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NAPHTHOQUINONES AND TRITERPENES FROM AFRICAN *DIOSPYROS* SPECIES

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Key Word Index—*Diospyros* spp; Ebenaceae; dimeric naphthoquinones; reduced naphthoquinones; isoshinanolone; epiisoshinanolone; triterpenes; lupane-type; glutinol; cerin.

Abstract—Investigation of the bark and/or wood of seventeen African species of *Diospyros* has revealed the presence of a number of triterpenes and naphthoquinones. The triterpenes lupeol, betulin and betulinic acid were detected in all samples but three other triterpenes were each found in only one species; betulinaldehyde in *D. canaliculata*, cerin in *D. iturensis*, and glutinol in *D. zenkeri*. Naphthoquinones were detected in fourteen of the seventeen species and the common dimeric compounds diospyrin, isodiospyrin and diosindigo-A were isolated. *D. canaliculata* differed from all other species in producing derivatives of plumbagin including its reduced form, isoshinanolone (1*R*,2*R*) and a novel stereoisomer which was given the trivial name epiisoshinanolone (1*S*,2*R*).

INTRODUCTION

The genus *Diospyros* L. is widespread throughout the tropics, notably in central Africa [1] and south east Asia [2]. The genus, and the family as a whole, is characterized by the ability to produce naphthoquinones, usually in the form of dimers, and triterpenes of the lupane series. In this paper we report the results of investigations of the barks, and in many cases the woods, of seventeen African species collected in either Ghana or Cameroon.

RESULTS AND DISCUSSION

The compounds isolated from or detected in the *Diospyros* species, together with compounds previously recorded from three of them [3], are given in Table 1. In all samples examined the three triterpenes lupeol (**1**), betulin (**2**) and betulinic acid (**3**) were present. In some cases these were isolated but in most they were confirmed by co-chromatography against authentic markers using three different TLC systems. Other triterpenes, when detected during TLC analysis of petrol extracts, were separated by either column chromatography or preparative TLC over silica gel.

Betulinaldehyde (**4**) was isolated from the petrol extract of *D. canaliculata* bark. This compound, which represents a stage in the C-28 oxidation sequence from lupeol to betulinic acid, has surprisingly not been reported before from the Ebenaceae. It was identified on the basis of the similarity of IR and ^{1}H NMR data to those of the typical lupane compounds with the addition of aldehyde signals, and by its conversion into **2** by reduction with sodium borohydride. The ^{13}C NMR spectrum of **4** was obtained for the first time and the data are listed in the Experimental.

An additional triterpene from the petrol extract of *D. zenkeri* bark analysed for $C_{30}H_{50}O$ but did not have the spectral characteristics of lupeol. The ^{1}H NMR spectrum showed a signal at δ 3.45 for an axial H-3 proton and a triplet at δ 5.65 for an olefinic proton, together with eight singlets for methyl groups resonating between δ 0.85 and 1.16. The EIMS gave major ions at *m/z* 274 and *m/z* 152, assignable to **5** and **6** respectively. This fission reveals the presence of the olefinic centre in ring-B and the absence of a C-10 methyl substituent. Physical and spectral data for the compound agree closely with that published [4, 5] for glut-5(6)-en-3β-ol (**7**), a rare triterpene previously recorded only from Labiatae [4], Euphorbiaceae [5] and Betulaceae [6].

D. iturensis bark yielded small amounts of a triterpene ($C_{30}H_{50}O_2$) which exhibited a weak UV absorption at 283 nm and an IR spectrum with bands for OH and CO. The EIMS gave a major ion at *m/z* 289 (**8**) characteristic of saturated friedelane derivatives substituted only in ring-A [7]. A comparison of the EIMS with that published for friedelin (**9**) [7] showed strong correlation but with those ions incorporating ring-A undergoing a 16 amu increase confirming the placement of the second oxygen in ring-A. On the basis of the presence of UV absorption, which requires a diosphenol-type system, oxygenation can be assigned to C-2 and C-3. Acetylation afforded a monoacetate the ^{1}H NMR spectrum of which exhibited a double-doublet ($J_1 = J_2 = 3$ Hz) for the oxymethine proton, requiring its placement at C-2 and in the equatorial configuration. Other significant features of the ^{1}H spectrum were a 3H doublet at δ 0.87 for the C-4 methyl group coupled to a 1H quartet at δ 2.67 for H-4, an acetyl signal at δ 2.12 and seven methyl singlets between δ 0.72 and 1.20. Both physical and spectral data on the acetate agreed well with those recorded [8] for cerin acetate (**10**) and on that basis the isolated triterpene can be identified as cerin (**11**), a compound previously reported only as a constituent of cork [9].

