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MONOTERPENE DIOL, IRIDOID GLUCOSIDE AND DIBENZO-α-PYRONE FROM *ANTHOCLEISTA DJALONENSIS*

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Key Word Index—*Anthocleista djalonensis*; Loganiaceae; djalonenoside; djalonensone; djalonenol; dibenzo-α-pyrone.

Abstract—*Anthocleista djalonensis* has provided a new monoterpene diol, djalonenol, as well as the known iridoid glucoside djalonenoside (also sweroside). Also isolated for the first time from a plant source is a dibenzo-α-pyrone-djalonensone, previously identified as a fungal metabolite. The structure of the new compound was elucidated on the basis of its chemical and spectral data as tetrahydro-3-hydroxy hydroxymethylene-4-(3-hydroxymethylene prop-1-ene)-2H-pyran-2-one.

INTRODUCTION

Anthocleista djalonensis (A. Chev.) is a plant of West African origin used in traditional medicine for the treatment of various diseases. The plant is known for its antipyretic, stomachic, analgesic and purgative actions [1, 2]. The aqueous extract of *A. djalonensis* was found to produce a rise in the blood pressure in cats and an increase in tone and amplitude of movement of rabbit duodenum preparations [3]. Most importantly, the root decoction of *A. djalonensis* and related species *Anthocleista vogelli* and *Anthocleista kerstingii* has been used in the treatment of diabetes mellitus. Herbalists claim a high percentage of 'cures' in their diabetic patients treated with members of these *Anthocleista* species [3].

A phthalide, djalonensin (**1**), which was the first report of its isolation from a natural source, lichexanthone (**2**) and an uncharacterized triterpene have been isolated from the hexane extract of the stem bark [4]. Poisson [5] reported the absence of swertiamarin in the leaves of *A. djalonensis*.

In continuation of our investigation of this medicinal plant [4] we now report chemical examination of the roots, leaves and stem, which gave a new monoterpene diol, djalonenol (**3a**), an iridoid glucoside, djalonenoside (**4a**) and a dibenzo-α-pyrone (**5**), djalonensone. Other compounds present include 3-oxo-$\Delta^{4,5}$-sitosterone (**6**), D-(+)-bornesitol (**7a**), ursolic acid (**8a**), an oligosaccharide, sitosterol and stigmasterol.

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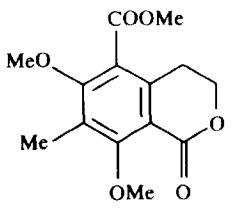
RESULTS AND DISCUSSION

Repeated dry column flash chromatography on silica gel of the resultant brown solid and dark brown viscous liquid from ethyl acetate and methanol soxhlet extraction, respectively, of the roots of *A. djalonensis* furnished two compounds (A and B). Compound B was found to be the major constituent of the plant, also being present and isolated from the methanol extracts of the leaves and stem. Also isolated from the hexane and ethyl acetate extracts of the leaves were two compounds (C and D). Three compounds (E–G) were isolated from the methanol extracts of the stem.

Compound B was isolated as a brown viscous liquid and was named djalonenoside. The structure of djalonenoside (**4a**), was deduced from IR, UV, ^{1}H NMR, ^{13}C NMR, mass spectral data (see Experimental) and confirmed by decoupling, NOE, ^{1}H–^{1}H and ^{13}C–^{1}H 2D COSY correlation experiments and by chemical evidence (acetylation, hydrogenation, and acid hydrolysis). The ^{13}C NMR spectrum (Table 1) showed 16 signals, of which six could be assigned to a β-glucopyranosyl moiety [6] and five to an iridoid dihydropyrane ring. Of the remaining five signals, two at δ 132.5 and 120.6, as well as the proton signals at δ 5.44 (1H, *dt*) and δ 5.25 (2H, *m*, exomethylene) in the ^{1}H NMR spectrum, indicated the presence of an exocyclic double bond: the other three were assigned to a conjugated lactone moiety. This is consistent with the absorption at ν_{max} 1700 cm^{-1} for a conjugated carbonyl observed in the IR spectrum and the vinylic proton resonance at δ 7.52 in the ^{1}H NMR spectrum.

Acetylation under mild conditions in pyridine and acetic anhydride provided the tetraacetate, mp 166–167°.



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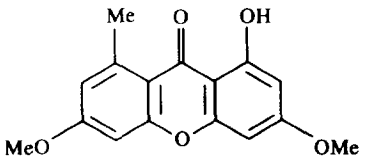

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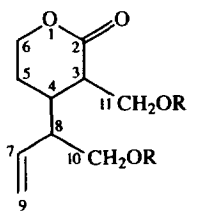

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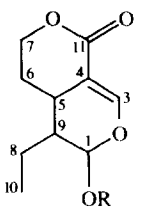

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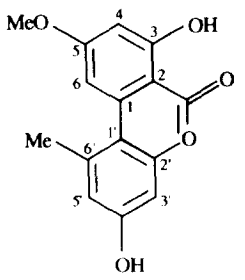

