Phytochemistry, Vol. 27, No. 9, pp. 2881–2886, 1988.
Printed in Great Britain.

0031–9422/88 $3.00+0.00

SESQUITERPENE GLYCOSIDES AND OTHER CONSTITUENTS FROM *OSTEOSPERMUM* SPECIES

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(*Received* 23 *September* 1987)

Key Word Index—*Osteospermum imbricatum*, *O. microcarpum* subsp. *septentrionale*, *O. corymbosum*, *O. rigidum* var. *elegans*, *O. caulescens*; *Gibbaria ilicifolia*; Compositae; sesquiterpene glycosides; *p*-hydroxyacetophenone derivatives; triterpenes; caffeic acid glycosides.

Abstract—The investigation of five South African *Osteospermum* species and one related *Gibbaria* species afforded several glycosides derived from aromatic compounds as well as from sesquiterpenes. Furthermore, five new *p*-hydroxyacetophenone derivatives, three oleanolic acid derivatives and three trachylobane derivatives were isolated. The structures were elucidated by high field NMR techniques and a few chemical transformations.

INTRODUCTION

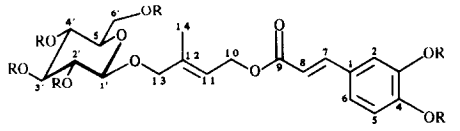
The South African genus *Osteospermum* with *ca* 70 species is the largest one in the small tribe Calendulaceae [1]. So far the representatives of this tribe are characterized by the occurrence of tridecapentaynene and diterpenes, mainly pimarane derivatives. From *Osteospermum* only a few species have been investigated chemically. In addition to the already mentioned constituents, some sesquiterpene glycosides have been reported [2]. We have re-examined some *Osteospermum* species and also one *Gibbaria* species, as the latter used to be part of the former genus.

RESULTS AND DISCUSSION

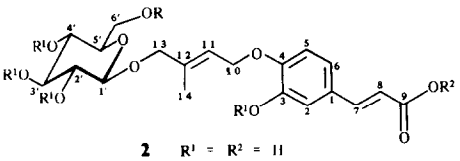
From *O. imbricatum* L., the subsp. *nervatum* (DC) T. Norl. has previously been investigated [2]. In addition to triterpenes, dimethoxycinnamaldehyde and tremetone derivatives were isolated. We now have re-investigated the roots and aerial parts. The former gave tridecapentaynene, 3,4-dimethoxycinnamaldehyde, the tremetone derivatives **3** [3] and **4** [3] as well as the resacetophenone derivatives **5** [4], **6** and **7**. The aerial parts afforded the glucopyranosides **1** and **2** which could only be obtained pure as their acetates **1a** and **2a**, the latter also being esterified.

The aerial parts of *O. microcarpum* subsp. *septentrionale*, T. Norl. collected in Namibia gave in addition to phytadiene and sesquiterpene hydrocarbons (see Experimental) the fucopyranosides **8–10** and **12** [5].

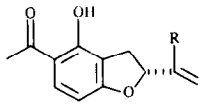
The roots of *O. corymbosum* L. have been studied previously [6]. A re-investigation afforded, in addition to compounds isolated previously, the resacetophenone derivatives **6** and **7**, the tremetone derivative **4** and caryophyllenepoxide. The aerial parts gave the tremetone derivative **3** and several triterpenes. In addition to oleanolic acid, the related acids **13–15** were isolated as their methyl esters.



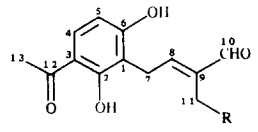
1 R = H
1a R = Ac



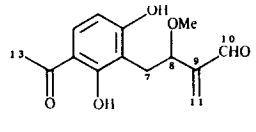
2 R^1 = R^2 = H
2a R^1 = Ac, R^2 = Me



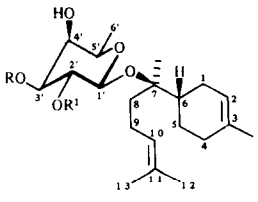
3 R = CH_2OH
4 R = CHO



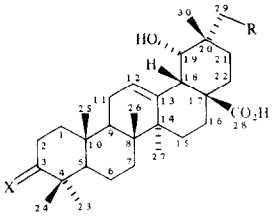
5 R = H
6 R = OMe



7

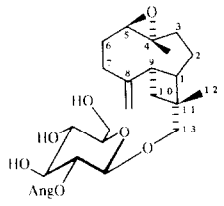


	8	**9**	**10**	**11**	**12**
R	Ac	Ac	Ang	H	H
R^1	Ang	MeBu	Ang	Ang	H

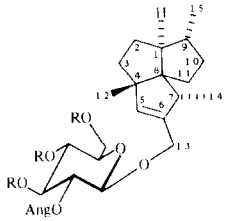


	13	14	15
X	βOH,H	O	O
R	H	H	OH

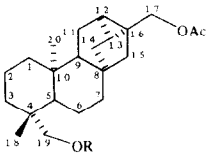
13a–15a are the methylesters



16



17 R = H
17Ac R = Ac



18 R = Ac
19 R = *i*Val
20 R = MeBu

The aerial parts of *Gibbaria ilicifolia* L. afforded 3,5-dimethoxystilbene, 8β,12β-dihydroxy and 8β,11α,12β-trihydroxypimarene, oleanonic acid, oleanolic acid, scopoletin and the glycoside **11**.