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Table 1. Distribution of triterpenes and naphthoquinones in the stem barks and woods of the *Diospyros* species examined

Species	Voucher	Source	Plant part	Compounds and yields (% × 10^3)												
				1	**2**	**3**	**4**	**7**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18/19**
D. abyssinica (Hiern) F. White	GC-46147	Sh	B	+	+	+	–	–	–	4	5	–	–	–	–	–
D. canaliculata De Wild	GC-46658	Ka	B	+	+	+	5	–	–	–	–	–	70	5	5	15
D. chevalieri De. Wild	GC-46622	Br	B	+	+	+	–	–	–	–	–	–	–	–	–	–
D. cinnabarina (Gürke) F. White	W/M-818	DE	B[3]	+	+	8	–	–	–	2	–	–	–	–	–	–
			W	+	+	+	–	–	–	–	–	–	–	–	–	–
D. crassiflora Hiern	T-685	K	B	+	+	+	–	–	–	–	–	–	–	–	–	–
D. dendo Welw. *ex* Hiern*	W/M-875	DE	B[3]	1	6	3	–	–	–	–	2	40	–	–	–	–
			W	+	+	+	–	–	–	?	?	–	–	–	–	–
D. fragrans Gürke	M/G-149	DE	W	+	+	+	–	–	–	10	–	–	–	–	–	–
D. gabunensis Gürke	T-548	K	B	+	+	+	–	–	–	?	?	–	–	–	–	–
D. gracilescens Gürke	W/M-851/884	DE	B[3]	29	12	6	–	–	–	–	56	–	–	–	–	–
			W	+	+	+	–	–	–	–	–	–	–	–	–	–
D. hoyleana F. White	W/M-803/866	DE	B	6	11	13	–	–	–	?	?	–	–	–	–	–
			W	12	19	28	–	–	–	–	–	–	–	–	–	–
D. iturensis (Gürke) Let. & F. White	M/G-183	DE	B	13	10	60	–	–	3	?	?	–	–	–	–	–
			W	+	+	+	–	–	–	–	–	–	–	–	–	–
D. kamerunensis Gürke	GC-46609	Br	B	+	+	+	–	–	–	5	–	–	–	–	–	–
D. longiflora Let. & F. White	W/M-822	DE	B	19	9	60	–	–	–	50	–	–	–	–	–	–
			W	+	+	+	–	–	–	–	–	–	–	–	–	–
D. mespiliformis Hochst. *ex.* D. C.	none	Sh	B	+	+	+	–	–	–	–	–	–	–	–	–	–
D. monobuttensis Gürke	none	Ghana	B	+	+	+	–	–	–	?	?	–	–	–	–	–
D. sanza-minika A. Chev.	GC-46634	Br	B	+	+	+	–	–	–	?	?	–	–	–	–	–
D. zenkeri (Gürke) F. White	M/G-125	DE	B	16	67	65	–	4	–	–	–	1	–	–	–	–
			W	36	7	6	–	–	–	–	–	–	–	–	–	–

*Previously reported [3] to be *D. bipindensis* Gürke.

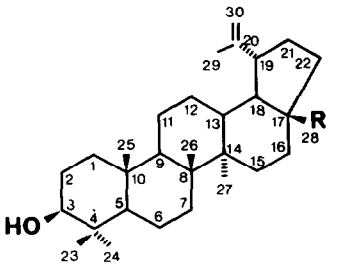
Vouchers: GC numbers are deposited at the Herbarium of the University of Ghana, Legon. W/M = Waterman and McKey, M/G = McKey and Gartlan, T = Thomas; all vouchers deposited at the Herbarium of the Royal Botanic Gardens, Kew. Sources: DE = Douala-Edea Forest Reserve, Cameroon; K = Korup National Park, Cameroon. Br = Bronikrom area, 30 km SSE of Samreboi, Ghana; Ka = Kade Agricultural Research Station, Ghana; Sh = Shai Hills, Ghana. Plant part: B = stem bark; W = wood.

+, Detected by TLC but not isolated; ?, compounds of the 7-methyljuglone dimer type present but in insufficient amounts for isolation; –, not detectable by TLC.

