Synthesis of Neobanone, a 12a-Methoxy-rotenoid

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Neobanone, a novel 12a-methoxyrotenoid from *Neorautanenia amboensis,* has been synthesised *via* chalcone, isoflavone, and rotenoid intermediates

OUR interest in the synthesis of neobanone (21), a novel 12a-methoxy-rotenoid from *Neorautanenia amboensis*,[1] followed from our preliminary finding of its high potency as insecticide [2] and consequent requirement of additional material for an evaluation of its relative rate of inhibition of cytochrome *c* reductase.

Its co-occurrence with the isoflavone dehydroneotenone (15) [3] and the demonstration by Crombie *et al.*[4] of the incorporation of [2′-^{14}C]methoxyisoflavones into [6-^{14}C]rotenoids, led to our consideration of a biosynthetically orientated total synthesis of neobanone (21) *via* chalcone and isoflavone intermediates. This entailed surmounting certain problems in the formation of complex 2′-hydroxychalcones;[5] their convenient oxidative rearrangement with thallium(III) nitrate (TTN) in methanol; and their concomitant cyclization to isoflavones.[6] From this point onward the route *via* a 2-vinylcoumaran-3-one, as pioneered by Crombie *et al.*,[7] led to the first synthesis of a 12a-methoxyrotenoid.

Our first synthetic objective was the construction of the chalcone (12) containing a benzofuranoid ring A. 6-Hydroxybenzofuran-3(2*H*)-one (1) was prepared by a Friedel–Crafts reaction of resorcinol with chloroacetyl chloride in nitrobenzene.[8] Huang-Minlon reduction gave a moderate yield of 2,3-dihydrobenzofuran-6-ol (2), together with traces of benzofuran-6-ol (4). This procedure gives a 15—20% higher yield than the alternative catalytic hydrogenation [8] of the same compound. Hoesch condensation smoothly converted the phenol (2) into its 5-acetyl derivative (3). Oxidation of the latter by 2,3-dichloro-5,6-dicyanobenzoquinone afforded high yields of 5-acetylbenzofuran-6-ol (5), representing the acetophenone ring A unit required for aldol condensation.

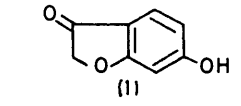
Preparation of 2-hydroxy-4,5-dimethoxybenzaldehyde (10), the ring B fragment, was first attempted *via* an Elbs oxidation of 2-hydroxy-4-methoxybenzaldehyde as the initial step. However, all attempts at methylation of the 5-hydroxy-group of the product failed. Use of an alternative approach, namely nitration of veratrole to give 1,2-dimethoxy-4-nitrobenzene (7); reduction to 3,4-dimethoxyaniline (8); conversion into 3,4-dimethoxyphenol (9); and formylation by a Gatterman reaction gave the desired 2-hydroxy-4,5-dimethoxybenzaldehyde (10) in moderate yield.

We have recently demonstrated that formation of a complex chalcone (12) by the standard procedure is unsuccessful when the 2-hydroxy-group is unprotected.[5] The difficulty was overcome in this instance by blocking the 2-hydroxy-groups of both acetophenone (5) and benzaldehyde (10) units by methoxymethylation, for which the use of a crown ether (18-crown-6) proved essential.[5] In the presence of these labile protecting groups high yields of the desired chalcone were obtained.

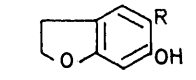
Formation of the isoflavone (14) failed in all attempts where the protecting methoxymethyl groups corresponding to positions 2 and 2′ in the chalcone had been removed prior to attempted rearrangement with TTN in methanolic solution. However, the oxidative rearrangement of the fully substituted chalcone (13) gave a complex mixture in which the desired isoflavone (14) was the major product. As a by-product, an aroylbenzofuran (16) was isolated; an analogous reaction has been recorded previously.[6] In the n.m.r. spectrum of the latter product (16) the characteristic H-7 signal (τ 1.47) of the isoflavone (14) is replaced by a singlet at τ 2.85, due to the 2-proton of the benzofuran.

