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DITERPENES AND SESQUITERPENES FROM *OSTEOSPERMUM* SPECIES*

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Key Word Index—*Osteospermum auriculatum*; *O. muricatum*; *O. barberiae*; *O. scariosum*; *O. jucundum*; *O. ciliatum*; *O. thodei*; Compositae; diterpenes; pimarene and cassane derivatives; sesquiterpenes; glycosides; cubebol and caryophyllene β-6-desoxyglucopyranosides; *p*-hydroxyacetophenone derivatives; triterpene palmitates.

Abstract—The investigation of several *Osteospermum* species afforded in addition to known compounds three diterpenes from the rare cassane type, two further sandaracopimarene derivatives, two 6-desoxyglucosides of cubebol and 13-hydroxycaryophyllene, respectively, an isomer of 7-hydroxycalamenene, two *p*-hydroxyacetophenone derivatives derived from toxol, a thymol derivative and the palmitates of lupeol, taraxasterol and 3β,20-dihydroxydammarene. The structures were elucidated by spectroscopic methods. The chemotaxonomy of the genus is discussed briefly.

INTRODUCTION

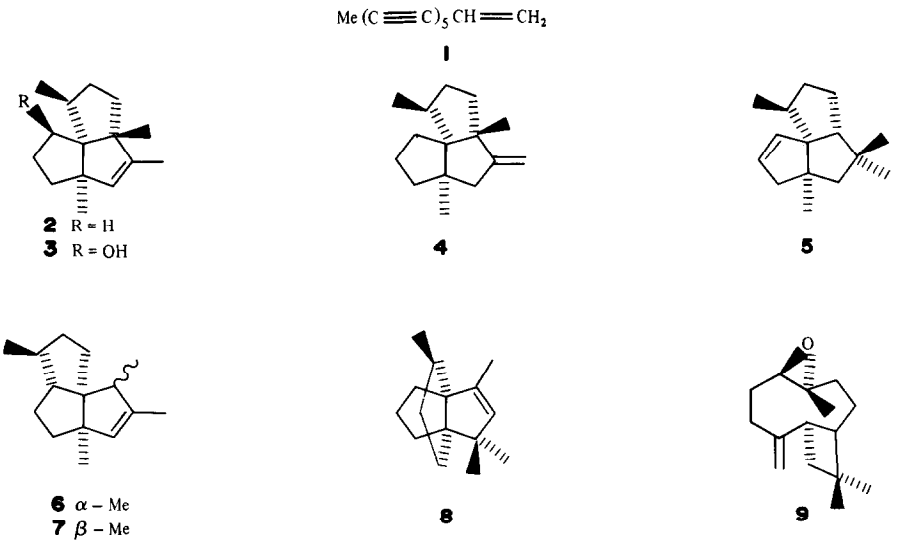
The South African genus *Osteospermum* is the largest one in the small tribe Calendaleceae. It has been divided into two subgenera [1]. Investigations have shown that sandaracopimarene derivatives are widespread in the subgenus *Osteospermum* [2, 3], while in *Tripteris* species only tridecapentaynene has been isolated as a characteristic compound. The latter compound was also present in the members of the subgenus *Osteospermum*. We have investigated seven further species of this subgenus and the results are discussed in this paper.

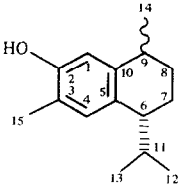
*Part 463 in the series "Naturally Occurring Terpene Derivatives". For Part 462 see Bohlmann, F., Jakupovic, J., Ahmed, M. and Schuster, A. (1983) *Phytochemistry* **22**, 1623.

RESULTS AND DISCUSSION

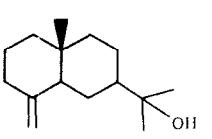
The roots of *Osteospermum auriculatum* afforded caryophyllene, bicyclogermacrene, tridecapentaynene (**1**), heptadec-1-ene, silphinene (**5**) [4] and the isomeric hydrocarbons **6** and **7** [4]. The more polar fractions gave the sandaracopimarene derivatives **16**–**20**, which were identified by direct comparison with authentic material [2].

