1, 20 mg **11** und 2 mg **12** lieferten.

Chrysanthemoides monolifera (*Herbar Nr. 73/20, bei Cape Town gesammelt*). 750 g Wurzeln ergaben 5 mg **1**, 30 mg **5**, 100 mg **7** und 200 mg **10**.

Chrysanthemoides incana (*Herbar Nr. 91/75, bei Cape Town gesammelt*). 150 g Wurzeln ergaben 0.5 mg **1** und 100 mg **10**.

Castilis nudicaulis *var.* gramminifolia (*Herbar Nr.* 75/82, *Botanic Gardens Kirstenbosch*). 120 g Wurzeln ergaben 0.5 mg **1**.

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TETRAHYDRODIOSPYRIN: A REDUCED BINAPHTHOQUINONE FROM THE BARK OF *DIOSPYROS MONTANA*

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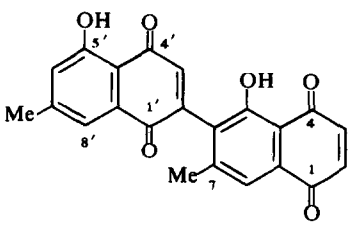
Key Word Index—*Diospyros montana*; Ebenaceae; tetrahydrodiospyrin; reduced binaphthoquinone.

Abstract—A new reduced dimeric 7-methyljuglone isolated from the fresh bark of *D. montana* is shown to be 3′,7-dimethyl-5′,6′,7′,8′-tetrahydro-1′,5,5′-trihydroxy [2,2′-binaphthalene]-1,4,8′-trione.

The occurrence of diospyrin [1] from *D. montana* was reported previously. In our search for biogenetic precursors, we isolated β-dihydrodiospyrin [2] from the fresh bark of *D. montana* and characterised some new derivatives of diospyrin [3], which are possible artifacts of the isolation procedure. The present paper describes the isolation and structure elucidation of another reduced derivative of diospyrin from the fresh bark of *D. montana*.

TLC of the chloroform extract of freshly cut *D. montana* bark gave in addition to diospyrin (**1**) and β-dihydrodiospyrin (**2**) an unknown polar orange-red compound, which was purified by PLC and repeated column chromatography. This compound gave a violet colour with aq. alkali and underwent reversible reduction with sodium dithionite indicating that it was a quinonoid pigment. It analysed for $C_{22}H_{18}O_6$ and its MW 378 (MS) indicates that it is a dimeric 7-methyljuglone with four additional hydrogens. The IR spectrum showed bands 3450 cm^{-1} (broad, —OH), 2920–2850 cm^{-1} (methylenes), 1640 cm^{-1} (bonded $\rangle C{=}O$) and 1670 cm^{-1} ($\rangle V{=}O$). However, proof that the new



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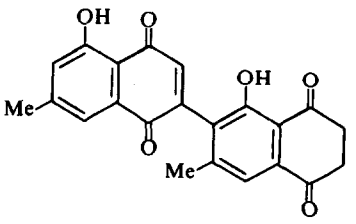

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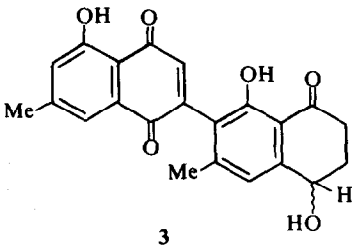

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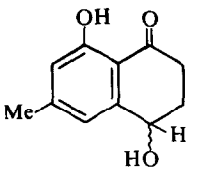