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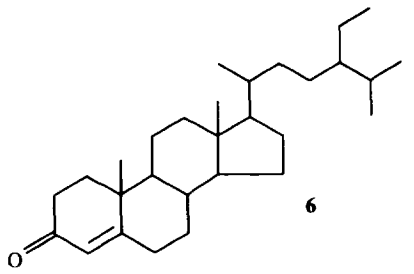

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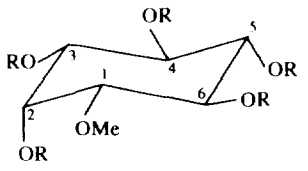

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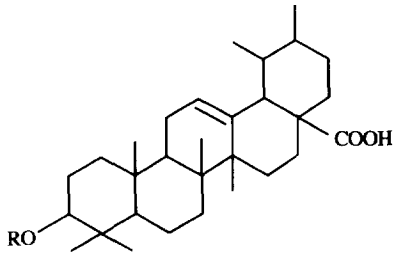

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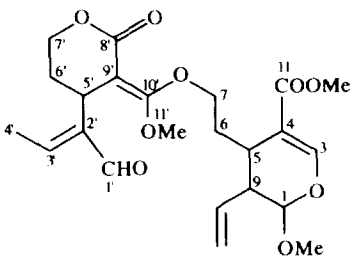

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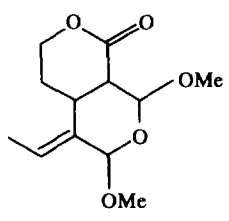

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Hydrogenation of the iridoid and its tetraacetate in the presence of hydrogen and 10% paladium on carbon afforded the dihydroiridoid as a liquid and the dihydroiridoid tetraacetate as a white crystalline compound mp 173–175°. All the protonated carbons of the tetraacetate were unambiguously assigned on the basis of 2D $^{13}C-^{1}H$ COSY (Table 1). Decoupling experiments on irradiation of protons 5 and 6 revealed that H-5 was coupled to H-3, H-6 and H-9 while H-6 was coupled to H-5 and H-7. Irradiation of protons H-8 and H-9 also revealed that H-8 was coupled to H-9, H-10 and H-9 to H-3 and H-8. ^{3}J couplings of H-5/H-6/H-7, H-5/H-9/H-8, H-9/H-8/H-10 observed in the $^{1}H-^{1}H$ COSY are consistent with the above decoupling result.

Irradiation of H-10 afforded positive NOEs at H-9, H-1′, H-3′ and H-5′, while irradiation of H-1′ afforded positive NOEs at H-10 and H-5′, indicating the close proximity of H-10 to H-1′ and H-5′. Comparison of the ^{13}C NMR data with those of secologanin, loganin and sweroside [7] revealed that djalonenoside had exact parallels with sweroside: djalonenoside is thus identical to sweroside. However, no previous report of a 2D COSY correlation experiment on sweroside was found in the literature. Hydrolysis in methanol and HCl gave three hydrolysis products: HYB-1, HYB-2 and HYB-3. The major product HYB-1 (**9**) was found to be a dimer of the other two (minor) products with opening of ring A in HYB-2 (**10**) and opening of ring B in HYB-3 (**4c**). This is

Table 1. ^1H and ^{13}C NMR spectral data of compound B $(OAc)_4$, djalonenoside tetraacetate (**4b**)

H	δ (ppm)	Decoupling experiment	NOE experiment	^1H ^1H-COSY correlated with	C	δ (ppm)	DEPT	^{13}C ^1H-COSY correlated with
1	5.29 *d*			H-9	1	96.2	CH	H-1
3	7.52 *d*	3 coupled to 5	(3) NOEs at 10a (< 1%)	H-5	3	151.2	CH	H-3
					4	105.1	C	
5	2.82 *ddd*	5 coupled to 3, 6a, b, 9		H-3, 6, a	5	27.2	CH	H-5
6a	1.64 *ddd*	6a, b coupled to 5, 7a, b		H-5, 7	6	24.4	CH_2	H-6a, b
6b	1.70 *ddd*							
7a	4.30 *ddd*	7a coupled to 7b, 6a, b		H-6, 7, 6′	7	68.0	CH_2	H-7
7b	4.42 *ddt*	7b coupled to 7a, 6a, b						
8	5.44 *dt*	8 coupled to 9, 10a, b		H-9, 10	8	130.8	CH	H-8
9	2.65 *ddd*	9 coupled to 8, 5	(10b) NOEs at 5′ (1%)	H-1, 3, 8	9	41.7	CH	H-9
10	5.25 *m*		(10a) NOEs at 9 (4%), 1′ (3%) 3 (1%)	H-6′	10	120.9	CH_2	H-10a, b
					11	164.8	C	
1′	4.87 *d*		(1′) NOEs at 5′ (4%), 10a (4%) 10b (4%)	H-2′	1′	95.7	CH	H-1′
2′	4.96 *dd*	2′ coupled to 10b		H-1′	2′	70.2	CH	H-2′
3′	5.05 *t*	3′ coupled to 5′		H-5′	3′	71.9	CH	H-3′
4′	5.21 *t*				4′	67.8	CH	H-4′
5′	3.72 *ddd*	5′ coupled to 3′, 6a′, 6b		H-3′, ′	5′	71.9	CH	H-5′
6a′	4.26 *dd*	6′ coupled to 6b′, 5′		H-5′, 6′b, 7	6′	61.4	CH_2	H-6′a, b
6b′	4.10 *dd*	6b′ coupled to 5′, 6a′		H-5′, 6′a	R	169.1, 169.2		
OAc–Me	1.88, 1.93					169.8, 170.3		
	1.95, 2.01				OAc–Me	20.5, 20.3 (× 3)		

