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THE OCCURRENCE OF THE ALKALOID ORICINE IN THE WOOD OF *ORICIA SUAVEOLENS**

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Abstract—Oricine, an alkaloid related structurally to Flindersine, was isolated from the heart-wood of *Oricia suaveolens* The MS, IR and NMR spectra were shown to agree with those of the synthesized compound

INTRODUCTION

Oricia suaveolens (Rutaceae) is a small under-storey plant, locally abundant in the forest reserves in Nigeria. Extraction of its heart-wood gave an alkaloid whose structure was found to be very closely related to flindersine (I) and atanine (II).

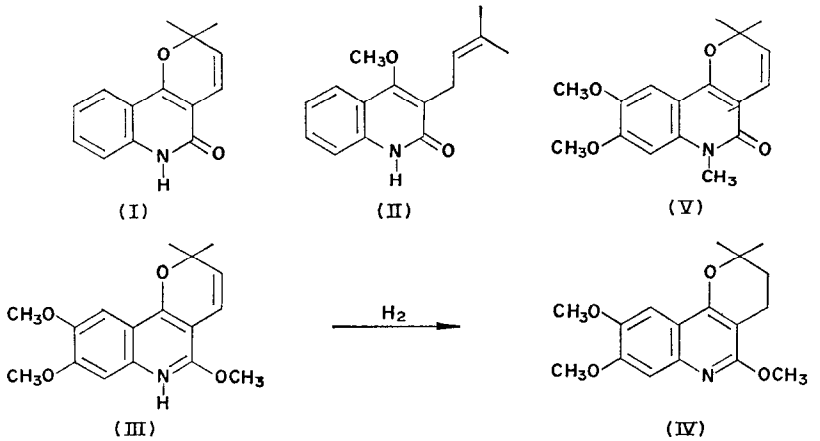
Flindersine was first isolated from the wood of the Australian tree *Flindersia australis*, (Rutaceae).[1] Atanine, which appears to be an intermediate in the biogenesis of flindersine, has been shown to be a major constituent of a West African member of the Rutaceae, *Fagara zanthoxyloides* (ata).[2] Cyclodehydrogenation of atanine gave flindersine in a quantitative yield.[3] The isolation of oricine from another Rutaceous plant, the elucidation by spectroscopic methods of its structure as a derivative of flindersine and the confirmation of this structure by synthesis are reported in this communication.

RESULTS AND DISCUSSION

Percolation of the pulverized heart-wood of *Oricia suaveolens* with light petroleum afforded a large amount of oil. Column chromatography of the oil on neutral alumina gave glassy, prism-like crystals of oricine m.p. 150–152° (from benzene). M^+ 301. The elemental analysis combined with the molecular weight determination suggested the empirical formula $C_{17}H_{19}O_4N$. The NMR spectrum showed a six-proton sharp singlet at δ 1·53 attributable to two methyl groups; a three-proton sharp singlet at δ 3·70 which was first thought to be attributable to the protons of a methoxy group, but later found to be due to the protons of a methylimino group (=N CH_3). The singlets at δ 3·98 and δ 4·02 counting for three protons each were assigned to two methoxy groups. There were two doublets at δ 5·48 (J = 10 c/s) and δ 6·75 (J = 10 c/s) due to the ethylenic protons of such grouping as —C—CH=CH—C— with no hydrogen atoms on the contiguous carbon atoms. The signal at δ 6·73 and δ 7·31 were attributed to two benzenoid protons and since they did not couple with each other, they were, perhaps, para to each other.

