and ajmaline.[5] Since this reaction has usually been carried out at temperatures about 300°, dehydrogenation has sometimes been accompanied by rearrangement and cleavage of the ring system of the alkaloids. I, therefore, thought it of some interest to investigate the dehydrogenation under milder conditions. The present paper describes the products of the dehydrogenation of methyl reserpate and yohimbine by palladium-carbon in boiling *p*-cymene.

Methyl reserpate (Ia) is a minor constituent of *Rauwolfia serpentina*,[6] but can most conveniently be obtained by methanolysis of reserpine[7] (Ib).

(1) Presented at the annual meeting of the Pharmaceutical Society of Japan held in Fukuoka, Japan, April, 1956.

(2) G. Barger and C. Scholtz, *Helv. Chim. Acta*, **16**, 1343 (1933); **18**, 923 (1935).

(3) P. Karrer and P. Enslin, *Helv. Chim. Acta*, **32**, 1390 (1949).

(4) J. M. Muller, E. Schlittler, and H. Bein, *Experientia*, **8**, 338 (1952).

(5) F. A. L. Anet, D. Chakravarti, R. Robinson, and E. Schlittler, *J. Chem. Soc.*, 1242 (1954).

(6) A. Hofmann, *Helv. Chim. Acta*, **37**, 849 (1954).

(7) L. Dorfman, A. Furlenmeier, C. F. Huebner, R. Lucas, H. B. Macphillamy, J. M. Mueller, E. Schlittler, and A. F. Andre, *Helv. Chim. Acta*, **37**, 59 (1954).