Coupling constants (Hz): $J_{\perp,9} = 1.6$, $J_{3,5} = 2.6$, $J_{5,6} = 7.9$, $J_{5,9} = 5.7$, $J_{6a,b} = 13$, $J_{6,7} = 7$, $J_{7,6'} = 3.6, 4.5$, $J_{7a,b} = 11$, $J_{8,9} = 9$, $J_{8,10} = 18$, $J_{10,4'} = 9.4$, $J_{10,2'} = 9$, $J_{1',2'} = 8$, $J_{3',5'} = 9.6$, $J_{5',6'} = 2.3, 4.5$, $J_{6'a,b} = 12.4$.

the first report of ring opening and dimerization of a hydrolysis (or methanolysis) product of such glucosides.

Compound E was isolated as a brown liquid and purified by repeated preparative TLC as a sweet-smelling liquid, which was named djalonenol (**3a**). Its structure was deduced on the basis of DEPT, ^{1}H NMR, UV and IR spectral data, comparison with spectral data of compound B, and confirmed by chemical evidence (acetylation). The IR absorption indicated the presence of hydroxyl (ν_{max} 3550–3100 cm^{-1}) and non-conjugated carbonyl (ν_{max} 1750 cm^{-1}) systems. Ten distinct signals were evident in the DEPT spectra, indicating that compound E is a monoterpene. The resonance at δ176.2 and the absorption at 1750 cm^{-1} of the ^{13}C NMR and IR, respectively, are consistent with an unconjugated lactone. The resonance at δ68.9 was assigned to the oxo-methylene carbon of the lactone moiety. Two signals at δ138.5 and δ118.5 (exomethylene), as well as the ^{1}H NMR signals at δ5.74 (1H, *m*, J = 8, 11, 18 Hz) and 5.13 (2H, *dd*, J = 11, 18 Hz) (exomethylene) indicated the presence of an exocyclic double bond. Two triplet carbon resonances at δ63.2 and 63.9 were attributed to primary hydroxy methylenes. Three of the remaining four signals were assigned to an unconjugated lactone moiety, with the resonance at δ48.2 bearing one of the hydroxy methylene carbons; the fourth resonance at δ50.9 was attributable to the allylic carbon to which the second hydroxy methylene carbon is attached.

The characterization was confirmed by the diacetate obtained on acetylation under mild conditions. Similarities observed in the ^{1}H NMR of djalonenol with djalonenoside suggests that djalonenol is a natural hydrolysis product of djalonenoside with cleavage of the pyran ring. Djalonenol was thus characterized as tetrahydro-3-hydroxymethylene-4-(3-hydroxymethylene prop-1-ene)2Hpyran-2-one. This is the first report of isolation of the monoterpene djalonenol.

Compound A formed needles, mp 264–266° and was named djalonensone (**5**). The IR spectrum indicated the presence of aromatic rings at ν_{max} 1615, 1590 and 1565 cm^{-1} and conjugated carbonyl at 1660 cm^{-1}, consistent with the singlet at δ165.5 in the ^{13}C NMR spectrum for conjugated lactones. The ^{13}C NMR DEPT spectrum revealed the presence of 15 carbon atoms. ^{1}H and ^{13}C NMR spectra indicate the presence of a methoxy group at δ3.79 and 55.4, an aromatic methyl at δ2.62 and 25.2, four aromatic protons at δ7.1 (J = 2.2 Hz), 6.3 (J = 2.2 Hz), 6.5 (2H, J = 2 Hz, narrow AB systerm). The narrow AB system was evident from decoupling experiments of the aromatic methyl. The coupling constants found for the aromatic ring protons are typical of meta-coupling, implying the presence of two aromatic rings, each bearing a pair of meta-related protons [8]. The mass spectrum indicated a parent peak at *m/z* 272 (100%) which, in addition to the ^{13}C NMR DEPT and ^{1}H NMR spectra, support a molecular formula of $C_{15}H_{12}O_5$. Sharpening of both the meta-AB quartets and one of the aromatic proton doublets on decoupling experiments on the aromatic methyl indicated that the molecule was angular, rather than linear like in xanthones. The structure of compound A was confirmed by NOE experiments (presented in Table 2) and characterized as 3,4′-dihydroxy-5-methoxy-6′-methyl dibenzo-α-pyrone (**5**). Comparison of the ^{13}C NMR spectrum with that of model benzo-α-pyrone revealed that djalonensone had an exact parallel with the monomethyl ether of the fungal metabolite, alternariol (mp 266–267°) [9], first isolated from *Alternaria tenius*. As the plant material was not mouldy before extraction and the extract itself was not mouldy, the isolation and characterization of djalonenosone is the first report of such a dibenzo-α-pyrone from a plant source.