The roots of *O. rigidum* var. *elegans* (Bol.) Norl. afforded the known isomeric 8β,11α, 12β-trihydroxypimarene 11-*O*- and 12-*O*-acetates [7]. The aerial parts gave phytadiene, nerolidol and two glycoside esters, the epoxycaryophyllene derivative **16** and the silphiperfol-5-ene derivative **17**. The aerial parts of *O. caulescens* Harv. gave phytadiene, 8β-hydroxypimarane and the trachylobane derivatives **18**–**20**.

The structure of **1a** followed from the ^{1}H NMR data (Table 1) and from the mass spectrum, though no molecular ion was observed. However, the highest peak corresponds to $C_{28}H_{34}O_{14}$, most likely formed by loss of two molecules of ketene. This was supported by the ion *m/z* 163 ($C_9H_7O_3$) which represents a dihydroxycinnamoyl ion. In agreement with this assumption the ^{1}H NMR spectrum displayed two phenolic acetate methyl singlets (δ2.32, 2.31). Furthermore, the chemical shifts of the aromatic protons agreed with the presence of an acetylated caffeic acid ester. In addition to the typical signals of a β-glucopyranoside tetraacetate signals at δ4.77 (*br d*, 2H), 5.65 (*br t*), 4.27 (*br d*) and 4.06 (*br d*) and 1.75 (*br s*) indicated a dihydroxyprenyl group esterified at C-1 with an ether oxygen at C-4. Accordingly, the three units, which followed from the ^{1}H NMR data, could only be combined to **1a**. The *E*-configuration of the Δ^{11}-bond followed from the NOE between H-14 and H-10.

Table 1. ^{1}H NMR spectral data of compounds **1a** and **2a** (400 MHz, $CDCl_3$, δ-values)

H	1a	2a
2	7.37 *d*	7.25 *d*
5	7.24 *d*	6.87 *d*
6	7.42 *dd*	7.38 *dd*
7	7.64 *d*	7.61 *d*
8	6.38 *d*	6.29 *d*
10	4.77 *br d*	4.76 *br d*
11	5.65 *br t*	5.64 *br t*
13	4.27 *br d*	4.26 *br d*
13′	4.06 *br d*	4.06 *br d*
14	1.75 *br s*	1.75 *br s*
1′	4.53 *d*	4.53 *d*
2′	5.04 *dd*	5.04 *dd*
3′	5.10 *t*	5.09 *t*
4′	5.21 *t*	5.21 *t*
5′	3.68 *ddd*	3.68 *ddd*
$6'_1$	4.28 *dd*	4.27 *dd*
$6'_2$	4.17 *dd*	4.17 *dd*
OAc	2.33, 2.32 *s*	2.34 *s*
	2.11, 2.07 *s*	2.11, 2.07 *s*
	2.03, 2.02 *s*	2.03, 2.02 *s*
OMe		3.89 *s*

J [Hz]: 2,6 = 2; 5,6 = 8.5; 7,8 = 16; 10,11 = 7; 13,13′ = 12; 1′,2′ = 8; 2′,3′ = 3′,4′ = 4′,5′ = 9.5; 5′,$6'_1$ = 5; 5′,$6'_2$ = 2.5; $6'_1$,$6'_2$ = 12.

The ^{1}H NMR spectrum of **2a** (Table 1) was in part close to that of **1a**. However, the signals of the caffeic acid part were typically shifted and only one phenolic acetate singlet was visible. Comparison of the shifts with similar compounds clearly indicated that the *p*-hydroxy group bore an ether residue while that in the *m*-position was acetylated. Furthermore, a methoxy singlet at δ3.89 after addition of CH_2N_2 showed that the natural product was a free acid. Therefore the dihydroxyprenyl group had to be placed in the *p*-position of the caffeic acid and again the C_5-unit was present as a β-glucopyranoside tetraacetate. All data therefore agreed with the proposed structure.

The ^{1}H NMR spectrum of **6** (Table 2) was close to that of **5** [4]. However, one olefinic methyl signal was replaced by a two proton singlet at δ4.43 and a methoxy signal at δ3.53. Therefore the corresponding methoxy derivative of **5** was present. The configuration of the Δ^8 bond followed from the chemical shift of H-8.

