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A BINAPHTHOQUINONE FROM *DIOSPYROS GREENIWAYI*

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Key Word Index—*Diospyros greeniwayi*; Ebenaceae; habibone, lupeol, diosindigo A; 7-methyljuglone.

Abstract—Lupeol, diosindigo A, 7-methyljuglone and a novel binaphthoquinone, 5,5′-dihydroxy-2,7′-dimethyl-3,8′-binaphthalene-1,1′,4,4′-tetrone, which we have named as habibone, were isolated from the root bark of *Diospyros greeniwayi*. This is the second example of a dimer derived from plumbagin and 7-methyljuglone. Its structure has been elucidated on the basis of its spectral data mainly, ^{1}H and ^{13}C NMR. Diosindigo A and 7-methyljuglone were also detected in the stem bark of the plant.

INTRODUCTION

The genus *Diospyros* comprises over 400 species, with a world wide distribution and are used extensively in local herbal medicine [1, 2]. From the leaves of *Diospyros greeniwayi* we isolated lupeol, and betulinic acid [3]. Now we report on the isolation and identification of a new binaphthoquinone, 5,5′-dihydroxy-2,7′-dimethyl-3,8′-binaphthalene-1,1′,4,4′-tetrone, we have named as habibone (**1**), along with other constituents from the root bark of the plant. 7-Methyljuglone, plumbagin and their respective dimers have been isolated from a number of plant species [4–6].

RESULTS AND DISCUSSION

Lupeol, diosindigo A, 7-methyljuglone and the new binaphthoquinone (**1**) were isolated from the root bark. The two known naphthoquinones were identified by comparison of their spectral and physical data with those of authentic samples.

Compound **1** was assigned the molecular formula (HRMS) $C_{22}H_{14}O_6$. The UV-VIS spectrum showed λ_{max}^{MeOH} (log. ϵ): 212 (3.97), 250 (3.63), 285 (3.32) and 420 (3.09) typical of the general pattern observed for *peri*-hydroxynaphthoquinones [4]. The IR spectrum showed characteristic chelated C=O absorption for *peri*-hydroxy-1,4-naphthoquinones [4]. The 1H NMR spectrum and the molecular formula indicated the compound to be an unsymmetrical dimeric hydroxynaphthoquinone.

The ^{1}H NMR indicated that the two moieties of the dimer were chemically non-equivalent and made up of plumbagin (moiety *A*) and 7-methyljuglone (moiety *B*). The ^{1}H NMR of moiety *A* was similar to that of plumbagin and the *B* part resembled the corresponding part of neodiospyrin (**3**). Moiety *A* gave rise to three aromatic proton signals at δ 7.27 (*dd*, H-6), 7.66 (*t*, H-7) and δ 7.74 (*dd* H-8); these were confirmed by irradiation at δ 7.66 which changed the other two into *meta* coupled doublets. The absence of H-3 (*q*), at around δ 6.7 and the presence of a singlet at δ 1.82 for Me-2, indicated the linkage to be at the 3 position. Moiety *B*, gave rise to two quinonoid protons as doublets at δ 6.94 and 6.77 (H-2′ and H-3′) and an *ortho* coupled quartet at δ 7.29 (H-6′). The 7′-methyl protons appeared as a *ortho* coupled doublet at δ 2.2. The absence of an H-8′ signal confirmed the 3,8′ linkage between the two moieties. These assignments were supported by the ^{13}C NMR data.

The ^{13}C NMR assignments were made by comparing the chemical shifts of **1** with those of isodiospyrin (**6**), 3,8′-biplumbagin (**5**), plumbagin (**2**) and 7-methyljuglone (**4**) [7]. Table 1 summarises the chemical shifts assignments. The 14 quaternary carbon atoms, which appeared as low intensities singlets, could easily be recognized from the DEPT spectrum. The more appropriate assignments where possible are given in bold.