It would be worthwhile to mention briefly that lichexanthone earlier isolated from *A. djalonensis* cooccurs with alternariol methyl ether in *Penicillin diversum*. Stinson *et al.* [10] claim alternariol, and thus its mono methyl ether, are biosynthesized via nor-lichexanthone. The co-occurrence of 3,4′-dihydroxy-5-methoxy-6′-methyl dibenzo-α-pyrone (mono methyl ether alternariol) with lichexanthone in *A. djalonensis* could be of chemotaxonomic importance as supportive evidence in favour of nor-lichexanthone as a precursor of alternariol methyl ether.

Compounds C, D, F and G were identified spectroscopically (UV, IR, ^{1}H NMR, ^{13}C NMR and MS) as 3-oxo-$\Delta^{4,5}$-sitosterone (**6**), ursolic acid (**8**), D-(+)-bornesitol (**7**) and an oligosaccharide (comprising two α- and β-D-glucose units), respectively. Sitosterol and stigmasterol were also isolated from the hexane extracts of the roots, leaves and stem.

EXPERIMENTAL

General. Mps: uncorr. ^{1}H NMR: 200.13 and 300.133 MHz (shifts relative to $CDCl_3$ at δ_H7.25 or CD_3OD at δ_H 3.30 or TMS). ^{13}C NMR: 50.3 and 75.5 (shifts relative to $CDCl_3$ at δ_C77.0 or CD_3OD at δ_C49.0). EIMS were obtained at 70 eV. CC: silica gel (Merck, 70–230 and 230–400 mesh). TLC: percolated silica gel F_{254} (Merck, 0.25 mm) spots visualized by UV (254 nm) and 60% H_2SO_4.

Plant material. Stem, roots and leaves of *A. djalonensis* collected from Ibadan, Nigeria were authenticated at source and confirmed at the Federal Department of Forest Research, Ibadan where a voucher specimen is deposited at the Herbarium.

Table 2. ^{1}H NMR and NOE effects on djalonensone (**5**)

Position	Irradiated species	NOE effects (approx. values)
C-8′	Me δ2.62	δ7.0 (~ 20%), 6.5 (~ 18%)
C-7′	OMe δ3.79	δ6.3 (~ 13%), 7.0 (~ 3%)
C-4	H- δ6.3	OMe (~ 5%)
C-3/5′	H- δ6.5	Me (~ 6%)
C-6	H- δ7.1	Me (~ 10%), OMe (~ 3%)
C-4′	OH- δ9.6	δ6.5 (~ 1%)
C-3	OH- δ12.0	δ6.3 (~ 1%)

Extraction and isolation. The dried powdered roots (1.5 kg), stem (500 g) and leaves (840 g) were Soxhlet extracted with refluxing C_6H_{12}, EtOAc and MeOH, respectively. The EtOAc concentrate of the roots gave a brown solid (34.22 g), which was fractionated by dry column flash chromatography on a column of silica gel eluting with Et_2O–petrol (40:60). Petrol–Et_2O (7:3) eluted dibenzo-α-pyrone compound A (0.038 g), djalonensone as needles (mp 264–266°) (R_f 0.5, C_6H_{12}–EtOAc, 9:1) (lit. 266–267°) [9]. EIMS (probe) 70 eV, *m/z* (rel. int.): 272 (M^+, 100), 243 [$M^+ - Co$] (25), 28 (39.4). IR ν_{max}^{KBr} cm^{-1}: 3420–3320 (OH), 1660 (C=O), 1615, 1590, 1565 (arom). ^1H NMR (200 MHz, $CDCl_3$): δ2.62 (3H, *s*), 3.79 (3H, *s*), 6.3 (1H, *d*, *J* = 2 Hz, H-4), 6.5 (2H, *d*, *J* = 2 Hz, H-3, H-5′), 7.1 (*d*, *J* = 2 Hz, H-6), 9.6 (OH), 12.0 (OH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ138.1 (*s*, C-1), 98.5 (*s*, C-2), 164.3 (*s*, C-3), 101.8 (*d*, C-4), 161.3 (*s*, C-5), 104.0 (*d*, C-6), 165.5 (*s*, C-7), 109.6 (*s*, C-1′), 152.8 (*s*, C-2′), 101.8 (*d*, C-3′), 157.9 (*s*, C-4′), 117.5 (*d*, C-5′), 138.2 (*s*, C-6′), 55.4 (*s*), 25.23 (*q*).

The MeOH concentrate of the roots afforded a dark brown viscous liquid (192.5 g), of which 30 g was fractionated by dry column flash chromatography on a column of silica gel eluting with EtOAc–MeOH (9.5:0.5). This yielded the iridoid glucoside compound B, djalonenoside, (**4a**) (also sweroside), as a brown viscous liquid (8.14 g) (R_f 0.2, MeOH–EtOAc, 1:1). UV λ_{max}^{MeOH} nm: 201, 243. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440–3380 (OH), 1700 (C=O), 1615 (C=C), 1280, 1070, 900, 840. ^{13}C NMR (50.3 MHz, CD_3OD): δ95.9 (*d*, C-1), 151.8 (*s*, C-3), 105.1 (*s*, C-4), 27.0 (*d*, C-5), 24.5 (*t*, C-6), 68.0 (*t*, C-7), 132.5 (*d*, C-8), 41.8 (*d*, C-9), 120.6 (*t*, C-10), 165.0 (*s*, C-11), 98.3 (*d*, C-1′), 73.3 (*d*, C-2′), 76.5 (*d*, C-3′), 70.2 (*d*, C-4′), 77.5 (*d*, C-5′), 61.3 (*d*, C-6′).

