

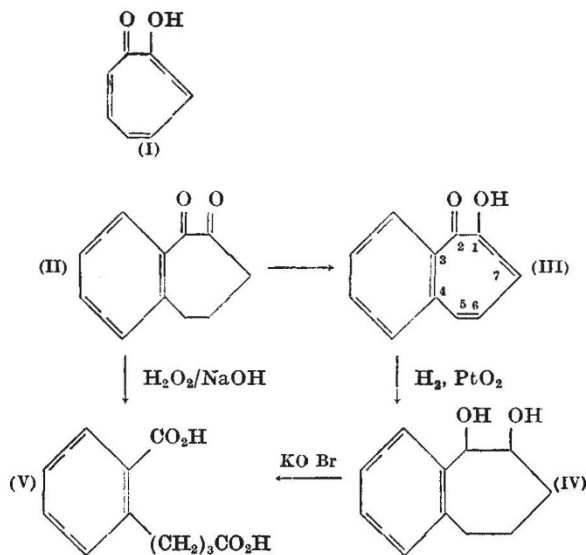
Synthesis of 3:4-Benzotropolone

DEWAR¹ has interpreted the chemistry of the mould metabolite, stipitatic acid, and of colchicine (the methyl ether of which is the alkaloid colchicine) by postulating that they are derived from the hypothetical *cycloheptatrienolone* (I). This he termed 'tropolone', and he attributed to it quasi-aromatic character. This interesting suggestion, for which no tangible evidence was advanced², has acquired more plausibility from the recent demonstration of Haworth, Moore and Pauson³ that purpurogallin is a trihydroxybenztropolone, as earlier suggested by Barltrop and Nicholson⁴, and from the finding of Erdtman and Gripenberg⁵ that the cedar-wood constituent γ -thujaplicin is an *isopropyltropolone*. Hitherto, a synthetic tropolone of established constitution has not been prepared, and the properties ascribed to such a structure have been based largely on speculation.

We have now synthesized one of the two possible benztropolones, namely, 3:4-benztropolone (III), and have made a preliminary survey of its properties. 2:3-Benz-1-suberone⁶ was oxidized by selenium dioxide in boiling ethanol to 3:4-benzsuberone-1:2-dione (II), a deep yellow liquid, b.p. 128–132°/0.4 mm., which gave a mono-2:4-dinitrophenylhydrazone, m.p. 230–232° (found: C, 57.5; H, 3.95; N, 15.8. $C_{17}H_{14}O_6N_4$ requires C, 57.6; H, 4.0; N, 15.8 per cent) and a semicarbazone, m.p. 190–192°. The diketone (II) was dehydrogenated to 3:4-benztropolone (III) by bromine in acetic acid at 100°. The tropolone, obtained by this method in small yield, crystallized from *cyclohexane* in pale yellow needles, m.p. 85–86° (found: C, 76.3, 77.0; H, 4.7, 4.6. *M* (Rast), 186. $C_{11}H_8O_2$ requires C, 76.7; H, 4.7 per cent. *M*, 172). Better results were obtained when the dehydrogenation was effected with 10 per cent palladized charcoal in boiling trichlorobenzene, under nitrogen (5 hours). The benztropolone was isolated in 10 per cent yield from the fraction of the products soluble in dilute sodium hydroxide solution. Two other products, not yet investigated, were also isolated. After the crude trichlorobenzene solution was diluted with benzene, shaking with sodium bicarbonate solution extracted a small amount of a compound which, after reprecipitation with acid, crystallized from light petroleum in yellow needles, m.p. 128–130°. Addition of sodium hydroxide solution to the benzene-trichlorobenzene liquors gave a buff-coloured neutral crystalline solid, m.p. 265–268°, the benztropolone being afterwards liberated by acidification of the alkaline liquors.

Benztropolone, of which purpurogallin is a trihydroxy derivative, had in most respects the chemical properties which would be expected from its structure and from the behaviour of natural products thought to be tropolone derivatives. Although, unexpectedly, not sufficiently acidic to undergo salt formation with sodium bicarbonate, it dissolved readily in sodium hydroxide solution. By fusion with 80 per cent potash at 180–185°, it was almost quantitatively converted into α -naphthoic acid.

The presence of a seven-membered ring, indicated by the method of synthesis, was confirmed by hydrogenation of benztropolone over Adams's catalyst to the diol (IV), which gave a yellow-green colour with Criegee's potassium tetramethylsulfate reagent⁷, was unaffected by alkaline hydrogen peroxide, but was oxidized by potassium hypobromite to γ -2-carboxyphenylbutyric acid (V), obtained also by oxidation



of benzsuberone with 2 per cent nitric acid⁸. Benztropolone showed no carbonyl reactivity, but was hydrogenated over palladized charcoal to a resinous product which gave an immediate precipitate with 2:4-dinitrophenylhydrazine and was oxidized by alkaline hydrogen peroxide to the acid (V), as also was benzsuberandione (II). Microhydrogenation of benztropolone using palladium-black led to absorption of three molecules of hydrogen. Haworth, Moore and Pauson³ recorded a similar behaviour in the hydrogenation of a methyltropolone, which they prepared by degradation of purpurogallin.

Benztropolone gave a brownish-red colour with ferric chloride, and dissolved in concentrated hydrochloric acid to a bright yellow solution. On dilution, the colour was destroyed and the benztropolone was precipitated. Benztropolone coupled with *p*-tolyl-diazonium chloride to give a crimson precipitate.

Details of this work, which is being extended, will be published elsewhere.

J. W. COOK
A. R. SOMERVILLE

Chemistry Department,
University of Glasgow.
Jan. 19.

¹ Dewar, M. J. S., *Nature*, **155**, 50, 141, 479 (1945).

² But compare Arnstein, H. R. V., Tarbell, D. S., Huang, H. T., and Scott, G. P., *J. Amer. Chem. Soc.*, **70**, 1669 (1948).

³ Haworth, R. D., Moore, B. P., and Pauson, P. L., *J. Chem. Soc.*, 1045 (1948).

⁴ Barltrop, J. A., and Nicholson, J. S., *J. Chem. Soc.*, 116 (1948).

⁵ Erdtman, H., and Gripenberg, J., *Nature*, **161**, 719 (1948).

⁶ Plattner, P. A., *Helv. Chim. Acta*, **27**, 804 (1944). Cook, J. W., Philip, R., and Somerville, A. R., *J. Chem. Soc.*, 169 (1948).

⁷ Criegee, R., Marchand, B., and Wannowius, H., *Annalen*, **550**, 111 (1942).

⁸ Kipping, F. S., and Hunter, A. E., *J. Chem. Soc.*, **83**, 250 (1903).

Amylopectin and Glycogen: Products of Irreversible and Reversible Synthesis

It is assumed that the molecules of amylopectin and glycogen have a ramified structure, the glucose residues being united by α -glucosidic 1,4- or 1,6-linkages, the latter representing the branching points. By β , the 'degree of ramification', we shall denote the ratio between the number of 1,6-linkages and the total number of glucose residues. For amylopectin, $\beta \sim 0.056$; for glycogen, $\beta \sim 0.09$.