[1] M. E. Oberholzer, G. J. H. Rall, and D. G. Roux, *Phytochemistry*, 1976, **15**, 1283.
[2] Tests performed by Professor P. H. Hewitt, Department of Entomology, U.O.F.S., Bloemfontein, South Africa.
[3] C. v. d. M. Brink, W. Nel, G. J. H. Rall, J. C. Weitz, and K. G. R. Pachler, *J. S. African Chem. Inst.*, 1966 **19**, 24.
[4] L. Crombie P. M. Dewick, and D. A. Whiting, *J.C.S. Perkin I*, 1973, 1285.
[5] G. J. H. Rall, M. E. Oberholzer, D. Ferreira, and D. G. Roux, *Tetrahedron Letters*, 1976, 1033.
[6] L. Farkas, A. Gottsegen, M. Nógrádi, and S. Antus, *J.C.S. Perkin I*, 1974, 305.
[7] L. Crombie, P. W. Freeman, and D. A. Whiting, *J.C.S. Perkin I*, 1973, 1277.
[8] J. S. H. Davies, P. A. McCrea, W. L. Norris, and G. R. Ramage, *J. Chem. Soc.*, 1950 3206.

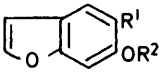
The reaction between the isoflavone (14) and dimethylsulphoxonium methylide [7] gave a new 2-vinylcoumaran-3-one (17) in 83% yield, characterized by its spectra. Heating the coumaranone in pyridine at 100 °C for 24 h afforded erosone (18),[9] and subsequent aerial oxidation in basic medium gave 12a-hydroxyerosone (19). Methylation of the latter with methyl iodide in acetone yielded (±)-neobanone (21), indistinguishable from natural optically active neobanone [1] by n.m.r. and mass spectrometry.



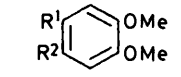
(1)



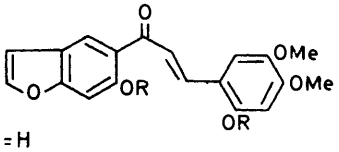
(2) R = H
(3) R = COMe



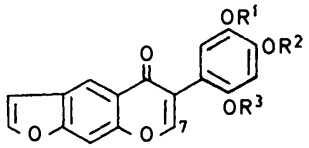
(4) R^1 = H, R^2 = H
(5) R^1 = Ac, R^2 = H
(6) R^1 = Ac, R^2 = CH_2OMe



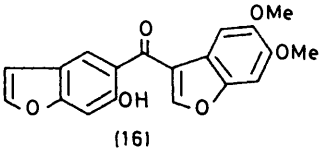
(7) R^1 = NO_2, R^2 = H
(8) R^1 = NH_2, R^2 = H
(9) R^1 = OH, R^2 = H
(10) R^1 = OH, R^2 = CHO
(11) R^1 = O·CH_2OMe, R^2 = CHO



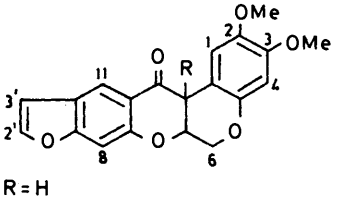
(12) R = H
(13) R = CH_2·OMe



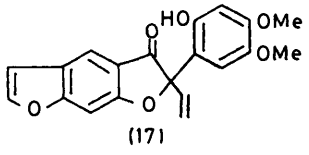
(14) R^1 = R^2 = Me, R^3 = H
(15) R^1 R^2 = CH_2, R^3 = Me



(16)



(18) R = H
(19) R = OH
(20) R = OAc
(21) R = OMe



(17)

Evaluation of the relative toxicity of both natural and synthetic neobanones is in hand.