The C_6H_{12} concentrate of the leaves gave a green oil (0.24 g) whose components were separated by dry column flash chromatography on a column of silica gel eluting with Et_2O–petrol (1:1). The steroid, compound C, 3-oxo-$\Delta^{4,5}$-sitosterone, eluted as a liquid purified by preparative TLC (R_f 0.46, C_6H_{12}–EtOAc, 8.6:1.4). Spectroscopic data are comparable with those of sitosterol [11] and 3,17-dioxo androstanes [12]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2850, 2860, 1660, 1435, 720. UV $\lambda_{max}^{CHCl_3}$ nm: 244. ^1H NMR (200 MHz, $CDCl_3$): δ5.71 (1H, *s*, H-4), 1.56 (*s*, 3H, H-19), 1.24, 1.17 (×2, *br s*, methylene), 0.84 (9H, *m*, H-26, H-27, H-29), 0.69 (3H, *s*, H-18). ^{13}C NMR (MHz, $CDCl_3$): δ35.7 (*t*, C-1), 29.7 (*t*, C-2), 199.7 (*s*, C-3), 123.7 (*d*, C-4), 171.8 (*s*, C-5), 32.0 (*t*, C-6), 33.0 (*t*, C-7), 35.6 (*d*, C-8), 53.8 (*d*, C-9), 38.7 (*s*, C-10), 21.0 (*t*, C-11), 39.6 (*t*, C-12), 42.5 (*s*, C-13), 56.0 (*d*, C-14), 24.2 (*t*, C-15), 28.2 (*t*, C-16), 55.9 (*d*, C-17), 12.0 (*q*, C-18), 19.0 (*q*, C-19), 36.1 (*d*, C-20), 18.8 (*q*, C-21), 34.0 (*t*, C-22), 29.8 (*t*, C-23), 45.8 (*d*, C-24), 29.1 (*d*, C-25), 17.4 (*q*, C-26), 19.8 (*q*, C-27), 23.0 (*t*, C-28), 12.0 (*q*, C-29).

The EtOAc concentrate of the leaves gave a greenish brown solid (22.5 g). On dry column flash chromatographic separation over a column of silica gel eluting with Et_2O–petrol (2:8), the triterpene compound D, ursolic acid, was eluted as crystals, mp 286–288° (R_f 0.2, C_6H_{12}–EtOAc, 8.6:1.4) (Lit. mp 290–291° [13]). EIMS, *m/z*, (rel. int.): 248 [203 + COOH]$^+$ (100), 207 (19.6), 203 [248–COOH]$^+$ (48.8), 202 [248 – HCOOH]$^+$ (5.2), 189 [207 – H_2O]$^+$ (13.1), 133 (34.9). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (OH), 2920–2860 (OH), 1695 (C=O). UV λ_{max}^{MeOH} nm: 241, 259. ^1H NMR (200 MHz, $CDCl_3$): δ0.76, 0.82, 0.93, 0.97, 1.10, 1.27 (6 × Me, *s*), 0.86 (3H, *d*, *J* = 1.3 Hz), 2.18 (1H, *d*, *J* = 2.5 Hz, H-18), 3.15 (1H, *m*, H-3), 5.23 (1H, *br s*, H-12). ^{13}C NMR (50.3 MHz, $CDCl_3$), 38.5 (*t*, C-1), 27.1 (*t*, C-2), 77.2 (*d*, C-3), 38.2 (*t*, C-4), 54.3 (*d*, C-5), 20.1 (*t*, C-6), 35.8 (*t*, C-7), 39.0 (*s*, C-8), 41.0 (*d*, C-9), 37.8 (*s*, C-10), 23.2 (*t*, C-11), 124.4 (*d*, C-12), 137.4 (*s*, C-13), 38.6 (*s*, C-14), 27.0 (*t*, C-15), 24.4 (*t*, C-16), 46.5 (*s*, C-17), 51.8 (*d*, C-18), 38.1 (*d*, C-19), 38.0 (*d*, C-20), 32.1 (*t*, C-21), 35.9 (*t*, C-22), 28.6 (*q*, C-23), 14.3 (*q*, C-24), 14.7 (*q*, C-25), 16.0 (*q*, C-26), 29.9 (*q*, C-27), 178.9 (*s*, C-28), 17.3 (*q*, C-29), 22.2 (*q*, C-30).