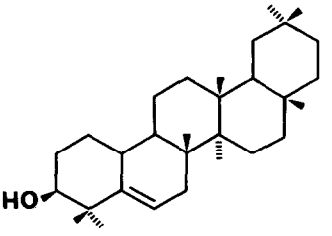
Naphthoquinones were detected in fourteen of the seventeen species that have been investigated (including those already reported [3] from the barks of *D. cinnabarina*, *D. dendo* and *D. gracilescens*). Where present in sufficient quantities they were isolated by column chromatography or by preparative TLC using acid-washed silica gel and protecting the extract from strong light. For five of the six species where isolation was possible the naphthoquinones obtained were dimers of 7-methyljuglone; diospyrin (**12**) from *D. abyssinica*, *D. fragrans*, *D. kamerunensis* and *D. longiflora*; isodiospyrin (**13**) from *D. abyssinica*; and diosindigo-A (**14**) from *D. zenkeri*. All three compounds were identified by comparison of spectral data with that published.

By contrast *D. canaliculata* yielded 2-methyljuglone (plumbagin, **15**) and two novel plumbagin/4-hydroxy-5-methylcoumarin adducts, canaliculatin (**16**) and cyclocanaliculatin (**17**), the characterization of which has been described elsewhere [10, 11]. In addition a colourless, yellow–green fluorescent material was isolated from the petrol extract of the bark. This substance analysed for $C_{11}H_{12}O_3$ which, together with a UV spectrum showing maxima at 258 and 333 nm, was in agreement with that required for isoshinanolone (**18**) [12], a reduced form of plumbagin. The ^{1}H NMR spectrum showed resonances anticipated for **18** [12]; most notably a doublet at δ 1.10 (J = 6 Hz) for the C-2 methyl group, a doublet at δ 4.62 (J = 2.5 Hz) for H-1 and a downfield resonance at δ 12.25 for the hydrogen-bonded OH proton at C-5.

However, the ^{1}H spectrum obtained for the material was more complex than required for **18**, the most striking additional feature being a doublet at δ 4.37 (J = 8 Hz) with an integral value about equal to that for the δ 4.62 signal assigned to H-1 of **18**. As chromium trioxide oxidation of the mixture in pyridine yielded only **15** it was clear that the isolated material must be a mixture of approximately equal amounts of **18** and of an isomer thereof. The stereochemistry of **18** has been resolved by Tezuka *et al.* [12] who have found that it exists with the reduced quinoid ring in the half-chair form with a 1*R*,2*R* absolute configuration on which H-1 and H-2 exist in pseudoequatorial and axial orientations respectively. The same workers report [12] that on reduction of **15** with lithium aluminium hydride they obtained the racemate of a diastereoisomer of **18** which exhibited a doublet at δ 4.44 (J = 7.5 Hz) indicating that H-1 and H-2 would be in pseudoaxial and axial orientations. Of the eight possible isomers of **18** the two which permit that pseudoaxial and axial orientation are 1*S*,2*R* in the half-chair conformation (**19**) and 1*R*,2*S* in the half-boat conformation (**20**).



1 R = Me
2 R = CH_2OH
3 R = COOH
4 R = CHO



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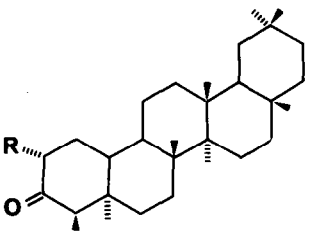
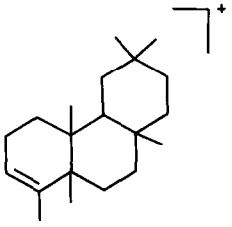


9 R = H
10 R = OAc
11 R = OH



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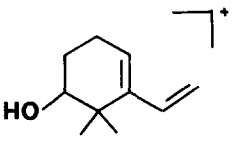

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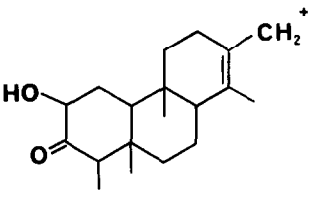

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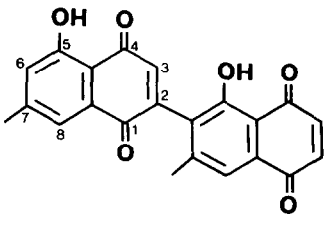