* This communication is an extract from the work approved for the award of the Ph.D. degree of the University of Ibadan, Nigeria (M.O.A. 1970)

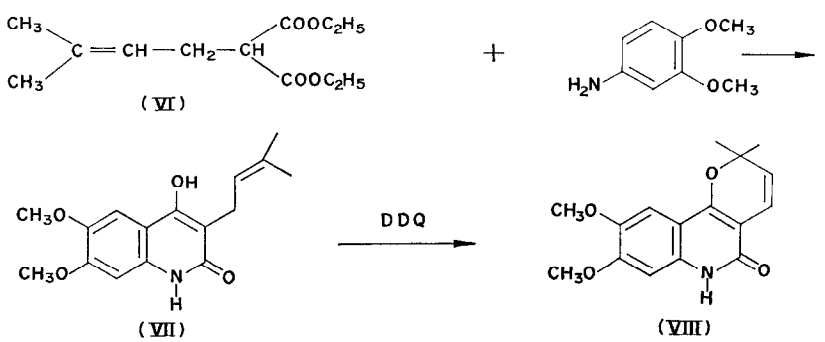
[1] F. R. C. BROWN *et al.*, *Austral. J. Chem.* 7, 348 (1954).
[2] I. T. U. ESHIET and D. A. H. TAYLOR, *Chem. Commun.* 114 (1966); *J. Chem. Soc.* 481 (1968).
[3] M O ABE, unpublished.



Hydrogenation of oricine with platinum oxide as catalyst in methanol gave dihydro-oricine, m.p. 150°. In the NMR of the dihydro oricine, there were two triplets centred at δ 1·83 (J = 7 c/s) and δ 2·65 (J = 7 c/s) which were not present in the spectrum of oricine. The doublets at δ 5·48 and δ 6·75 in the NMR spectrum of oricine disappeared in that of dihydrooricine. The molecular weight (M^+ from mass spectra) of dihydrooricine was 303 showed an addition of two units to that of oricine, indicating that it had only one reducible ethylenic bond. The presence of two triplets in the NMR spectrum of dihydrooricine in place of the doublets at δ 5·48 and δ 6·75 of the NMR spectrum of oricine showed the reduction of —CH=CH— to —CH_2—CH_2—.

The UV spectrum of oricine was comparable with that of flindersine and atanine. It appeared, therefore, that oricine had the same nucleus as flindersine and structures (III), (IV) were suggested for oricine and dihydrooricine.

The three proton signal at δ 3·70 in the NMR spectrum of oricine was thought to be due to the protons of one of the methoxy groups. If so, it was wondered why the protons of the methoxy groups should resonate at a higher field than the protons of the other two methoxy groups. It was assumed, therefore, that the methoxy group was in the heterocyclic ring and close to the hetero-atom. The methoxy group was, therefore, thought to be in the 2-position of the alkaloid as in structure (III). But on a close inspection of the IR spectrum of oricine, it was found that the characteristic imino band =NH expected at about ν_{max} 3333 cm^{-1} was absent. Again, the characteristic carbonyl band at ν_{max} 1639 cm^{-1} for a 2-quinolone was very prominent, showing that oricine could not have been 2-*O*-methylated as in (III). From the above facts, it was suggested that the structure of oricine was 1-methyl-6,7-dimethoxy flindersine (V).



This structure was confirmed synthetically by the method of Poizzi *et al.*[4] Refluxing an excess amount of diethyl-($\gamma\gamma$-dimethylallyl)-malonate (VI) with aminoveratrole gave the intermediate 6,7-dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone (VII) which was cyclodehydrogenated to give demethyl oricine (VIII). *N*-methylation of demethyloricine gave a compound whose NMR and IR were superimposable on those of oricine (V).

EXPERIMENTAL

Isolation of oricine. The pulverized wood (14·75 kg) was extracted continuously for over 2 days with light petroleum (60–80°). Evaporation of the solvent afforded an oily material (300 g) which was chromatographed on alumina and a fraction eluted with 20% benzene in Et_2O gave a yellow crystalline substance, oricine. Recrystallization from benzene gave large, prism-like crystals (1·5 g) m.p. 150–152°, optically inactive. (Found C, 67·05, H, 6·2; $C_{17}H_{19}O_4N$ requires C, 67·17, H, 6·34%.) M^+ (from mass spectrum) 301 ν_{max} 1639 cm^{-1} (carbonyl of 2-quinolone).