The MeOH concentrate of the stem gave a dark brown viscous liquid (25 g). Dry column flash chromatography of the extract (20 g) over a column of silica gel afforded three compounds E–G. MeOH–EtOAc (0.2:9.8) eluted a sweet-smelling monoterpene compound E, djalonenol (0.087 g) (**3a**) as a liquid purified by prep. TLC: (R_f 0.63, MeOH–EtOAc, 3.3:6.7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550–3100 (OH), 3000–2890 (OH), 1750 (C=O). UV $\lambda_{max}^{CHCl_3}$ nm: 242, 280. ^1H NMR (200 MHz, $CDCl_3$): 1.98 (1H, *m*, $J_{3,4}$ = 2, $J_{3,11}$ = 5 … Hz, H-3), 2.26 (1H, *m*, $J_{4,3}$ = 2, $J_{4,8}$ = 6.5, $J_{4,5}$ = 7.6 … Hz, H-4), 1.76 (2H, *m*, $J_{5,6}$ = 5.6, $J_{5,4}$ = 7.9, $J_{5a,b}$ = 11 … Hz, H-5), 4.35 (2H, *m*, $J_{6,5}$ = 6, $J_{6a,b}$ = 10 Hz, H-6), 5.74 (1H, *m*, $J_{7,8}$ = 8, $J_{7,9}$ = 18 … Hz, H-7), 2.69 (1H, *m*, $J_{8,10}$ = 4, $J_{8,4}$ = 6.5, $J_{8,7}$ = 8.1 … Hz, H-8), 5.13 (2H, *dd*, $J_{9a,b}$ = 11, $J_{9,7}$ = 18 Hz, H-9), 3.72 (2H, *dd*, $J_{10,8}$ = 4, $J_{10a,b}$ = 11 Hz, H-10), 4.07 (2H, *dd*, $J_{11,3}$ = 5, $J_{11a,b}$ = 15 Hz, H-11). ^{13}C NMR (50.3 MHz, $CDCl_3$): 176.2 (*s*, C-2), 48.2 (*d*, C-3), 34.9 (*d*, C-4), 27.1 (*t*, C-5), 68.9 (*t*, C-6), 138.5 (*d*, C-7), 50.9 (*d*, C-8), 118.5 (*t*, C-9), 63.2 (*t*, C-10), 63.9 (*t*, C-11).

MeOH–EtOAc (1:9) eluted a cyclitol, compound F, D-(+)-bornesitol (also D-1-methoxy myoinositol), (0.041 g) mp 200–202°, (R_f 0.35, MeOH–EtOAc, 2.5:7.5). Lit. mp 201–203° [14, 15]. Spectroscopic data are comparable with those of Weber [15]. IR ν_{max} cm^{-1}: 3500–3000. UV $\lambda_{max}^{CHCl_3}$ nm: 206, 271, 325. ^{13}C NMR (50.3 MHz; CD_3OD): δ82.8 (*d*, C-1), 69.7 (*d*, C-2), 74.0 (*d*, C-3), 73.1 (*d*, C-4), 76.3 (*d*, C-5), 73.3 (*d*, C-6), 57.7 (*s*).

MeOH–EtOAc (1.5:8.5) eluted an oligosaccharide compound G (1.99 g) as a viscous liquid (R_f 0.6, MeOH–EtOAc 2.5:7.5) with spectroscopic data comparable with those found by Gorin [6] and Wehri [12]. IR ν_{max} cm^{-1}: 3500–3000 (OH). ^{13}C NMR: (Cs-2): δ82.0 (*d*), 79.7 (*d*), 75.3 (*d*), 75.0 (*d*), (Cs-4): 70.5 (*d*), 70.4 (*d*), 69.7 (*d*), 68.1 (*d*). (Cs-4): 79.1 (*d*), 78.4 (*d*), 76.4 (*d*), 72.1 (*d*). (Cs-6): 64.5 (*t*), 63.5 (*t*), 63.4 (*t*), 61.6 (*t*).

Djalonenoside tetraacetate (**4b**). Djalonenoside (2.16 g) was acetylated (AC_2O–pyridine, 2:5:1), 16 hr room temp. and the mixture partitioned between H_2O and $CHCl_3$. The $CHCl_3$ extract on concn and crystallization afforded a substance (2.64), mp 166–167° (R_f 0.6, MeOH–EtOAc, 1:1). EIMS: *m/z* (rel. int.): 330 [M – CO]$^+$ (16.1), 168 [330 – $C_6H_{11}O_5$]$^+$ (63.1), 127 (19.5), 109 (42.2), 43 (100), 28 (15.5). IR ν_{max} cm^{-1}: 1760 (C=O), 1705 (C=O), 1620 (C=C), 1230, 1070, 1050. UV

$\lambda_{max}^{CHCl_3}$ nm: 257. ^{1}H NMR data: see Table 1. Decoupling, NOE, ^{1}H–^{1}H [300 MHz, $CDCl_3$] and ^{13}C–^{1}H COSY [75.5 MHz, $CDCl_3$] 2D correlation experiments are presented in Table 1.

Hydrogenation of djalonenoside-B and B-tetraacetate. Catalytic hydrogenation (10% paladium on carbon) (0.309 g) of B (0.797 g) in HOAc (glacial) (12 ml) at room temp. was carried out for 2 hr until one mol H_2 had been absorbed. H_2O was added and filtered through celite, filtrate neutralized with $NaHCO_3$ and extracted repeatedly with $CHCl_3$. Dihydrodjalonenoside was obtained as a liquid (0.015 g), (R_f 0.7, MeOH–EtOAc, 2.5:7.5). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000–2970 (OH), 1730 (C=O). UV $\lambda_{max}^{CHCl_3}$ nm: 244.