The ^{1}H NMR spectrum of **7** (Table 2) was in part similar to that of **6**. However, the changed substitution of the prenyl side chain followed from the corresponding signals. Due to the chiral centre at C-8, the signals of H-7 now displayed a pair of double doublets and the olefinic triplet was replaced by a pair of broadened singlets at δ6.18 and 6.08 indicating the presence of a conjugated exomethylene group. Thus all data required the presence of the isomeric aldehyde **7**.

The structures of **8**–**11** also followed from the ^{1}H NMR spectra (Table 3) which were close to that of **12** [5].

Table 2. ^{1}H NMR spectral data of compounds **6** and **7** (400 MHz, $CDCl_3$, δ-values)

H	**6**	**7**
4	7.59 *d*	7.58 *d*
5	6.44 *d*	6.48 *d*
7	3.85 *d*	3.12 *dd* 3.05 *dd*
8	6.74 *t*	4.60 *dd*
10	9.40 *s*	9.62 *s*
11	4.43 *s*	6.18 *br s*
11′		6.08 *br s*
13	8.59 *s*	2.56 *s*
OMe	3.53 *s*	3.37 *s*
OH	8.75 *s*, (13.30) *s*	8.74 *s*, (12.96) *s*

J [Hz]: 4,5 = 8.5; compound **6**: 7,8 = 8; compound **7**: 7,7′ = 14.5; 7,8 = 5; 7′,8 = 2.5.

Table 3. ^{1}H NMR spectral data of compounds **8**–**11** (400 MHz, $CDCl_3$, δ-values)

H	**8**	**9***	**10**	**11**	Multiplicity
1	1.95	1.95	1.95	1.95	*m*
2	5.33	5.33	5.30	5.50	*br s*
4,9	1.95	1.95	1.95	1.95	*m*
10	5.04	5.04	5.04	5.06	*br t*
12	1.63	1.63	1.63	1.63	*br s*
13	1.60	1.60	1.59	1.59	*br s*
14	1.07	1.06	1.04	1.07	*s*
15	1.68	1.68	1.68	1.68	*br s*
1′	4.63	4.61	4.67	4.60	*d*
2′	5.26	5.32	5.38	5.01	*dd*
3′	4.96	4.91	5.06	4.37	*dd*
4′	3.90	3.82	3.90	3.68	*br s*
5′	3.70	3.68	3.73	3.67	*br q*
6′	1.30	1.29	1.31	1.36	*d*
OAng	6.12	6.12	6.03, 6.10	6.14	*qq*
	1.98	1.98	1.97, 1.92	2.01	*dq*
	1.88	1.88	1.86, 1.82	1.92	*dq*
OAc	1.99*s*	1.99 *s*	—	—	

*OMeBu, 2.45*tq*, 0.88*t*, 1.14*d*, 1.60*m*, 1.47*m*.

J [Hz]: 9,10 = 7; 1′,2′ = 8; 2′,3′ = 9; 3′,4′ = 3; 4′,5′ ~ 1; 5′,6′ = 7; OAng: 3,4 = 7; 3,5 = 4,5 = 1.3; OMeBu: 2,3 = 2,5 = 3,4 = 7.

Careful ^{1}H NMR studies, however, showed that the configuration of the sugar moiety had to be revised. As can be shown by the nOe's and by comparison with the spectra of β-fucopyranosides [8], the bisabolol-glycoside **12** also had this sugar moiety which obviously had to be present in the glycosides **8**–**11** which only differed in the nature of the ester group. Spin decoupling allowed the assignment of the signals of the pyranoside protons and the chemical shifts clearly indicated which of the hydroxy groups was esterified. Thus the downfield shift of H-2′ and H-3′ together with the presence of the signals of two angelate residues in the case of **10** determined the structure. The spectrum of **8** clearly showed that one angeloyl group was replaced by an acetyl group. The upfield shift of H-3′favoured the 3′-*O*-position of the latter. Similarly the relative position of the 2-methylbutyrate was assigned while in the case of **11** the shift of H-2′ showed that a 2′-*O*-angelate was present. The relative position of the ester groups of **8**–**10** was strongly supported by the chemical shifts of the olefinic angelate proton. In the spectrum of **11** and **8** the shift of the 2′-*O*-angelate protons was identical. Most likely the chemical shift of the ester proton at C-2′ is influenced by the neighbouring acetal carbon.

The structure of **13a** followed from its ^{1}H and ^{13}C NMR spectra (Table 4) which were close to those of methyl oleanolate [9] while that of **14a** was similar to that of methyl oleanonate. The ^{1}H NMR spectrum of **15a** indicated that the latter differed from **14a** by an additional primary hydroxy group. The relative positions of the hydroxy groups and the stereochemistry of **15a** followed from the observed NOE's which also allowed us to assign the methyl singlets. Thus clear effects were observed between H-26, H-25 and OMe, between H-30, H-18 and H-19, between H-18, H-12 and H-19, between H-29 and H-30 as well as between H-19, H-18 and H-12. As the ^{1}H NMR signals of the protons in the neighbourhood of H-19 in the spectra of **13a** and **14a** were very close to those of **15a** the secondary hydroxyl surely was in the same position in all three compounds.