Hydrogenation of oricine. Oricine (0·135 g) was dissolved in MeOH (50 ml) and Pt_2O (0 1 g) added. The mixture was shaken up with H_2 at atmospheric pressure until no more uptake. The filtrate was evaporated to give white crystalline, dihydrooricine m p. 150°. (Found C, 67·02, H, 6·81, $C_{16}H_{21}O_4N$ requires C, 67·32, H, 6·93%.) M^+ (from mass spectrum) 303.

Preparation of 6,7-dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone. A mixture of aminoveratrole (3 g) and diethyl—($\gamma\gamma$-dimethylallyl)-malonate (6 g) in diphenyl ether (50 ml) was refluxed in N_2 for 5 hr. When cool, the solid 2-quinolone was precipitated with petrol (40°–60°), collected and washed. The solid was shaken with $CHCl_3$ and filtered to give an ash-coloured powder. Yield 1·8 g, m.p. 200°–201°. (Found: C, 66·51, H, 6·84%; $C_{16}H_{19}O_4N$ requires C, 66·42, H, 6·58%). M^+ (mass spectrum) 289. γ_{max} 1639 cm^{-1} (Carbonyl of a 2-quinolone).

Preparation of demethyl-oricine. 6,7-Dimethoxy-3-isopentenyl-4-hydroxy-2-quinolone (0·1042 g) and 2,3-dicyano-5,6-dichloro benzoquinone (DDQ) (0·1056 g) in dry benzene (100 ml) was refluxed for 4 hr. The mixture was cooled, filtered, evaporated and the residue extracted with $CHCl_3$, washed with 10% $NaHCO_3$ (*ca.* 500 ml) and H_2O. The $CHCl_3$ extract was dried (Na_2SO_4) and evaporated to give a crystalline substance m.p. 210°–212°. Yield (*ca.* 0 1 g). (Found: C, 68 01; H, 6 01%; $C_{16}H_{17}O_4N$ requires C, 67·92; H, 5 98%) M^+ (mass spectrum) 287.

Methylation of N-demethyloricine to oricine. *N*-demethyloricine (0 05 g), MeI (2 ml) K_2CO_3 (5 g) in acetone (40 ml) was refluxed for 6 hr on a steam bath. The filtrate was evaporated to give a residue which was taken up in $CHCl_3$, washed (H_2O), dried (Na_2SO_4) and evaporated to give oricine. Recrystallized from benzene, m.p. 150°. Yield (0 03 g). (Found: C, 67·51; H, 6·30%.) The IR and NMR spectra were identical with those of the authentic oricine.

[4] F Piozzi, P. Venturella and A. Bellino, *Gazz. Chim. Ital.* **99**, 711 (1969); *Chem. Abs.* **71**, 91709 (1969).

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NEUTRAL CONSTITUENTS OF *ORIXA JAPONICA*

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Plant. Orixa Japonica Thunb. *Uses.* Not known. *Previous work.* Alkaloids.[1]

Leaves. Extracted with MeOH, steam distillation. Chromatographed using Al_2O_3. *Bergapten.* $C_{12}H_8O_4$, m.p. 191–192°. M.p., mixed m.p., superimposable IR and NMR spectra. *Xanthotoxin.* $C_{12}H_8O_4$, m.p. 146–148°. M.p., mixed m.p., superimposable IR and NMR spectra. *Friedelin.* $C_{30}H_{50}O$, m.p. 260–261°. M.p., mixed m.p., superimposable IR and NMR spectra. *Isoarborinol.* $C_{30}H_{50}O$, m.p. 298–299°. M.p., mixed m.p., superimpos-

* On leave of absence from Kojin Co. Ltd.

[1] M. Terasaka, T. Ohta and K. Narahashi, *J Pharm. Soc Japan* **73**, 773 (1953), *idem. Chem. Pharm. Bull. Japan* **2**, 159 (1954) M. Terasaka, *ibid*, **8**, 523 (1960).