Catalytic hydrogenation (10% paladium on carbon) (0.030 g) of B $(OAc)_4$ (0.063 g) in HOAc (glacial) (12 ml) for 2 hr yielded dihydrodjalonenoside tetraacetate as a crystalline compound (0.030 g), mp 173–175° (R_f 0.65, MeOH–EtOAc, 1.7:8.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755 (C=O), 1700 (C=O), 1230. UV $\lambda_{max}^{CHCl_3}$ nm: 258. ^{1}H NMR (200 MHz, $CDCl_3$): 5.40 (1H, *d*, H-1), 7.50 (1H, *d*, H-3), 2.88 (1H, *m*, H-5), 1.77 (1H, *m*, H-6a), 1.65 (1H, *m*, H-6b), 4.48 (1H, *m*, H-7a), 4.30 (1H, *m*, H-7b), 1.08–1.5 (2H, *m*, H-8), 1.90 (1H, *m*, H-9), 0.98 (3H, *t*, H-10), 4.90 (1H, *d*, H-1′), 4.98 (1H, *m*, H-2′), 5.08 (1H, *t*, H-3′), 5.21 (1H, *t*, H-4′), 3.75 (1H, *m*, H-5′), 4.17 (1H, *m*, H-6′a), 4.10 (1H, *m*, H-6′b). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ96.0 (*d*, C-1), 151.4 (*s*, C-3), 105.6 (*s*, C-4), 28.6 (*d*, C-5), 24.2 (*t*, C-6), 68.4 (*t*, C-7), 17.5 (*t*, C-8), 37.5 (*d*, C-9), 11.8 (*q*, C-10), 165.2 (*s*, C-11), 95.5 (*d*, C-1′), 70.4 (*d*, C-2′), 72.2 (*d*, C-3′), 68.1 (*d*, C-4′), 72.2 (*d*, C-5′), 61.7 (*d*, C-6′), 169.5 (*s*), 169.3 (*s*), 170.0 (*s*), 170.5 (*s*), 20.5 (OAc–Me, *s*), 20.7 (OAc–Me, *s*, ×3).

Hydrolysis of djalonenoside B. Hydrolysis of B (0.653 g) was carried out in 10% HCl in MeOH (75 ml) under reflux for 5 hr. The reaction mixt. was poured into H_2O, neutralized and extracted with $CHCl_3$, giving a crude product (0.247 g). The crude material was separated by prep. TLC, which afforded three hydrolysis products, all liquids: HYB-1, HYB-2, HYB-3.

HYB-1 (**9**). (0.039 g) (R_f 0.7, C_6H_{12}–EtOAc, 6.7:3.3). UV $\lambda_{max}^{CHCl_3}$ nm: 261. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000–2840 (OH), 1700 (C=O), 1620 (C=C), 1090, 1000. ^{1}H NMR (200 MHz, $CDCl_3$): δ4.87 (1H, *d*, $J_{1,9}$ = 1.7 Hz, H-1), 7.62 (1H, *d*, $J_{3,5}$ = 2.5 Hz, H-3), 2.92 (1H, *ddd*, $J_{5,3}$ = 2.6, $J_{5,9}$ = 5.7, $J_{5,6}$ = 8.0 Hz, H-5), 1.72 (1H, *ddd*, $J_{6a,b}$ = 12, $J_{6a,7}$ = 7, $J_{6a,5}$ = 8 Hz, H-6a), 1.66 (1H, *ddd*, $J_{6b,a}$ = 12, $J_{6b,7}$ = 7, $J_{6b,5}$ = 8 Hz, H-6b), 4.26 (1H, *ddd*, $J_{7a,b}$ = 11.7, $J_{7a,6}$ = 6.7 Hz, H-7a), 4.08 (1H, *ddd*, $J_{7b,a}$ = 11.7, $J_{7b,6}$ = 7 Hz, H-7b), 5.48 (1H, *dt*), $J_{8,10}$ = 17.4, $J_{8,9}$ = 9.6 Hz, H-8), 2.57 (1H, *ddd*, $J_{9,8}$ = 9.6, $J_{9,5}$ = 5.5, $J_{9,1}$ = 1.7 Hz, H-9), 5.20 (2H, *m*, $J_{10,8}$ = 17 Hz, H-10), 3.55 (3H, *s*, H-12), 3.48 (3H, *s*, H-13), 9.28 (1H, *d*, $J_{1',5'}$ = 1.55 Hz, H-1′), 6.61 (1H, *q*, $J_{3',4'}$ = 7 Hz, H-3′), 1.98 (1H, *d*, $J_{4',3'}$ = 7 Hz, H-4′), 3.05 (1H, *ddd*, $J_{5',7'}$ = 9.6), $J_{5',10}$ = 4.9, $J_{5',1'}$ = 1.4 Hz, H-5′), 1.72 (1H, *ddd*, $J_{6a',b'}$ = 12, $J_{6a',7'}$ = 7, $J_{6a',10'}$ = 8 Hz, H-6a′), 1.66 (1H, *ddd*, $J_{6b',a'}$ = 12, $J_{b',7'}$ = 7, $J_{6b',10}$ = 8 Hz, H-6b′), 4.44 (1H, *ddd*, $J_{7a',b}$ = 12, $J_{7a',5'}$ = 8.6, $J_{7a',6}$ = 7 Hz, H-7a′), 4.38 (1H, *ddd*, $J_{7b',a}$ = 13, $J_{7b',5'}$ = 9.0, $J_{7b',6}$ = 7 Hz, H-7b′), 3.10 (1H, *ddd*, $J_{10',6'}$ = 8.8, $J_{10',5'}$ = 4.0, $J_{10',11'}$ = 1.2 Hz, H-10′), 3.66 (1H, *d*, $J_{11',10'}$ = 1.9 Hz, H-11′), 3.45 (3H, *s*, H-12′). Characterization was done by comparing spectral data of hydrolysis products with those of the natural product B (**4a**).