The structure of **1** was thus established to be 5,5′-dihydroxy-2,7′-dimethyl-3,8′-binaphthalene-1,1′,4,4′-

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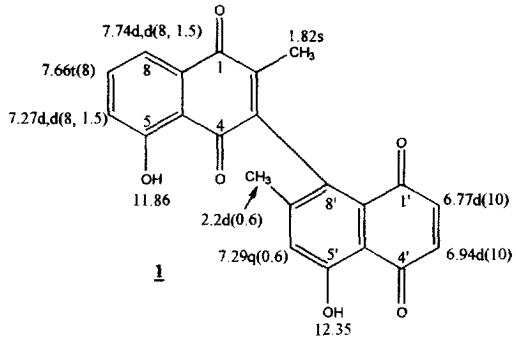

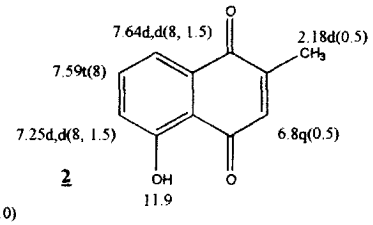

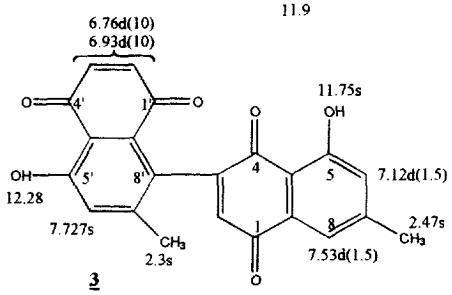

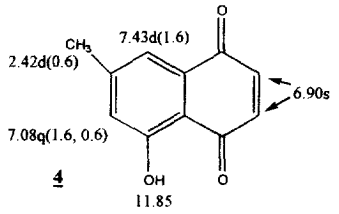

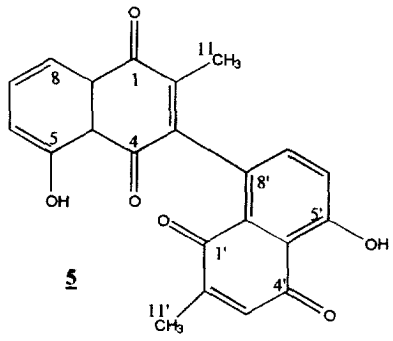

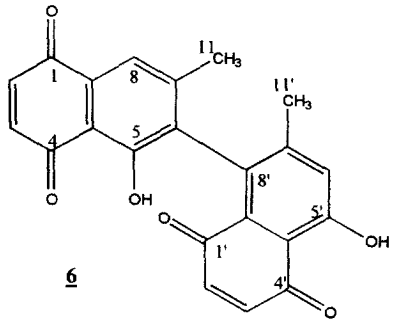

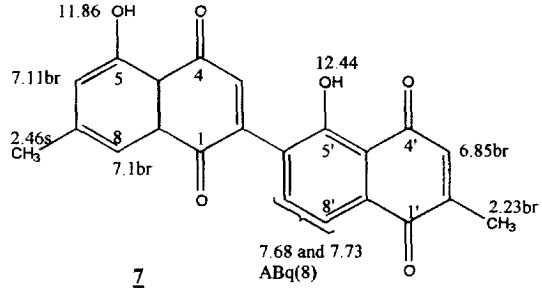

tetrone, which we have named habibone. This is the second example of a dimer involving plumbagin and 7-methyljuglone out of the 16 theoretically possible isomers. The previously reported dimer was ehretione (7) from *D. ehretioides* [5]. From *D. greeniwayi*, as expected, we isolated 7-methyljuglone but unexpectedly did not detect plumbagin in any part of the plant.

EXPERIMENTAL

Mp: uncorr.; IR: KBr; UV: EtOH; ^{1}H NMR: 500 MHz; ^{13}C NMR: 125.759 MHz; EIMS (probe): 30 eV; TLC: silica gel 60 F254 (0.22 mm) for Analytical; 2 mm for prep.); CC: (70–230 mesh). *Diospyros greeniwayi* root and stem barks were collected from Pangani in Tanga region, Tanzania in November 1988. The plant was authenticated at the Herbarium of the Botany Department, University of Dar es Salaam, where a voucher specimen is deposited.

