Wood. (500 g) Chromatography (SiO_2) of the petrol extract (1 g) gave β-sitosterol (0·02%) and of the MeOH extract (5 g) complex mixtures which were not further investigated.

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RUTACEAE

A QUINOLONE ALKALOID FROM *ORICIA SUAVEOLENS*

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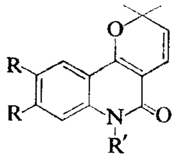
Abstract—The timber of *Oricia suaveolens* has been found to contain 6,7-dimethoxy-*N*-methylflindersine, which has been synthesized. Roots of *Clausena anisata* yielded the known coumarins imperatorin and coumarrayin.

Oricia suaveolens (Engl.) Verdoon is a small under-storey tree locally common in West Africa, belonging to the family Rutaceae. In the course of work designed to find new limonoids, we extracted the timber of this tree. Chromatography of the light petroleum extract gave a new compound which we call oricine, m.p. 150–155°. The mass spectral molecular weight was 301; elemental analysis suggested the formula $C_{17}H_{19}O_4N$. The NMR spectrum showed two methoxy groups at about δ 4·0, a methyl group at δ 3·7, two coupled vinyl protons ($J = 10$ cycles/sec) at δ 5·48 and 6·75, two single proton singlets at δ 6·73 and 7·31, and a six proton singlet at δ 1·53. Catalytic hydrogenation gave dihydro-oricine, m.p. 150°, in which the two vinyl doublets were missing, being replaced by two triplets at δ 1·83, 2·65 each corresponding to two hydrogen atoms. The i.r. spectrum of oricine (ν_{max} 1630 cm^{-1}) suggested a quinolone, the u.v. spectrum (λ_{max} 260, 355, 373 nm) was similar to that of flindersine (Ia).[1]

Since the two aromatic protons are not strongly coupled, we assumed they were *para* to each other, which means the methoxy groups must be at positions 6 and 7 of the benzene ring. The final methyl group can be accommodated as an *N*-methyl group, which is shifted downfield from the usual position of an amide methyl by the deshielding due to the aromatic nucleus. Consequently we concluded that oricine was 6,7-dimethoxy-*N*-methylflindersine (Ib).

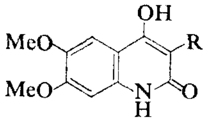
[1] R. F. C. BROWN *et al.*, *Australian J. Chem.* **7**, 348 (1954).

This was confirmed by synthesis. 4-Aminoveratrole was refluxed with excess malonic ester in diphenyl ether to give 6,7-dimethoxy-4-hydroxy-2-quinolone (II); repetition of this synthesis with diethyl dimethylallyl malonate gave the 3-dimethylallylquinolone (IIa) m.p. 200–201°. Cyclisation of this with hydrochloric acid gave demethyldihydro-oricine (III), which on methylation with methyl iodide and potassium carbonate in acetone gave dihydro-oricine, identical with a sample prepared from the natural product. This confirmed the structure assigned to oricine. Cyclodehydration of (IIb) with dichlorodicyanobenzoquinone, following the recent synthesis of flindersine,[2] then gave demethyl oricine m.p. 210–212°, which on methylation gave oricine identical with the natural material.



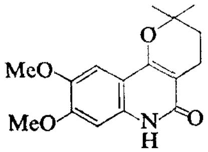
I

Flindersine (a) R=R′=H
Orincine (b) R=OMe, R′=Me.

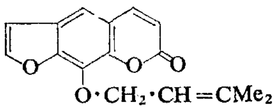


II

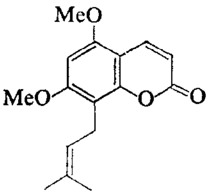
(a) R=H
(b) R=Me_2C=CH·CH_2—



III



Imperatorin (IV)



Coumarrayin (V)

We have also examined the Rutaceous shrub, *Clausena anisata.* This gave us the known coumarins imperatorin (IV) and coumarrayin (V),[3] identical with a sample supplied by Dr. Dreyer.