EXPERIMENTAL

The following experimental conditions apply, except where otherwise stated. M.p.s were determined with a Kofler hot-stage microscope. U.v. data were recorded for solutions in methanol ($\log_{10}$ ε values follow $\lambda_{max.}$) with a Perkin-Elmer 402 spectrophotometer. I.r. spectra were obtained for solutions in chloroform with a Unicam SP 1000 spectrophotometer. N.m.r. spectra were obtained with a Varian T-60 spectrometer for solutions in deuteriochloroform (tetramethylsilane as internal standard). Hydroxylic protons were located by exchange with deuterium oxide. Mass spectra were recorded with a Varian CH-5 instrument at 70 eV. Preparative thin-layer chromatography (p.l.c.) was carried out on Kieselgel 60 PF_{254} (Merck) plates (1 mm thick); Kieselgel 60 (230—400 mesh; Merck) was used for column chromatography.

6-*Hydroxybenzofuran*-3(2H)-*one* (1).—Compound (1) was prepared according to the procedure of Davies *et al.*[8] and crystallised from methanol–pyridine as golden plates, m.p. 245—246° (lit.,[8] 245°); M^+ 150; $\nu_{max.}$ (KBr) 3 150, 1 680, and 1 480 cm^{-1}; $\lambda_{max.}$ 320 (3.64) and 275 nm (3.55); τ (C$_5$D$_5$N) 2.05br (s, OH), 3.58 (d, *J* 8 Hz, 4-H), 4.42 (dd, *J* 8 and 2 Hz, 5-H), 4.48 (d, *J* 2 Hz, 7-H), and 6.55 (s, CH_2).

2,3-*Dihydrobenzofuran*-6-*ol* [8] (2).—This was prepared according to the following modified procedure. A mixture of hydrazine hydrate (90%; 7 ml) and 6-hydroxybenzofuran-3(2*H*)-one (1) (10 g) in ethanol (50 ml) was refluxed for 1 h. After removal of the solvent, potassium hydroxide (10 g) in diethylene glycol (80 ml) was added. The mixture was heated at 185—190 °C for 1 h, steam distilled for 1 h, cooled, acidified with 3N-hydrochloric acid and extracted with ether. Removal of the solvent, and separation on a

[9] L. B. Norton and R. Hansberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1609.

column in hexane–benzene–ethyl acetate (5 : 5 : 2) gave two products. Compound (2), of lower mobility, was obtained as light yellow oil (4.4 g), b.p. 268° at 644 mmHg (lit.,[8] 128° at 2 mmHg) (Found: M^+, 136.051. Calc. for $C_8H_8O_2$: M, 136.052); $\nu_{max.}$ 1 510 and 1 470 cm^{-1}; $\lambda_{max.}$ 325 (2.94), 287 (3.56), and 265 nm (3.26); τ 3.04 (d, J 8 Hz, 4-H), 3.62 (dd, J 8 and 2 Hz, 5-H), 3.63 (d, J 2 Hz, 7-H), 4.00br (s, OH), 5.45 (t, J 8 Hz, O·CH_2), and 6.93 (t, J 8 Hz, CH_2).

6-Hydroxybenzofuran (4), the compound of higher mobility from the above column, was obtained as a light yellow oil (180 mg) (lit.,[10] m.p. 56°); M^+ 134; τ 2.70 (d, J 6 Hz, 4-H), 3.17 (dd, 2- and 5-H), 3.37 (d, J 1.6 Hz, 7-H), 3.70 (d, J 2 Hz, 3-H), and 5.50br (s, 6-OH).

5-*Acetyl*-2,3-*dihydrobenzofuran*-6-*ol* (3).—This was prepared according to the standard Hoesch procedure,[8] and was obtained as needles (7.2 g) (from methanol), m.p. 107—108° (lit.,[8] 107—108°); M^+ 178; τ −3.03 (s, OH), 2.48br (s, 4-H), 3.70 (s, 6-H), 5.35 (t, J 8 Hz, O·CH_2), 6.87 (t, J 8 Hz, CH_2), and 7.47 (s, CH_3).