The structure of **16** followed from the molecular formula and the ^{1}H NMR data which were close to those of caryophyllenepoxide and 2-*O*-angeloyl-β-D-glucopyranosides respectively. Comparison of the ^{1}H NMR spectrum with that of 12- and 13-hydroxycaryophyllene-epoxide [10] showed that **16** was a 13-hydroxy derivative. A corresponding caryophyllene glucoside in which the epoxide is missing, has been reported from another *Osteospermum* species [2].

The structure of **17**, which on acetylation gave the triacetate **17Ac**, also followed from the ^{1}H NMR data which were close to those of one of the silphiperfol-5-ene epimers [11]. The chemical shift of H-7 differ typically in these isomers [11, 12]. Therefore the configuration at C-7 could be proposed and was established by NOE between H-1, H-14 and H-15 which could be observed in deuteriomethanol while in $CDCl_3$ the methyl signals were overlapped.

The ^{1}H NMR spectrum of **18** (Table 5) was in part similar to that of trachylobanic acid. Especially the signals of H-12 and H-13 were typical. However, the new compound was obviously a diacetate and had no carboxyl group. The position of the oxygen functions which had to be primary [δ4.07 *br s* (2H), 4.20 *d* and 3.86 *d*, one proton each], were determined by spin decoupling and the observed NOEs. Thus clear effects were obtained between H-18, H-19 and H-19′, between H-20, H-19, H-19′, H-14 and H-11, between H-11 and H-12, between H-14, H-13 and H-20 as well as between H-17, H-15, H-15′, H-12 and H-13. Also the ^{13}C NMR data (Table 5) agreed with the structure. The ^{1}H NMR spectra of **19** and **20** (Table 5), which could not be separated, differed only very slightly from that of **18**. However, one acetate singlet was replaced by the typical signals of an isovalerate and a methylbutyrate respectively. The relative position of the ester groups could only be deduced from the mass spectra. In all three compounds (**18**–**20**) a typical fragment, [M − HOAc

Table 4. ^{1}H NMR spectral data of compounds **13a**–**15a** and ^{13}C NMR data of compound **13a** ($CDCl_3$, δ-values)

H	**13a**	**14a**	**15a**	C	**13a**	C	**13a**
2	1.63 *m*	2.57 *ddd*	2.57 *ddd*	1	38.7	16	24.1
2′		2.36 *ddd*	2.36 *ddd*	2	27.2	17	46.2
3	3.23 *dd*	—	—	3	78.9	18	44.3
12	5.46 *br t*	5.47 *br t*	5.49 *br t*	4	39.1	19	81.6
18	3.15 *br s*	3.16 *br s*	3.12 *br s*	5	55.9	20	35.1
19	3.35 *br d*	3.35 *br t*	3.64 *d*	6	18.8	21	33.1
23	0.98 *s*	1.11 *s*	1.10 *s*	7	33.1	22	27.9
24	0.81 *s*	1.07 s	1.07 s	8	40.0	23	28.2
25	0.92 *s*			9	48.2	24	15.8
26	0.70 *s*	0.77 *s*	0.76 *s*	10	37.4	25	15.3
27	1.25 *s*	1.25 *s*	1.25 *s*	11	27.2	26	17.2
29	1.00 *s*	1.00 *s*	3.52 *d* 3.48 *d*	12	124.7	27	24.9
30	0.99 *s*	0.99 *s*	0.92 *s*	13	143.4	28	179.0
OMe	3.63 *s*	3.64 *s*	3.64 *s*	14	41.6	29	28.3
				15	27.9	30	24.6

J [Hz]: 11,12 = 18,19 = 3.5; compounds **14a** and **15a**: 1,2 = 7; 1′,2 = 11; 1,2′ = 6; 1′,2′ = 3; 2,2′ = 15; compound **15a**: 29,29′ = 10.

Table 5. NMR spectral data of compounds **18**–**20** ($CDCl_3$, δ-values)

H	**18**	*J* [Hz]	C	**18**	C	**18**
5	1.37 *dd*	4,11	1	39.1 *t*	13	27.3 *d*
9	1.18 *br dd*	7,11	2	17.7 *t*	14	32.7 *t*
11	1.91 *ddd*	3,11,14	3	36.4 *t*	15	45.9 *t*
11′	1.68 *ddd*	2,5,7,14	4	38.2 *s*	16	26.5 *s*
12	0.87 *br ddd*	2,5,3,8	5	53.1 *d*	17	69.4 *t*
13	1.14 *m*		6	19.6 *t*	18	19.3 *q*
14	2.07 *br d*	11	7	39.1 *t*	19	67.2 *t*
14′	1.14 *m*		8	40.5 *s*	20	15.2 *q*
15	1.51 *br d*	11	9	56.7 *d*	OAc	171.42 *s*
15′	1.38 *br d*	11	10	36.7 *s*		171.37 *s*
17	4.07 *br s*		11	20.3 *t*		21.1 *q*
18	0.93 *s*		12	22.7 *d*		21.0 *q*
19	4.20 *d*	11				
19′	3.86 *d*	11				
20	0.96 *s*					
OAc	2.06 *s*					
	2.04 *s*					