4

compound is tetrahydrodiospyrin (3) may be found in the PMR spectrum. Thus, resonance signals at δ ($CDCl_3$): 2.27 (3H, *s*) and 2.48 (3H, *s*) are assignable to C-7 and C-7′ methyl groups, respectively; 6.92 (1H, *s*) to a C-3′ olefinic hydrogen; 7.17 (1H, *b*, $W_{\frac{1}{2}} = 3$ Hz) and 7.55 (1H, *b*, $W_{\frac{1}{2}} = 3$ Hz) to the two *meta*-coupled H-6′ and H-8′ protons, respectively; 7.05 (1H, *s*) to a C-8 hydrogen, shielded due to the absence of the peri carbonyl group and 11.63 (1H, *s*) and 12.45 (1H, *s*), both D_2O exchangable, are assignable to C-5 and C-5′ chelated hydroxyl groups. The C-1 carbinol proton appears as a multiplet at 5.00 and the remaining methylenes as multiplets at 2.2–3.0. In the aromatic region, the PMR spectrum has all the features of diospyrin (1) and β-dihydrodiospyrin (2), except that it showed only one olefinic proton at 6.92 and the H-8 aromatic proton is shielded to 7.05 from 7.58 in diospyrin (1) and 7.52 in β-dihydrodiospyrin [2] (2). Hence, the C-1 carbonyl group of (2) is reduced in tetrahydrodiospyrin (3) and this is further substantiated by the presence of two chelated hydroxyl groups at 11.63 and 12.45. Thus, the new natural product is tetrahydrodiospyrin (3). The UV spectrum of 3 λ_{max} (EtOH): 216 (4.5), 263 (4.1), 330 (3.5) and 430 (3.7) nm is comparable with that of tetrahydro-7-methyljuglone (4) (shinanolone) [4]: 218 (4.24), 268 (4.08) and 333 (3.54) nm. The absorption at 430 nm is due to the presence of the juglone moiety. The structure was further confirmed by oxidation of tetrahydrodiospyrin (3) to diospyrin (1) with active manganese dioxide. The identity of the oxidation product with diospyrin was established by superimposable IR, mmp, TLC and identical MS.

The MS of tetrahydrodiospyrin (3) showed peaks at *m/e* 360 (M-18), 350 (M-28) and in the low mass region 163, 135, 134 and 106 which are characteristic fragments of diospyrin [3, 5]. The natural product exhibited a weak optical rotation $[\alpha]_D^{27}$ +15° but the absolute stereochemistry of the hydroxyl group could not be determined due to lack of sufficient material.

Although shinanolone (4) [4] has been reported earlier, this is the first report of the natural occurrence of a tetrahydrobinaphthoquinone. The co-occurrence of diospyrin (1), β-dihydrodiospyrin (2) and tetrahydrodiospyrin (3) in the bark of *D. montana* is of biogenetic significance.

EXPERIMENTAL

Isolation of tetrahydrodiospyrin. The $CHCl_3$ extract of freshly cut *D. montana* bark was evapd and the residue repeatedly washed with Et_2O. TLC of the Et_2O washings showed the presence of tetrahydrodiospyrin (3), diospyrin (1) and β-dihydrodiospyrin (2). Tetrahydrodiospyrin was first isolated in crude form by PLC ($CHCl_3$–EtOAc, 95:5) and was later purified by column chromatography on Si gel (0.08, mesh) using $CHCl_3$–EtOAc (95:5) as eluent. Finally it was crystallized from $CHCl_3$–petrol (40–60°) as red needles, mp 198°. (Found: C, 69.21; H, 4.39. $C_{22}H_{18}O_6$ requires: C, 69.83; H, 4.80%). $[\alpha]_D^{27}$ +15° ($CHCl_3$, 2%); ν_{max}^{KBr} (cm^{-1}): 3450, 2950–2850, 1670, 1640, 1570, 1490, 1445, 1380, 1360, 1330, 1300(sh), 1260, 1210, 1195(sh), 1150, 1110, 1050, 985, 960, 940, 910, 870, 850, 820 and 720; λ_{max}^{EtOH} nm (log ε): 216 (4.5), 263 (4.1), 330 (3.5) and 430 (3.7); MS *m/e* (rel. int.): 378 (M^+; 100), 360 ($M^+ - 18$; 10), 350 ($M^+ - 28$; 3), 180 (8), 163 (11), 135 (17), 134 (13), 106 (18) and 77 (10).

Oxidation of tetrahydrodiospyrin to diospyrin. Tetrahydrodiospyrin (10 mg) was dissolved in C_6H_6 and shaken with active manganese dioxide (electrolytic grade) for 30 min. The manganese dioxide was filtered, the filtrate evapd to dryness and the residue chromatographed on a Si gel column in $CHCl_3$–C_6H_6 (7:3). The bright red compound in the eluate was crystallized from CH_2Cl_2 to yield dark red crystals of diospyrin (8 mg), mp 259° (decomposition). Both the IR and MS of the oxidation product are superimposable with that of diospyrin earlier isolated from *D. montana* [1].

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