5-*Acetylbenzofuran*-6-*ol* (5).—A mixture of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (13 mmol, 3 g) and 5-acetyl-2,3-dihydrobenzofuran-6-ol (3) (11 mmol, 2 g) in dry benzene (30 ml) was refluxed for 3 h. Methanol (30 ml) was added and the solvent evaporated off. The mixture was separated on a column with benzene–hexane–ethyl acetate (5 : 5 : 3). Recrystallisation from benzene–methanol gave light yellow crystals (1.5 g), m.p. 94—95° (lit.,[8] 96°); M^+ 176; $\nu_{max.}$ 3 080, 1 650, and 1 550 cm^{-1}; $\lambda_{max.}$ 345 (3.70) and 275 nm (3.84); τ −2.46 (s, OH), 2.13 (s, 4-H), 2.50 (d, J 2 Hz, 2-H), 3.03 (s, 7-H), 3.32 (d, J 2 Hz, 3-H), and 7.38 (s, CH_3).

5-*Acetyl*-6-(*methoxymethoxy*)*benzofuran* (6).—A mixture of 5-acetylbenzofuran-6-ol (5) (2 g) and potassium hydroxide (590 mg) in water–methanol (30 ml) was heated on a water-bath for 1 h, then evaporated. The residue was dried overnight at 120 °C. 18-Crown-6 (700 mg) was dissolved in dry acetonitrile and the potassium salt of (5) added. The mixture was stirred for 30 min, chloromethyl methyl ether (0.98 g) was added, and stirring was continued for 1 h. Aqueous 7% potassium hydroxide (20 ml) was added and the organic solvents were removed. The aqueous phase was extracted with ether, washed, dried (Na_2SO_4), and concentrated to a yellow *oil* (1.5 g); τ 2.03 (s, 4-H), 2.38 (d, J 2 Hz, 2-H), 2.68 (s, 7-H), 3.27 (d, J 2 Hz, 3-H), 4.70 (s, O·CH_2·OMe), 6.47 (s, O·CH_2·O·CH_3), and 7.32 (s, CH_3) (Found: C, 65.3; H, 5.7%; M^+, 220.072. $C_{12}H_{12}O_4$ requires C, 65.4; H, 5.6%; M, 220.073).

1,2-*Dimethoxy*-4-*nitrobenzene* (7).—Prepared according to the procedure of Cardwell and Robertson,[11] this crystallised from ethanol as yellow-brown crystals, m.p. 97—98° (lit.,[12] 98°); M^+ 183; τ 1.98 (d, J 2 Hz, 2-H), 2.17 (dd, J 8 and 2 Hz, 4-H), 5.97 (s, 3-OMe), and 6.00 (s, 4-OMe).

3,4-*Dimethoxyaniline* [13] (8).—This was prepared according to the following modified procedure. Sodium sulphide (62 g) and 1,2-dimethoxy-4-nitrobenzene (7) (25 g) in water (20 ml) were refluxed for 2 h, and then steam distilled for 1 h. The mixture was cooled and extracted with chloroform; the extract was washed with 3N-hydrochloric acid and the aqueous phase basified. Extraction with ethyl acetate, evaporation, and column chromatography in benzene–acetone (8 : 1.5) gave grey plates (8.0 g), m.p. 86—87° (lit.,[14] 85—86°); M^+ 153; τ 3.29br (d, J 8 Hz, 6-H), 3.72br (s, 2-H), 3.80br (d, J 8 Hz, 5-H), 6.24 (s, OMe), and 6.45 (s, NH_2).

3,4-*Dimethoxyphenol* (9).—3,4-Dimethoxyaniline (8) was diazotised according to the procedure of Fargher,[13] and the product chromatographed on a column in benzene–acetone (9 : 2). Crystallisation from benzene–acetone gave plates (3.7 g), m.p. 45—46° (lit.,[13] 46°) (Found: M^+, 154.062. Calc. for $C_8H_{10}O_3$: M 154.063); τ 3.25 (d, J 8.5 Hz, 5-H), 3.63 (dd, J 8.5 Hz, 6-H), 3.48 (d, J 2 Hz, 2-H), 4.00—5.00br (s, OH), and 6.25 and 6.22 (each s, 2 × OMe).