*Compound **19**: H-19 4.21 and 3.83 *d*; OCOR: 2.19 (*d*), 2.10 *m*, 0.95 *d*; OAc: 2.06 *s*; compound **20**: H-19 4.23 and 3.85 *d*; OCOR: 2.37 *tq*, 1.14 *d*, 0.91 *t*.

$-C_4H_6]^+$, was present which was assigned to the cyclopropane part of the molecule. In agreement with this assumption the elimination of HOAc was followed by loss of CH_2OCOR. Furthermore, the H-19 signals were slightly different in the esters of **18**–**20** which also supported the proposed position of the C_5-ester groups.

The overall picture of the chemistry of the genus *Osteospermum* indicates that sesquiterpene glycosides may be characteristic. However, some species have other constituents. The presence of 8β-hydroxypimarene derivatives gives a link to related genera like *Garuleum* [7, 13], *Chrysanthemoides* [14] and *Dimorphotheca* [15], where these diterpenes are widespread. All the other constituents reported in this paper seem to be less characteristic as similar compounds are isolated from many, in part very different Compositae.

EXPERIMENTAL

The plant material was collected in South Africa in Sept. 1986. The air-dried material was extracted and worked-up as reported previously [16].

The aerial parts of *O. imbricatum* (780 g, collected near Port Elizabeth along the road to George, R.S.A., voucher 86/80) gave an extract which afforded a polar fraction by CC (Et_2O–MeOH, 4:1). TLC gave no separation. Even after addition of CH_2N_2 no pure esters were obtained. Acetylation (Ac_2O, $CHCl_3$, *p*-dimethylaminopyridine, 1 hr, 60°) gave a mixture which was separated by HPLC (MeOH H_2O, 7:3, always RP 18, *ca* 100 bar) affording 10 mg **1a** (R_t 8.2 min) and 20 mg **2a** (R_t 11.8 min). The extract of the roots (250 g) gave by CC two crude fractions (1: petrol, 2: Et_2O). TLC (petrol) of fraction 1 gave 2 mg tridecapentaynene. TLC of **2** (Et_2O-petrol 1:1) gave three bands (2/1–2/3). HPLC of 2/1 (MeOH–H_2O, 7:3) gave 3 mg **4** (R_t 6.0 min). HPLC of 2/2 (MeOH–H_2O, 7:3) afforded 3 mg **7** (R_t 2.3 min) and HPLC of 2/3 (MeOH–H_2O, 7:3) gave 2 mg 3,4-dimethoxycinnamaldehyde (R_t 1.8 min.), 2 mg **5** (R_t 5.2 min) and a mixture (R_t 3.5 min.) which gave by TLC (Et_2O-petrol, 3:1) 5 mg **3** (R_f 0.55) and 3 mg **6** (R_f 0.45).

The aerial parts of *O. microcarpum* subsp. *septentrionale* (70 g, collected in Namibia, Bosua pass, Swakopmund road, 110 km W of Windhoek, voucher 2216 CA) gave an extract which gave by CC (silica gel) three crude fractions (1: petrol and Et_2O–petrol, 1: 10; 2: Et_2O and Et_2O–MeOH, 9:1 and 3: MeOH). TLC of fraction 1 (Et_2O–petrol, 1:19) gave 2 mg phytadiene, 50 mg γ-bisabolene, 48 mg α- and 130 mg γ-curcumene. HPLC of fraction 2 (MeOH–H_2O, 9:1) gave 24 mg **8** (R_t 7.5 min), 4 mg **9** (R_t 4.9 min) and 2 mg **10** (R_t 5.1 min): TLC of fraction 3 ($CHCl_3$–MeOH, 9:1) gave 35 mg **12** (R_f 0.50).

The extract of the roots of *O. corymbosum* (100 g, collected on the Outeniqua pass, R.S.A., Sept. 1986, voucher 86/93) gave by CC and TLC in addition to the compounds reported previously [5] 5 mg caryophyllenepoxide, 80 mg **4**, 6 mg **6** and 3 mg **7**. The extract of the aerial parts (270 g) gave two polar fractions. TLC of fraction 1 gave 5 mg stigmasterol and 9 mg **3**. After addition of CH_2N_2 fraction 2 gave by TLC (Et_2O–petrol, 7:3) 15 mg **13a** (R_f 0.50), 13 mg **15a** (R_f 0.45) and a mixture which was further separated by HPLC (MeOH–H_2O, 4:1) affording 16 mg **13a**, 15 mg methyl oleanolate and crude **14a** (R_t 9.5 min.) which gave by TLC ($CHCl_3$–MeOH, 19:1) 2 mg **14a** (R_f 0.80).