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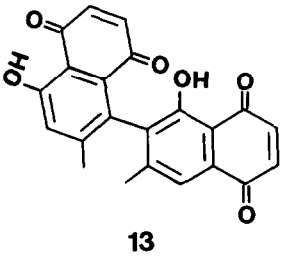

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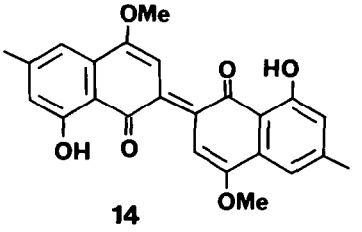

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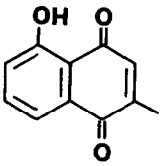
The isomer present with **18** in the mixture was determined by a comparison of the OR values for shinanolone (**21**), a reduced form of 7-methyljuglone, (−22.8°) [13], for isoshinanolone (−7°) [12], and for the mixture obtained (+16°). Shinanolone contains a 1*R* chiral centre with a half-chair conformation [13] and as the 1*R* chiral centre of isoshinanolone is identical to it then the 2*R* centre of the latter must produce an OR of +15.8° to give the observed OR of −7° (−22.8° + 15.8° = −7°). On this basis the anticipated OR for the 1*S*,2*R* isomer (**19**) would be +38.6° (+22.8° + 15.8° = 38.6°) and the 1*R*,2*S* isomer (**20**) would be the corresponding −38.6°. Considering



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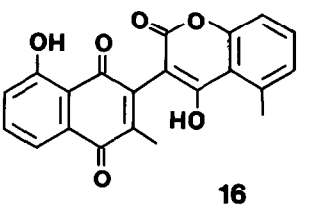

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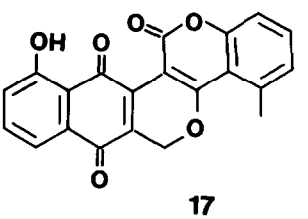

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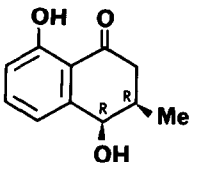

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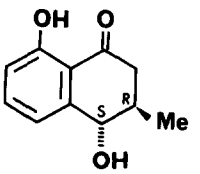

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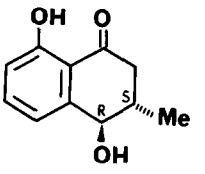

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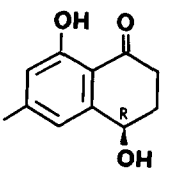

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that the OR of the mixture obtained was + 16° and that it was made up of about equal amounts of **18** (− 7°) and the second isomer it is obvious that the second component must be the 1*S*,2*R* isomer (**19**) as this mixture would give an OR of [(− 7° + 38.6°)/2 = + 15.8°], in close agreement with that found. This is the first time that **19**, which we have assigned the trivial name of epiisoshinanolone, has been reported.

The occurrence of naphthoquinones and triterpenes in the species analysed generally reveals the biochemical conservatism that appears to be typical of *Diospyros* [14]. For those species where naphthoquinones were present TLC usually revealed a mixture, presumably of dimers with different positions of attachment, but with one of the products predominating over all others. The only exceptional species was *D. canaliculata*, the most widespread *Diospyros* in the Guineo-Congolian region [1], which was at variance from all other species examined in producing plumbagin and derivatives rather than 7-methyljuglone and dimers and also in producing significant amounts of betulinaldehyde. Finally it should be noted that there does appear to be variability within a species with respect to the production of naphthoquinone compounds. In this study no trace of naphthoquinones could be detected in the bark of *D. mespiliformis* whereas an earlier study [15] had recorded the presence of 7-methyljuglone, **12** and **13**.

EXPERIMENTAL

Mps: uncorr; UV: MeOH; IR: KCl discs; NMR: $CDCl_3$ using TMS as int. standard unless otherwise stated; EIMS: elevated temp. (160–190°) and 70 eV using direct probe insertion; OR were determined with a Perkin-Elmer 240 polarimeter. Petrol refers to the bp 40–60° fraction unless otherwise stated.

Plant material. Bark and wood samples were collected in 1976 and 1979 and were sun dried. Details of vouchers are given in Table 1.