HYB-2 (**10**). (0.007 g) (R_f 0.4, C_6H_{12}–EtOAc 6.7:3.3). UV $\lambda_{max}^{CHCl_3}$ nm: 261. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 300–2860 (−OH), 1720 (C=O), 1700 (C=O), 1680 (C=O), 1610 (C=C), 1160, 1100. ^{1}H NMR (200 MHz, $CDCl_3$): δ3.45 (O–Me, *s*), 3.64 (O–Me, *s*), 6.2 (1H, *q*, H-8), 1.89 (3H, *d*, H-10). The remaining resonances are similar to that of B, difference being only in the absence of the resonance due to the glucose moiety as a result of the cleavage of the C–O glycoside bond.

HYB-3 (**4c**). (0.003 g) (R_f 0.3, C_6H_{12}–EtOAc, 6.7:3.3). UV $\lambda_{max}^{CHCl_3}$ nm: 262. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3010–2820 (OH), 1720 (C=O), 1650–1620 (C=C), ^{1}H NMR (200 MHz, $CDCl_3$): δ3.59 (O–Me, *s*). Remaining resonances similar to that of compound B, but with absence of the glucose moiety resonance.

Acetylation of ursolic acid, compound D. Ursolic acid acetate (0.099 g) was obtained by acetylation of D (0.46 g), (AC_2O–pyridine (2:1) at room temp. for 16 hr), mp 286–288° (MeOH–Me_2CO) (R_f 0.58, C_6H_{12}–EtOAc, 8.6:1.4). IR, UV, ^{1}H NMR spectra were identical to published data [13].

Acetylation of djalonenol, compound E. Djalonenol diacetate (0.076 g) was obtained by acetylation of E (0.059 g) (AC_2O–pyridine (2:1) at room temp. for 16 hr) as a liquid purified by repeated prep. TLC (R_f 0.63, MeOH–EtOAc, 3.3:6.7). EIMS *m/z* 241 $[M - COMe]^+$ (0.9), 182 $[241 - OCOMe]^+$ (4.3), 169 $[241 - CH_2OCOMe]^+$ (17.1), 140 $[169 - CO]^+$ (7.6), 109 $[140 - OCH_2H]^+$ (132), 43 (100), 28 (29.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (C=O), 1650 (C=O), 1600 (C=C), 1370, 1230. UV $\lambda_{max}^{CHCl_3}$ nm: 244, 281, 302. ^{1}H NMR (200 MHz, $CDCl_3$): δ4.37 (2H, *m*, H-6), 5.68 (1H, *m*, H-7), 2.84 (1H, *m*, H-8), 5.22 (2H, *m*, H-9), 4.09 (2H, *m*, H-10), 4.29 (2H, *m*, H-11), 2.06 (Ac-Me, *s*). ^{13}C NMR (50.3 MHz, $CDCl_3$): 171.2 (*s*, C-2), 43.7 (*d*, C-3), 35.2 (*d*, C-4), 29.3 (*t*, C-5), 67.4 (*t*, C-6), 135.5 (*d*, C-7), 46.1 (*d*, C-8), 127.4 (*t*, C-9), 64.0 (*t*, C-10), 64.5 (*t*, C-11), 170.6 (*s*), 170.8 (*s*), 20.8 (OAc-Me, *s*), 20.8 (OAc-Me, *s*).

Acetylation of D-(+)-*bornesitol, compound F.* Bornesitol pentaacetate (0.028 g) obtained by acetylation of F (0.041 g) (Al_2O–pyridine 2:1 at room temp. for 16 hr), mp 143–146° (R_f 0.72, MeOH–EtOAc, 2.5:7.5). EIMS *m/z*: 373 $[M - OMe]^+$ (0.2), 345 $[M - OMe - CO]^+$ (0.7), 303 $[M - OMe - CO - COMe]^+$ (0.5), 43 $[COMe]^+$ 100, 28 $[CO]^+$ (18). UV $\lambda_{max}^{CHCl_3}$ nm: 214, 300. IR, ^{1}H NMR spectra were identical to published data [15].

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