The extract of aerial parts of *Gibbaria ilicifolia* (170 g, collected in September 1986, Franshoek pass, RSA, voucher 86/146) gave by CC three crude fractions (1: petrol; 2: Et_2O and 3: Et_2O–MeOH, 9:1). TLC of fraction 1 (petrol) gave 4 mg phytadiene and HPLC of fraction 2 (MeOH–H_2O, 9:1) afforded 13 mg 3,5-dimethoxystilbene (R_t 4.5 min), 11 mg 8β,11α,-12β-trihydroxy-pimar-14-ene and 11 mg oleanonic acid. TLC of fraction 3 gave 10 mg 8β,12β-dihydroxypimar-14-ene, 4 mg oleanolic acid and a mixture which gave by HPLC (MeOH–H_2O, 4:1) 20 mg scopoletin (R_t 3.0 min) and 5 mg **11** (R_t 13.7 min).

The extract of aerial parts of *O. rigidum* var. *elegans* (90 g, collected on Pakkhuis pass, R.S.A., voucher 86/238) gave by CC three crude fractions (1: petrol, 2: Et_2O–petrol, 1:3, and 3: Et_2O and Et_2O–MeOH, 3:1). Fraction 1 gave by TLC 40 mg phytadiene, fraction 2 80 mg nerolidol and fraction 3 afforded by HPLC (MeOH–H_2O, 17:3) 3 mg **16** (R_t 5.5 min) and 30 mg **17** (R_t 12.0 min.). The extract of 23 g roots afforded by TLC (Et_2O) 20 mg of the 11-*O*-acetate and 40 mg of the 12-*O*-acetate of 8β,11α,12β-trihydroxypimarene.

The extract of *O. caulescens* (200 g, from Botanic Gardens, Kirstenbosch, R.S.A., voucher 86/168) gave by CC (silica gel) two crude fractions. The first one afforded by TLC 40 mg phytadiene and the second one (Et_2O and Et_2O–MeOH) was separated by TLC and HPLC (MeOH–H_2O, 9:1) affording 3 mg 8β-hydroxypimarene (R_t 8.5 min), 6 mg **19** and **20** (*ca* 1:1, R_t 10.8 min) and 9 mg **18** (R_t 7.0 min).

Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

Caffeic acid [4-*hydroxyprenyl*]-*ester* β-D-*glucopyranoside* (**1**). Isolated as its hexa acetate **1a**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOAc), 1760 (OAc), 1715, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 594.195 [M − 2 × ketene]$^+$ (2) (calc. for $C_{28}H_{34}O_{14}$: 594.195), 331 $[C_6H_5O(OAc)_4]^+$ (83), 271 [331–HOAc]$^+$ (7), 211 [271–HOAc]$^+$ (3), 169 [221 − ketene]$^+$ (100), 163 $[(HO)_2C_6H_3CH{=}CHCO]^+$ (41), 109 [169 − HOAc]$^+$ (42).

4-O-[4-*hydroxyprenyl*]-*Caffeic acid* 4′-O-β-D-*glucopyranoside* (**2**). Colourless gum which could not be purified; ^{1}H NMR ($CDCl_3$–MeOD): 6.96 (*d*, H-2), 6.72 (*d*, H-5), 6.83 (*dd*, H-6), 7.44 (*d*, H-7), 6.15 (*d*, H-8), 4.64 (*d*, H-10), 5.63 (*br t*, H-11), 4.13 and 3.94 (*br d*, H-13), 1.71 (*br s*, H-14), 4.21 (*d*, H-1′), 4.0 − 3.0 (*m*, H-2′–H-6′). Pentaacetate methyl ester **2a**: Colourless gum, 1770 (PhOAc), 1760 (OAc), 1715, 1635, 1605 (PhC=CCO_2R); MS *m/z* (rel. int.): 622.226 [M]$^+$ (1) (calc. for $C_{30}H_{38}O_{14}$: 622.226), 331 (21), 271 (4), 211 (4), 191 (52), 177 (81), 169 (100), 109 (48); $[\alpha]_D^{24}$ −13 ($CHCl_3$; *c* 0.57).

1-[5-*methoxy*-4-*oxo*-*prenyl*]-*Resacetophenone* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3240, 1630, 1620 (PhCO hydrogen bonded), 2720, 1690 (C=CCHO); MS *m/z* (rel. int.): 264.100 [M]$^+$ (8) (calc. for $C_{14}H_{16}O_5$: 264.100), 232 [M − MeOH]$^+$ (38), 217 [232 − Me]$^+$ (9), 204 [232 − CO]$^+$ (10), 203 [232 − CHO]$^+$ (22), 189 [217 − CO]$^+$ (24), 176 [204 − CO]$^+$ (100), 161 [176 − Me]$^+$ (52).