General isolation and purification methods. Powdered samples were extracted in a Soxhlet, firstly with petrol and then with $CHCl_3$ followed by MeOH, or directly with MeOH or EtOAc. Extracts were filtered and concd under red. pres. (max. temp. 40°) before initial TLC examination (silica gel plates with toluene–EtOAc–AcOH (40:9:1) or $CHCl_3$–MeOH (19:1) as eluting solvents). CC was carried out over silica gel eluting with petrol followed by petrol containing increasing amounts of EtOAc. Further purification of fractions from the column was achieved by prep. TLC employing solvents of petrol–EtOAc mixtures. Where naphthoquinones were present all operations were performed in subdued light and with columns wrapped in Al foil.

Isolation and identification of individual substances. Compounds from the bark of D. zenkeri. Concentration of the petrol extract of the bark (150 g) gave a ppt. which on recrystallization from EtOH yielded **14** (2 mg). CC of the supernatant gave, on elution with

petrol containing increasing amounts of EtOAc, **7** (5 mg), **1** (24 mg), **2** (86 mg) and a mixture. Prep. TLC of the mixture gave further **14** (1 mg) and **3** (5 mg). CC of the MeOH extract gave **2** (14 mg) and **3** (92 mg). *Lupeol* (**1**). Needles from $CHCl_3$, mp 214° (lit. [16] 215°, $[\alpha]_D^{20}$ +26° (*c* 0.2, $CHCl_3$) (lit. [17] +27°). Found: $[M]^+$ 426.3856; $C_{30}H_{50}O$ requires 426.3861. IR, ^1H NMR and EIMS identical with authentic material. *Betulin* (**2**). Needles from Me_2CO, mp 256–258° (lit. [12] 256–257°), $[\alpha]_D^{20}$ +18° (*c* 0.1, $CHCl_3$) (lit. [16] +20°). Found: $[M]^+$ 442.3818; $C_{30}H_{50}O_2$ requires 442.3811. IR, ^1H NMR and EIMS identical with authentic material. *Betulinic acid* (**3**). Colourless needles from MeOH, mp 314° (lit. [16] 316°), $[\alpha]_D^{20}$ +8° (*c* 0.25, pyridine) (lit. [17] +8°). Found: $[M]^+$ 456.3600; $C_{30}H_{48}O_3$ requires 456.3603. IR, ^1H NMR and EIMS identical with authentic material. *Glutinol* (**7**). Prisms from petrol (bp 60–80°), mp 207–210° (lit. [4] 207–210°), $[\alpha]_D^{25}$ +22° (*c* 0.14, $CHCl_3$) (lit. [4] +30°). Found: $[M]^+$ 426.3884; $C_{30}H_{50}O$ requires 426.3861. IR ν_{max} cm^{-1}: 3400, 2950, 2870, 1460, 1385; ^1H NMR (90 MHz): δ 0.85, 0.95, 0.99, 1.01, 1.04, 1.10, 1.14, 1.16 (8 × *s*, 8 × Me), 3.45 (1H, *dd*, $W_{1/2}$ = 5 Hz, H-6); EIMS *m/z* (rel. int.): 426 (12), 275 (22), 274 (100), 259 (41), 205 (19), 152 (13), 150 (10), 137 (18), 136 (11), 135 (13), 134 (23). *Diosindigo-A* (**14**). Blue prisms from MeOH, mp > 300° (lit. [18] 317°). Found: $[M]^+$ 404.1258; $C_{24}H_{20}O_6$ requires 404.1260. UV λ_{max} nm: 246, 293, 340, 697; (+ NaOH) 328, 526, 657; IR ν_{max} cm^{-1}: 3400 (*br*), 2960, 2880, 1740, 1575; ^1H NMR (100 MHz): δ 2.40 (6H, *s*, 7, 7′-Me), 6.83 (2H, *s*, H-2, H-2′), 7.14 (2H, *s*, H-6, H-6′), 8.43 (2H, *s*, H-8, H-8′), 13.52 (2H, *s*, OH-5, 5′); EIMS *m/z* (rel. int.): 404 (70), 389 (50), 373 (100), 202 (31), 191 (10), 189 (25).