EXPERIMENTAL

Extraction of Timber of Oricia suaveolens

The pulverised timber (14·75 kg) was extracted with refluxing light petroleum (b.p. 60–80°). Evaporation gave an oil (300 g). This was chromatographed over alumina, it appeared to be mostly fatty oil, but a fraction eluted with benzene–ether (1:4) gave a yellow solid; which after crystallisation from benzene gave *oricine* (Ib) (1·5 g), m.p. 150–155°. (Found C, 67·5; H, 6·2; M^+ 301. $C_{17}H_{19}O_4N$ requires C, 67·8; H, 6·3%. ν_{max} 1639 cm^{-1}, no optical rotation.)

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[2] F. PIOZZI, P. VENTURELLA and A. BELLINO, *Gazz. Chim. Ital.* **99**, 711 (1969).

[3] D. L. DREYER, *J. Org. Chem.* **33**, 3574 (1968).

Extraction of Clausena anisata

The pulverised root (6·76 kg) was extracted with refluxing light petroleum (b.p. 60–80°). Evaporation gave crystals and oil. The crystals were separated from the oil; crystallisation from methanol gave imperatorin (IV), m.p. 95–98°, identical with an authentic sample. The oil (17 g) was chromatographed on alumina. Elution with benzene–ether (9:1) gave white crystals of coumarrayin (V) (1·3 g) m.p. 150–155°; the i.r. spectrum was identical with that of an authentic sample supplied by Dr. Dreyer.

6:7-*Dimethoxy-4-hydroxy-2-quinolone*

4-Aminoveratrole (20 g) was added to excess diethyl malonate (40 g) in diphenyl ether (100 ml) and the whole refluxed for 2 hr. After cooling, a solid separated. This was filtered and washed with petrol ether to give the *quinolone* (12·5 g); insoluble in organic solvents, but purified by dissolving in NaOH solution and reprecipitating with HCl. (Yellow crystals, m.p. over 300°) [Found C, 60·1; H, 4·7; M^+ 221. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). ν_{max} 3448, 1639 cm^{-1} (quinolone).]

3-*Dimethylallyl*-6,7-*dimethoxy-4-hydroxy-2-quinolone*

4-Aminoveratrole (3 g) and diethyldimethylallyl malonate (6 g) in diphenyl ether (50 ml) were refluxed for 5 hr under N_2. After cooling, the product was filtered and washed with light petroleum to give the *dimethylallylquinolone* (1·8 g) m.p. 200–201°. (Found C, 66·5; H, 6·8. M^+ 289. $C_{16}H_{19}O_4N$ requires C, 66·4; H, 6·6%) ν_{max} 1639 cm^{-1}.

Dihydro-oricine

(a) Oricine (135 mg) was hydrogenated in methanol (50 ml) over PtO catalyst (100 mg). The product crystallised from methanol to give *dihydro-oricine*, m.p. 150°. (Found: C, 67·0; H, 6·8. M^+ 303. $C_{17}H_{21}O_4N$ requires C, 67·3; H, 6·9%.)

(b) The above dimethylallylquinolone (50 mg) was refluxed with conc. HCl (2 ml) for 2 hr. The product was extracted with $CHCl_3$; evaporation left demethyl dihydro-oricine m.p. 222–226°. This was dissolved in acetone (80 ml) and refluxed overnight with MeI (5 ml) and anhydrous K_2CO_3 (10 g). The acetone was evaporated and the product extracted with $CHCl_3$. Evaporation of the $CHCl_3$ left a gum, showing three spots on TLC. One of these, isolated by preparative TLC, was identified as dihydro-oricine by comparison of the NMR spectrum with the sample prepared above.

Oricine

The above dimethylallylquinolone (104 mg) and dichlorodicyanobenzoquinone (105 mg) was refluxed in benzene for 4 hr. After filtration, the solution was evaporated and the residue, in $CHCl_3$, washed with aqu. $NaHCO_3$ and with water. Evaporation of the $CHCl_3$ gave *demethyloricine* (100 mg) m.p. 210–212°. (Found: C, 68·0; H, 6·0; M^+ 287. $C_{16}H_{17}O_4N$ requires C, 67·2; H, 5·9%.) This (50 mg) was dissolved in acetone (40 ml) with MeI (2 ml) and anhydrous K_2CO_3 (5 g) and refluxed 6 hr. The mixture was filtered and the filtrate evaporated. The residue was dissolved in $CHCl_3$ and washed with water, evaporation gave oricine, (30 mg), m.p. 150° (from benzene). (Found: C, 67·5; H, 6·3. The NMR and i.r. spectra were identical with those of a natural sample.)