2-*Hydroxy*-4,5-*dimethoxybenzaldehyde* (10).—This was prepared according to the standard Gatterman procedure.[15] The product was chromatographed on a column in benzene–hexane–ethyl acetate (5 : 5 : 3) and crystallised from benzene–ethyl acetate to give fine needles (3.7 g), m.p. 105—106° (lit.,[15] 105°); M^+ 182; $\nu_{max.}$ 3 000, 2 860, 1 670, and 1 590 cm^{-1}; $\lambda_{max.}$ 345 (3.59) and 275 nm (3.75); τ −1.43br (s, OH), 0.03 (s, CHO), 3.07 (s, 6-H), 3.53 (s, 3-H), and 6.07 and 6.13 (each s, 2 × OMe).

4,5-*Dimethoxy*-2-(*methoxymethoxy*)*benzaldehyde* (11).—This was obtained (84%) from 4,5-dimethoxy-2-hydroxybenzaldehyde (10) by the same procedure as described for 5-acetyl-6-(methoxymethoxy)benzofuran (6) and crystallised from benzene as yellow *needles*, m.p. 54—55°; τ −0.35 (s, CHO), 2.72 (s, 6-H), 3.22 (s, 3-H), 4.73 (s, O·CH_2·OMe), 6.15 and 6.07 (each s, 2 × OMe), and 6.47 (s, O·CH_2·O·CH_3) (Found: C, 58.3; H, 6.3%; M^+, 226.085. $C_{11}H_{14}O_5$ requires C, 58.4; H, 6.2%; M, 226.084).

3-[4,5-*Dimethoxy*-2-(*methoxymethoxy*)*phenyl*]-1-[6-(*methoxymethoxy*)*benzofuran*-5-*yl*]*prop*-2-*en*-1-*one* (13).—A mixture of 5-acetylbenzofuran-6-ol (6) (500 mg) in ethanol (10 ml) and aqueous 70% (w/v) potassium hydroxide (10 ml) was stirred for 30 min. 4,5-Dimethoxy-2-(methoxymethoxy)benzaldehyde (11) (513 mg) in ethanol (10 ml) was added while stirring was continued for 2 h. Removal of the ethanol under reduced pressure and recrystallisation from methanol gave fine yellow *needles* (800 mg), m.p. 119—121°; $\nu_{max.}$ 1 660, 1 630, 1 610, 1 580, 1 520, 1 480, and 1 295 cm^{-1}; $\lambda_{max.}$ 370 (3.92), 303 (3.77), and 270 nm (3.91); τ 1.98 (d, J 15 Hz, CH·CO), 2.18 (s, benzofuran 4-H), 2.38 (d, J 2 Hz, benzofuran 2-H), 2.73 (d, J 15 Hz, CO·CH·C*H*), 2.65 (s, phenyl 6-H), 2.87 (s, benzofuran 7-H), 3.23 (s, phenyl 3-H), 3.25 (d, J 2 Hz, benzofuran 3-H), 4.70 (s, benzofuran 6-OCH_2·OMe), 4.82 (s, phenyl 2-O·CH_2·OMe), 6.13 and 6.10 (each s, 2 × OMe), 6.48 (s, benzofuran 6-O·CH_2·O·CH_3), and 6.52 (s, phenyl 2-O·CH_2·O·CH_3) (Found: C, 64.3; H, 5.7%; M^+, 428.148. $C_{23}H_{24}O_8$ requires C, 64.5; H, 5.6%; M, 428.147).

6-(2-*Hydroxy*-4,5-*dimethyoxyphenyl*)*furo*[3,2-g][1]*benzopyran*-5-*one* (14).—This was prepared from the chalcone (13) according to the procedure of Farkas *et al.*[6] The resulting mixture was separated on a column in benzene–hexane–ethyl acetate (5 : 5 : 3) and the compound of lower mobility was obtained as plates (from methanol) (200 mg), m.p. 207—209° (lit.,[16] 200—201°) (Found: M^+, 338.078. Calc. for $C_{19}H_{14}O_6$: M, 338.079); $\nu_{max.}$ 1 610, 1 590, 1 520, and 1 450 cm^{-1}; $\lambda_{max.}$ 300 (3.69) and 270 nm (3.84); τ 1.47

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[11] D. Cardwell and R. Robertson, *J. Chem. Soc.*, 1915, **107**, 257.
[12] L. L. Sergeeva and N. N. Shorygina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965 **9**, 1630.
[13] R. G. Fargher, *J. Chem. Soc.* 1920 **117**, 869.
[14] C. Alberti and C. Tironi *Farmaco (Pavia), Ed. Sci.*, 1964, **19**, 459.
[15] F. S. H. Head and R. Robertson, *J. Chem. Soc.*, 1930, 2440.
[16] V. Chandrashkar, M. Krishnamurti and T. R. Seshadri, *Current Sci.*, 1967, **36**, 623.