Diospyrin from D. longiflora *bark*. The bark (150 g) was extracted successively with petrol, $CHCl_3$ and MeOH. Normal work-up of the petrol extract gave, in order of elution from the silica gel column, **1** (16 mg), **12** (8 mg), **2** (5 mg) and **3** (3 mg). Similar treatment of the $CHCl_3$ extract gave **1** (12 mg), **12** (52 mg), **2** (10 mg) and **3** (56 mg). *Diospyrin* (**12**). Orange plates from $CHCl_3$, mp 254–256° (lit. [19] 254–256°). Found: $[M]^+$ 374.0802; $C_{22}H_{14}O_6$ requires 374.0790. UV λ_{max} nm: 254, 434 (+ NaOH) 270, 550; IR ν_{max} cm^{-1}: 3400 (*br*), 2920, 1664, 1640, 1605, 1595; ^1H NMR (90 MHz): δ 2.30 (3H, *s*, 7′-Me), 2.45 (3H, *s*, 7-Me), 6.90 (1H, *s*, H-3), 6.95 (2H, *s*, H-2′, H-3′), 7.13 (1H, *s* (*br*), H-6), 7.50 (1H, *s* (*br*), H-8), 7.58 (1H, *s*, H-8′), 11.87 (1H, *s*, OH-5), 12.15 (1H, *s*, OH-5′); EIMS *m/z* (rel. int.): 374 (100), 359 (15), 357 (11), 356 (14), 187 (18).

Cerin from D. iturensis *bark*. The bark (180 g) was extracted successively with petrol, $CHCl_3$ and MeOH. On concentration the combined petrol and $CHCl_3$ extracts gave **3** (29 mg). CC over silica gel gave **1** (20 mg) followed by a mixture of triterpenes. Recrystallisation of the mixture yielded **11** (5 mg) and prep. TLC of the supernatant gave **2** (18 mg) and **3** (70 mg). *Cerin* (**11**). Needles from toluene–MeOH, mp 246–250° (lit. [9] 247–251°), $[\alpha]_D^{20}$ −35° (*c* 0.04, MeOH) (lit. [16] −41°). Found: $[M]^+$ 442.3816; $C_{30}H_{50}O_2$ requires 442.3811. UV λ_{max} nm: 283; IR ν_{max} cm^{-1}: 3500, 3400, 2980, 1705, 1460; EIMS *m/z* (rel. int.): 442 (46), 341 (5), 318 (40), 290 (26), 289 (29), 273 (33), 264 (13), 262 (14), 248 (18), 246 (16), 234 (13), 231 (13), 220 (10), 218 (15), 205 (60), 179 (54). *Cerin acetate* (**10**). Compound **11** (4 mg) was acetylated using normal procedures to give **10** (3 mg) as needles from Et_2O, mp 261–264° (lit. [8] 260–262°). ^1H NMR (250 MHz): δ 0.72–1.20 (8 × Me), 2.12 (3H, *s*, 2-OAc), 2.67 (1H, *q*, *J* = 7 Hz, H-4), 4.95 (1H, *dd*, *J* = 3 Hz and 3 Hz, H-2).

Isodiospyrin from D. abyssinica. The bark (120 g) was extracted with petrol and then $CHCl_3$. The extracts were identical and were bulked and after concentration subjected to CC to give **13** (6 mg) followed by **12** (5 mg). *Isodiospyrin* (**13**). Orange plates from $CHCl_3$, mp 228–230° (lit. [12] 229–230°). Found: $[M]^+$ 374.0803; $C_{22}H_{14}O_6$ requires 374.0790. UV λ_{max} nm: 253, 430 (+ NaOH) 295, 550; IR ν_{max} cm^{-1}: 3400 (*br*), 2920, 1660, 1640, 1600, 1590; ^1H NMR (90 MHz): δ 2.01 (3H, *s*, 7′-Me), 2.03 (3H, *s*, 7-Me), 6.77, 6.89 (2H, *ABq*, *J* = 10 Hz, H-2, H-3), 6.90 (2H, *s*, H-2′, H-3′), 7.29 (1H, *s*, H-6), 7.60 (1H, *s*, H-8′), 12.02 (1H, *s*, OH-5′), 12.40 (1H, *s*, OH-5); EIMS *m/z* (rel. int.): 374 (100), 359 (49), 357 (10), 345 (5), 341 (3), 331 (8), 329 (4), 187 (21).