1-[2-*methoxy*-3-*formyl*-*but*-3-*en*-1-*yl*]-*Resacetophenone* (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3280, 1620 (PhCO hydrogen bonded), 2720, 1690 (C=CCHO); MS *m/z* (rel. int.): 264.100 [M]$^+$ (7) (calc for $C_{14}H_{16}O_5$: 264.100), 232 [M − MeOH]$^+$ (7), 204 [232 − CO]$^+$ (4), 165 [acetyl-dihydroxytropylium ion]$^+$ (100).

3′-O-*Acetyl*-2′-O-*angeloyl*-α-*bisabolol*-β-D-*fucopyranoside* (**8**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (0H), 1760 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 492 [M]$^+$ (0.06) (calc. for $C_{28}H_{44}O_7$), 271 $[C_{13}H_{19}O_6]^+$ (19), 205 $[C_{15}H_{25}]^+$ (28), 204 $[C_{15}H_{24}]^+$ (62), 171 [271 − AngOH]$^+$ (62), 119 $[C_9H_{11}]^+$ (100), 83 [RCO]$^+$ (78); $[\alpha]_D^{24}$ +4 ($CHCl_3$; *c* 1.0).

2′-O-[2-*methylbutyryl*]-3′-O-*Acetyl*-α-*bisabolol*-β-D-*fucopyranoside* (**9**). Colourless oil, not free from **10**; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1735 (CO_2R), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 311 $[C_{16}H_{23}O_6]^+$ (12), 85 [RCO]$^+$ (62), 57 [85 − CO]$^+$ (100).

2′-O,3′-O-*Diangeloyl*-α-*bisabolol*-β-D-*fucopyranoside* (**10**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 311 $[C_{16}H_{23}O_6]^+$ (12), 211 [311 − AngOH]$^+$ (24), 204 $[C_{15}H_{24}]^+$ (26), 119 (36), 83 [RCO]$^+$ (100); CIMS *m/z* (rel. int.): 311 (100); $[\alpha]_D^{24}$ +12 ($CHCl_3$; *c* 0.18).

2′-O-*Angeloyl*-α-*bisabolol*-β-D-*fucopyranoside* (**11**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 229 [M − $C_{15}H_{25}O$]$^+$ (42), 211 [229 − H_2O]$^+$ (51), 83 [RCO]$^+$ (100), 55 [83 − CO]$^+$ (44); $[\alpha]_D^{24}$ +15 ($CHCl_3$; *c* 0.2).

Methyl-19α-*hydroxyoleanolate* (**13a**). Colourless crystals, mp. 198–200°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 486.371 [M]$^+$ (4) (calc. for $C_{31}H_{50}O_4$: 486.371), 468 [M − H_2O]$^+$ (4.5), 427 [M − CO_2Me]$^+$ (4), 278 [RDA] (44), 260 (40), 201 (100).

Methyl-19α-*hydroxyoleanonate* (**14a**). Colourless crystals, mp 187–190°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730 (CO_2R), 1710 (C=O); MS *m/z* (rel. int.): 484.355 [M]$^+$ (3) (calc. for $C_{31}H_{48}O_4$: 484.355), 466 [M − H_2O]$^+$ (2.5), 425 [M − CO_2Me]$^+$ (4), 307 (2), 278 (12), 260 (12), 91 (64), 57 (100).

Methyl-19α,29-*dihydroxyoleanonate* (**15a**). Colourless crystals, mp 190–193°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730 (CO_2R), 1710 (C=O); MS *m/z* (rel. int.): 500.349 [M]$^+$ (6) (calc. for $C_{31}H_{48}O_5$: 500.340), 482 [M − H_2O]$^+$ (6), 451 [482 − CH_2OH]$^+$ (20), 294 [$C_{17}H_{26}O_4$: RDA]$^+$ (34), 245 [294 − H_2O, CH_2OH]$^+$ (66), 55 (100).

13-*Hydroxy*-4α,5β-*epoxycaryophyllen*-[4-O-*angeloyl*-β-D-*glucopyranoside*] (**16**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580, 3400 (OH), 1720, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 480.272 [M]$^+$

(0.1) (calc. for $C_{26}H_{40}O_8$: 480.273), 245 $[C_{11}H_{17}O_6]^+$ (21), 83 $[RCO]^+$ (100); ^1H NMR ($CDCl_3$): 2.88 (*br dd*, H-5), 2.61 (*br q*, H-9), 1.81 and 1.82 (*dd*, H-10), 1.01 (*s*, H-12), 3.72 and 3.11 (*d*, H-13), 1.18 (*s*, H-14), 4.97 and 4.82 (*br s*, H-15), 4.50 (*d*, H-1′), 4.88 (*dd*, H-2′), 3.78 (*m*, H-3′, H-4′, H-5′), 4.01 and 3.94 (*br dd*, H-6′); OAng: 6.16 *qq*, 2.00 *dq*, 1.90 *dq*; *J* [Hz]: 1,9 = 13,13′ = 9,10 = 9,10′ ~ 10; 5,6 = 10.5; 5,6′ = 4; 1′,2′ = 8; 2′,3′ = 9; 5′,$6'_1$ = 3.5; 5′,$6'_2$ = 4.5; 6′,6′ = 11.5; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5 $[\alpha]_D^{24}$ −100 ($CHCl_3$; *c* 0.05).