(s, 7-H), 1.83 (s, 4-H), 2.28 (d, *J* 2 Hz, 2-H), 2.43br (s, 9-H), 3.12 (d, *J* 2 Hz, 3-H), 3.30 (s, phenyl 6-H), 3.34 (s, phenyl 3-H), 6.13 (s, 5-OMe), and 6.17 (s, 4-OMe).

5,6-Dimethoxybenzofuran-3-yl 6-hydroxybenzofuran-5-yl ketone (16), obtained as a by-product, gave yellow *crystals*, m.p. 159—161° (from methanol–benzene); $\nu_{max.}$ 3 010, 1 630, 1 610, 1 590, 1 445, and 1 320 cm^{-1}; $\lambda_{max.}$ 345 (3.94), 330 (3.98), 312 (3.68), 300 (3.58), 283 (3.61), and 270 nm (3.43); τ 2.09 (s, 4-H), 2.42 (d, *J* 2 Hz, 2-H), 3.22 (d, *J* 2 Hz, 3-H), 2.84 (s, 2-H and 4-H), 2.94 (s, 7-H and 7-H), 2.84 (s, OH), and 6.09 (s, 2 × OMe) (Found: C, 67.3; H, 4.2%; M^+, 338.078. $C_{19}H_{14}O_6$ requires C, 67.5; H, 4.2%; *M*, 338.079).

2-(2-Hydroxy-4,5-dimethoxyphenyl)-2-vinylbenzo[1,2-*b* : 5,4-*b'*]*difuran-3*(2*H*)*-one* (17).—Trimethyloxosulphonium iodide (180 mg), sodium hydride (20 mg), and dry dimethyl sulphoxide (10 ml) were stirred under dry nitrogen for 15 min. After addition of the furobenzopyranone (14) (230 mg) the mixture was left for 2.5 h at room temperature, diluted with water, acidified with 3N-hydrochloric acid, and extracted with ethyl acetate. The extracts were washed with aqueous 1% sodium hydrogen carbonate and water, dried (Na_2SO_4), concentrated, and chromatographed on a column in benzene–methanol (9 : 1) to provide light yellow *needles* (150 mg) (from benzene–methanol), m.p. 134—136°; $\nu_{max.}$ 1 690, 1 625, and 1 440 cm^{-1}; $\lambda_{max.}$ 350 (3.52), 290 (3.80), and 277 nm (3.94); τ 1.33br (s, OH), 2.13 (s, 4-H), 2.40 (d, *J* 2.2Hz, 6-H), 2.72 (s, phenyl 6-H), 2.90 (s, 8-H), 3.23 (d, *J* 2.2 Hz, 5-H), 3.43 (s, phenyl 3'-H), 3.88 (d, J_{cis} 10.5, J_{trans} 17 Hz, −CH=), 5.40 and 5.70 (dd, J_{cis} 10.5, J_{trans} 17, J_{gem} 1, $=CH_2$), and 6.20 (s, 2 × OMe) (Found: C, 68.0; H, 4.7%; M^+, 352.094. $C_{20}H_{16}O_6$ requires C, 68.2; H, 4.6%; *M*, 352.095).