The dried ground root-bark (400 g) was successively extracted three times with petrol (40–60°) (2.5 l) and then $CHCl_3$ (2.5 l). The concentrated petrol extract (6.5 g, 1.6%) on CC using toluene–EtOAc (4:1) yielded a white solid which formed white crystals of lupeol, mp 211–213°, 0.07 g (0.02%) (Me_2CO). The $CHCl_3$ extract on evaporation to dryness gave a solid mass (7 g, 1.8%) which afforded three fractions on a silica gel CC using toluene–EtOAc (1:1) 300 ml and (1:5) 100 ml. The first fraction on concentration and rechromatography using toluene–EtOAc (4:1) deposited dark blue crystals of diosindigo A which on recrystallisation from petrol–CH_2Cl_2 (1:1) deposited deep blue microscopic needles 4 mg), mp 310°. The second fraction on evaporation and recrystallization from petrol deposited orange crystals (0.43 mg), mp 124–5°, of 7-methyljuglone.

Table 1. ^{13}C NMR chemical shifts assignments for habibone (**1**) and compounds **2**, **4**, **5** and **6**.

C	1	5	6	2	4
1	184.14	184.53	184.43	**183.94**	184.52
	or	or	or		
1′	184.83	**185.05**	**184.92**	—	—
2	146.84	147.78	140.19	149.16	139.35
		or	or		
2′	139.67	149.86	**139.63**	—	—
3	143.14	**142.54**	138.76	134.91	138.76
3′	137.92	137.86	**137.71**	—	—
4	188.76	**188.64**	190.38	189.63	189.76
		or	or		
4′	190.05	190.44	**190.10**	—	—
5	161.50	**161.87**	158.79	160.64	161.83
		or	or		
5′	162.04	162.79	**162.07**	—	—
6	124.03	**124.00**	135.20	123.64	124.13
		or			
6′	125.63	124.56	**125.71**	—	—
7	136.26	**136.10**	148.18	135.67	148.49
		or	or		
7′	146.20	135.10	**145.52**	—	—
8	119.24	**119.20**	121.37	118.71	120.47
8′	126.99	**126.55**	130.40	—	—
9	132.47	**132.65**	128.65	131.55	131.69
		or	or		
9′	129.10	130.24	**129.00**		
10	115.30	**115.45**	113.31	114.59	113.12
		or	or		
10′	113.92	115.82	**114.36**	—	—
11	13.85	**14.32**	20.40	16.09	22.17
		or	or		
11′	20.59	16.55	**20.55**	—	—

The third fraction on evaporation and repeated recrystallization from cyclohexane deposited habibone (**1**) as a deep red compound, mp 260–61°, 12.4 mg (0.003%), $[\alpha]^{25.1}$ −33.64° ($CHCl_3$; *c* 0.1). EIMS (probe) 30 eV, *m/z* (rel. int): 374 $[M]^+$ (49) (HRMS found: *m/z* 374.0785 $[M]^+$ $C_{22}H_{14}O_6$ requires: 374.0790), 359 (11) $[M-CH_3]^+$, 331 (71) $[M-CH_3-CO]^+$, 127 (11), 121 (10), 120 (30), 120 (21), 115 (42), 97 (16), 95 (14), 94 (21), 92 (60), 92 (71), 91 (19), 89 (10), 88 (13), 85 (12), 83 (16), 81 (13), 77 (22), 76 (21), 75 (18), 73 (10), 71 (22), 69 (21), 67 (15), 65 (28), 64 (50), 63 (100) and 57 (73).

The dried powdered stem-bark (10 g) was extracted in CH_2Cl_2 for 48 hr. The extract was evaporated to dryness and subjected to comparative TLC on silica gel against the authentic samples. This led to the detection of diosindigo A and 7-methyljuglone.

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