

THE CHEMICAL CONSTITUENTS OF AUSTRALIAN *FLINDERSIA* SPECIES

VIII. THE STRUCTURE OF MACULINE

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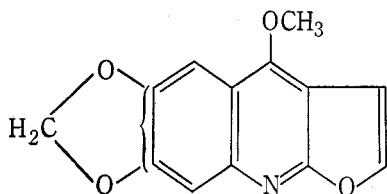
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Summary

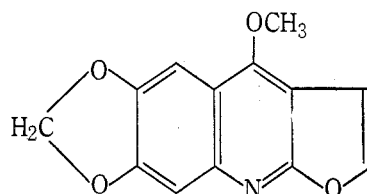
Maculine is shown by degradation to be 6,7-methylenedioxydictamnine (II).

I. INTRODUCTION

In Part V of this series (Brown *et al.* 1954), the isolation of maculine from the bark of *Flindersia maculosa* Lindl. together with a preliminary examination of the alkaloid was described. Maculine analysed for $C_{13}H_9O_4N$, contained one methoxyl group, and gave a positive Labat methylenedioxy test. It was isomerized to *isomaculine* on heating with methyl iodide, and had an ultraviolet absorption spectrum similar to those of kokusagine and skimmianine. This evidence suggested that maculine was a methylenedioxydictamnine (I).



(I)



(II)

As kokusagine, which is different from maculine, has already been shown to be 7,8-methylenedioxydictamnine (Narahashi, Ohta, and Terasaka 1954), this leaves only the 5,6- and 6,7-positions possible for the methylenedioxy group in maculine. In order to distinguish between these alternate structures, maculine was hydrogenolysed and demethylated to the 3-ethyl-2,4-dihydroxyquinoline, after the method used for the degradation of evolatine (Gell, Hughes, and Ritchie 1955). 3-Ethyl-6,7-methylenedioxy-2,4-dihydroxyquinoline was synthesized from 3,4-methylenedioxyaniline and diethyl ethyl malonate in boiling diphenyl ether. This product was identical with that obtained from maculine as shown by direct comparison (mixed melting points and X-ray powder photographs) of the dihydroxyquinolines themselves and their acetyl derivatives. Maculine is therefore 6,7-methylenedioxydictamnine (II).

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II. EXPERIMENTAL

Melting points are uncorrected. Powder photographs were taken in a 19 cm X-ray Powder Camera, using CuK α radiation. Microanalyses are by Miss B. Stevenson, University of Sydney.

(a) *Degradation of Maculine*.—Maculine (0.18 g) was dissolved in ethanol (20 ml) and hydrogenolyzed at room temperature and pressure in the presence of Adams's catalyst. The product was demethylated by heating under reflux with hydrochloric acid (5N; 15 ml) for 30 min. The precipitate which separated on cooling to 0 °C was dissolved in aqueous sodium hydroxide (charcoal) and the product precipitated with acetic acid. The product (0.04 g) crystallized from ethanol in colourless plates, m.p. 300–303 °C (Found: C, 61.6; H, 4.8%. Calc. for C₁₂H₁₁O₄N: C, 61.8; H, 4.7%).

(b) *Synthesis of 3-Ethyl-6,7-methylenedioxy-2,4-dihydroxyquinoline*.—Diethyl ethyl malonate (1.88 g) and 3,4-methylenedioxyaniline (1.40 g) in diphenyl ether (20 ml) were heated under reflux for 45 min. The mixture was cooled, hexane (50 ml) added, and the precipitate collected. The crude material was dissolved in aqueous sodium hydroxide (charcoal) and the product precipitated with acetic acid. The product (0.70 g, 30% yield) crystallized from ethanol in colourless plates, m.p. 300–303 °C (Found: C, 61.9; H, 5.0; N, 5.7%. Calc. for C₁₂H₁₁O₄N: C, 61.8; H, 4.7; N, 6.0%). The mixed m.p. with the substance obtained in (a) was not depressed. The X-ray powder photographs of the two substances were identical.

The acetyl derivative (presumably the 4-acetoxy-) was prepared by heating the dihydroxyquinoline (0.4 g) with acetic anhydride (5.0 ml) and pyridine (1 drop) on the water-bath for 2 hr. The product crystallized from ethanol in colourless needles, m.p. 292–295 °C (Found: C, 61.0; H, 4.8; N, 5.3%. Calc. for C₁₄H₁₃O₅N: C, 61.1; H, 4.7; N, 5.1%). By the same method, an acetyl derivative was prepared from the substance obtained from maculine. It crystallized from ethanol in colourless needles, m.p. 292–295 °C, undepressed on admixture with the above. The X-ray powder photographs of the two substances were identical.

III. ACKNOWLEDGMENT

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IV. REFERENCES

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