Erosone (18).—The benzodifuranone (17) (80 mg) was heated overnight at 100 °C in dry pyridine (3 ml) in a sealed tube. The solvent was evaporated off and the residue separated on a column in chloroform–ether (97 : 3) to give light yellow crystals (53 mg) (from chloroform), m.p. 214—216° (lit.,[9] 218°) (Found: M^+, 352.096. Calc. for $C_{20}H_{16}O_6$: *M*, 352.095); $\nu_{max.}$ 1 685, 1 635, 1 525, and 1 475 cm^{-1}; $\lambda_{max.}$ 340 (3.41), 276 (3.85), and 305 nm (3.51); τ 1.78 (s, 11-H), 2.45 (d, *J* 2 Hz, 2'-H), 2.95 (s, 8-H), 3.23 (s, 1-H), 3.28 (d, *J* 2 Hz, 3'-H), 3.53 (s, 4-H), 4.95 (m, 6a-H), 5.34 (d, *J* 13 Hz, 6*ax*-H), 5.83 (dd, *J* 13 Hz, 6*eq*-H), 6.10 (d, $J_{6a,12a}$ 5 Hz, 12a-H), and 6.22 and 6.27 (each s, 2 × OMe).

12a-Hydroxyerosone (19).—To erosone (18) (25 mg) suspended in ethanol (50 ml) aqueous 10% potassium hydroxide (1 ml) was added, and a fast stream of oxygen was passed through the solution for 12 h. After acidification with 3N-hydrochloric acid, evaporation, and column chromatography in chloroform–ether (97 : 3), yellow *needles* (20 mg) were obtained (from chloroform–ether), m.p. 185—187°; $\nu_{max.}$ 3 508, 3 200, 1 692, 1 630, 1 595, 1 515, and 910 cm^{-1}; $\lambda_{max.}$ 277 (3.82), 306 (3.56), and 330 nm (3.42); τ 1.87 (s, 11-H), 2.52 (d, *J* 2 Hz, 2'-H), 3.05 (s, 8-H), 3.34 (d, *J* 2 Hz, 3'-H), 3.52 (s, 1-H), 3.57 (s, 4-H), 5.67br (s, 12a-OH), 5.50 (m, 6-H_2 and 6a-H), and 6.28 and 6.38 (each s, 2 × OMe) (Found: C, 65.1; H, 4.5%; M^+, 368.010. $C_{20}H_{16}O_7$ requires C, 65.2; H, 4.4%; *M*, 368.099).

12a-Acetoxyerosone (20).—Acetylation of 12a-hydroxyerosone (19) (20 mg) with acetic anhydride–pyridine (2 ml) gave a pale yellow *oil* (19 mg); τ 1.77 (s, 11-H), 2.47br (d, *J* 2.2Hz, 2'-H), 2.98 (s, 8-H), 3.12 (s, 1-H), 3.25 (d, *J* 2.2 Hz, 3'-H), 3.50 (s, 4-H), 4.53 (m, 6a-H), 5.38 (dd, $J_{ax,eq}$ 13, 6*ax*-H), 5.67 (dd, $J_{ax,eq}$ 13, 6*eq*-H), 6.20 and 6.25 (each s, 2 × OMe), and 7.87 (s, OAc) (Found: C, 64.2; H, 4.5%; M^+, 410.101. $C_{22}H_{18}O_8$ requires C, 64.4; H, 4.4%; *M*, 410.100).

Neobanone (21).—Methylation of 12a-hydroxyerosone (19) (10 mg) with methyl iodide (5 ml) and potassium carbonate (100 mg) in dry acetone (10 ml) gave a pale yellow *oil* (7 mg); $\nu_{max.}$ 1 680, 1 630, 1 520, and 1 475 cm^{-1}; $\lambda_{max.}$ 275 nm (4.81); τ 1.76 (s, 11-H), 2.44 (d, *J* 2.2 Hz, 2'-H), 3.00 (s, 8-H), 3.33 (s, 1-H), 3.34 (d, *J* 2.2 Hz, 3'-H), 3.46 (s, 4-H), 5.32 (m, 6a-H), 5.47 (m, 6-H_2), 6.17 and 6.24 (each s, 2 × OMe), and 6.44 (s, 12a-OMe) (Found: C, 65.9; H, 4.8%; M^+, 382.105. $C_{21}H_{18}O_7$ requires C, 66.0; H, 4.7%; *M*, 382.104). The n.m.r. and mass spectra were identical with those of the natural product.[1]

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