Compounds from the bark of D. canaliculata. The powdered bark (200 g) was extracted with petrol, then MeOH. On concentration and CC the petrol extract gave **15** (85 mg) and a mixture of triterpenes. The isolation of further **15** (10 mg), **16** (4 mg) and **17** (10 mg) from the MeOH extract has been reported elsewhere [10, 11]. Similar extraction of a second bark sample (300 g) gave further **15** (15 mg), **16** (14 mg) and **17** (10 mg) from the $CHCl_3$ extract while CC of the petrol concentrate over silica gel yielded, on elution with petrol containing increasing amounts of $CHCl_3$, **15** (200 mg), **4** (15 mg) and a mixture of **18** and **19** (80 mg). *Plumbagin* (**15**). Orange–yellow needles from petrol, mp 75° (lit. [12] 75°). UV, IR, ^1H NMR and EIMS identical with those of an authentic sample. *Betulinaldehyde* (**4**). Plates from MeOH–Me_2CO, mp 197–200° (lit. [20] 199–200°), $[\alpha]_D^{20}$ +27° (lit. [20] +28°). Found: $[M]^+$ 440.3632; $C_{30}H_{48}O_2$ requires 440.3654. IR ν_{max} cm^{-1}: 3380, 3060, 2950, 2880, 1730, 1470; ^1H NMR (90 MHz): δ 0.73 (3H, *s*, 27-Me), 0.80 (3H, *s*, 25-Me), 0.90 (3H, *s*, 26-Me), 0.95 (6H, *s*, 23-Me, 24-Me), 1.68 (3H, *s* (*br*), 29-Me), 2.80 (1H, *m*, H-19), 3.15 (1H, *dd*, *J* = 11 Hz and 6 Hz, H-3), 4.60, 4.72 (2H, 2 × *s* (*br*), H-30), 9.65 (1H, *s*, H-28); ^{13}C NMR (62.9 MHz): δ_C 14.7 (*q*, C-27), 15.3 (*q*, C-24), 16.0 (*q*, C-26), 16.1 (*q*, C-25), 18.3 (*t*, C-6), 19.4 (*q*, C-29), 20.9 (*t*, C-11), 25.5 (*t*, C-12), 27.4 (*t*, C-2), 28.0 (*q*, C-23), 29.8 (*t*, C-21), 30.6 (*t*, C-15), 32.2 (*t*, C-16), 34.3 (*t*, C-7), 37.0 (*t*, C-22), 37.2 (*s*, C-10) 38.4 (*d*, C-13), 38.7 (*t*, C-1), 38.9 (*s*, C-4), 40.7 (*s*, C-8), 42.4 (*s*, C-14), 46.9 (*d*, C-18), 49.3 (*d*, C-19), 50.5 (*d*, C-9), 55.4 (*d*, C-5), 56.3 (*s*, C-17), 79.0 (*d*, C-3), 109.3 (*t*, C-30), 150.4 (*s*, C-20), 197.2 (*d*, C-28); EIMS *m/z* (rel. int.): 440 (85), 412 (44), 411 (26), 410 (16), 220 (15), 218 (12), 207 (100), 204 (19), 203 (26), 202 (15), 189 (90), 187 (34), 177 (17), 175 (29), 161 (17). Compound **4** (10 mg) in THF (4 ml) and EtOH (0.5 ml) was reacted with $NaBH_4$ for 1 hr at room temp. Work up of the reaction mixture gave **2** (3 mg), identical in all respects with authentic material. *Isoshinanolone* (**18**) *and epiisoshinanolone* (**19**). Oil, $[\alpha]_D^{20}$ +16°). Found: $[M]^+$ 192.0782; $C_{11}H_{12}O_3$ requires 192.0786. UV λ_{max} nm: 258, 333 (+ NaOH) 340; IR ν_{max} cm^{-1}: 3340, 2930, 1640, 1624, 1450; ^1H NMR (90 MHz): δ 1.10 (3H, *d*, *J* = 6 Hz, 2-Me), 2.10–3.10 (4H, *m*, H-2, H-3 and OH-1), 4.37 ($\frac{1}{2}$H, *d*, *J* = 8 Hz, H-1 of 19), 4.62 ($\frac{1}{2}$H, *d*, *J* = 2.5 Hz, H-1 of 18), 6.80–7.41 (3H, *m*, H-6, H-7, H-8), 12.25 (1H, *s*, OH-5); EIMS *m/z* (rel. int.): 192 (100), 177 (7), 175 (11), 150 (21), 122 (19), 121 (8). **18** + **19** (15 mg) in pyridine (1 ml) was added to CrO_3 (20 mg) in pyridine (2 ml) with continuous stirring. After 12 hr the reaction mixture was diluted with H_2O and after normal work up yielded **15** (6 mg).

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