13-*Hydroxy*-7*βH*-*silphiperfol*-5-*ene*-[4-O-*angeloyl*-*β*-D-*gluco*-*pyranoside*] (**17**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 464.278 $[M]^+$ (0.05) (calc. for $C_{26}H_{40}O_7$: 464.277), 245 $[C_{11}H_{17}O_6]^+$ (26), 216 $[C_{15}H_{20}O]^+$ (36), 202 $[C_{15}H_{22}]^+$ (92), 83 $[RCO]^+$ (100); ^1H NMR ($CDCl_3$): *δ* 5.19 (*br s*, H-5), 2.69 (*br q*, H-7, *J* = 7 Hz), 0.90 (*s*, H-12), 4.26 and 3.93 (*d*, H-13), 0.93 (*d*, H-14, H-15), 4.47 (*d*, H-1′), 4.88 (*dt*, H-2′, *J* = 8, 9), 3.65 (*t*, H-3′, *J* = 9), 3.73 (*t*, H-4′, *J* = 9), 3.32 (*dt*, H-5′, *J* = 9, 3), 3.87 (*d*, H-6′, *J* = 3); OAng: 6.08 *qq*, 1.97 *dq*, 1.88 *dq*; *J* [Hz]: 3,4 = 7; 3,5 = 4,5 = 1.5; in MeOH-d_4: *δ* 2.72 (*br q*, H-7), 1.86 (*dtq*, H-9), 0.98 (*d*, H-14), 0.97 (*d*, H-15). Acetylation of **17** (Ac_2O, CH_2Cl_2, DMAP) afforded **17Ac**; colourless oil; MS *m/z* (rel. int.): 430.236 [M–HOAng, HOAc]$^+$ (0.7) (calc. for $C_{25}H_{34}O_6$: 430.236), 371 $[430-OAc]^+$ (12), 202 $[C_{15}H_{22}]^+$ (71), 83 $[RCO]^+$ (100); ^1H NMR ($CDCl_3$): *δ* 5.21 (*d*, H-5, *J* = 2 Hz), 2.71 (*br q*, H-7, *J* = 7), 0.92 (*s*, H-12), 4.27 and 3.90 (*d*, H-13, *J* = 12.5), 0.95 (*d*, H-14, H-15, *J* = 7), 4.55 (*d*, H-1′, *J* = 8), 5.14 (*t*, H-2′, *J* = 9.5), 5.27 (*t*, H-3′, *J* = 9.5), 5.10 (*t*, H-4′, *J* = 9.5), 3.69 (*ddd*, H-5′, *J* = 9, 4.5, 2.5), 4.26 (*dd*, H-$6'_1$, *J* = 12.5, 4.5), 4.16 (*dd*, H-$6'_2$, *J* = 12.5, 2.5); OAng: 6.07 *qq*, 1.95 *dq*, 1.85 *dq*.

17,19-*Diacetoxytrachylobane* (**18**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245; MS *m/z* (rel. int.): 388.261 $[M]^+$ (21) (calc. for $C_{24}H_{36}O_4$: 388.261), 328 $[M-HOAc]^+$ (42), 274 $[328-C_4H_6]^+$ (50), 268 $[328-HOAc]^+$ (57), 255 $[328-CH_2OAc]^+$ (60), 149 $[268-C_9H_{11}]^+$ (200), 91 (71); $[\alpha]_D^{24}$ −45 ($CHCl_3$; *c* 0.2).

17-*Acetoxy*-19-*isovaleryloxy*- *and* 2-[*methylbutyryloxy*]-*trachylobane* (**19** and **20**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R); MS *m/z* (rel. int.): 430.308 $[M]^+$ (12) (calc for $C_{27}H_{42}O_4$: 430.308), 370 $[M-HOAc]^+$ (26), 316 $[370-C_4H_6]^+$ (18), 268 $[370-RCO_2H]^+$ (46), 255 $[370-CH_2OCOR]^+$ (29), 149 (46), 85 $[RCO]^+$ (31), 57 $[85-CO]^+$ (100).

Acknowledgement—We thank Dr J. Rourke (Botanic Gardens, Kirstenbosch, R.S.A.) for identification of the plant material and Dr Müller (SWA Herbarium, Windhoek), for plant material.

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