The aerial parts afforded amyrone, **16**, **17** and the cubebol derivative **14**. The structure of **14** followed from the mass spectrometric fragments at *m/z* 229 ($C_{11}H_{17}O_5$), *m/z* 205 ($C_{15}H_{25}$) and *m/z* 83 (C_4H_7CO), which indicated the presence of a sesquiterpene linked with an esterified sugar moiety. The ^{1}H NMR spectrum (Table 1) supported this assumption and showed that the sugar part was 6-desoxyglucose esterified with angelic acid at C-4. Irradiation of the most downfield signal (δ 4.77 *dd*) collapsed the signal at δ 3.56 to a quartet and the double





10 α – Me
11 β – Me



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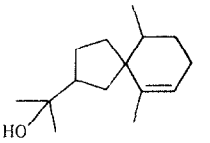

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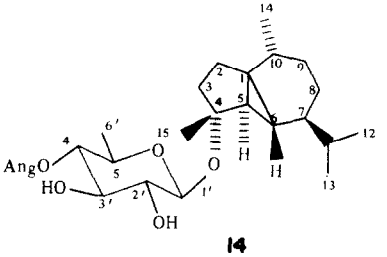

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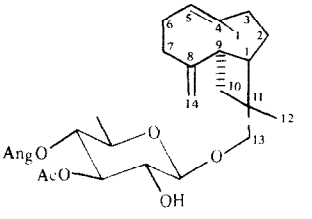

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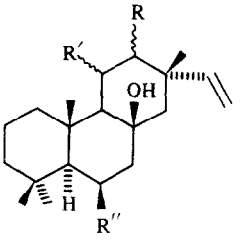
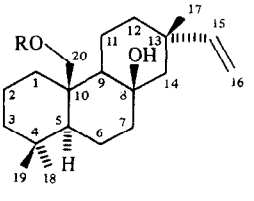
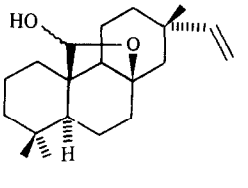


	16	**17**	**18**	**19**	**20**
R	H	β–OAc	α–OH	H	H
R′	H	α–OH	β–OAc	H	H
R″	H	H	H	OH	OAc



21 R = H
21a R = Ac



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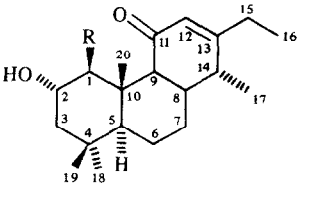


23 R = OH
24 R = H, Δ 15, 16
25 R = OH, Δ 15, 16

doublet at 3.70 to a doublet. The latter was coupled with the proton responsible for the double doublet at 3.43, which itself collapsed to a doublet on irradiation at 4.63, the signal for H-1′. The couplings showed that H-1′–H-5′ were axially orientated thus confirming the presence of a β-6-desoxy glucoside. The nature of the sesquiterpene part also followed from the ^{1}H NMR spectral data, which were close to those of 11-hydroxycubebol [5], though some signals were shifted slightly due to the influence of the sugar moiety. However, the splitting of the characteristic signals was identical.

The roots of *Osteospermum muricatum* subsp. *muricatum* afforded squalene, 2-hydroxycalamenene (**11**), hinesol (**13**), **16**, **17**, the cassane derivatives **23**–**25** and the *p*-hydroxyacetophenone **27**. The structure of the latter followed from the spectroscopic data. The molecular formula was $C_{13}H_{14}O_3$, while the base peak at *m/z* 147 was formed by loss of methyl from the fragment at *m/z*

Table 1. ^{1}H NMR spectral data of compound **14** (400 MHz, $CDCl_3$, TMS as int. standard)

H-2	1.86 *m*	H-1′	4.63 *d*
H-3	1.55 *m*	H-2′	3.43 *dd*
H-5	0.89 *d*	H-3′	3.70 *dd*
H-6	0.85 *dd*	H-4′	4.77 *dd*
H-7	1.13 *dddd*	H-5′	3.56 *dq*
H-8α	1.40 *dddd*	H-6′	1.26 *d*
H-8β	0.83 *br ddd*	OAng	6.13 *qq*
H-9α	0.53 *dddd*		2.00 *dq*
H-9β	1.60 *m*		1.90 *dq*
H-10	1.69 *m*		
H-11	1.63 *m*		
H-12, H-14	0.91 *d* 0.96 *d* 0.94 *d*		
H-15	1.34 *s*		

J (Hz): 5, 6 = 4; 6, 7 = 3.5; 8α, 8β = 14; 8α, 9α = 2; 8α, 9β ~ 10; 8β, 9α = 11; 8β, 9β ~ 3; 9α, 9β = 13; 9α, 10β = 11; 10, 14 = 11, 12 = 11, 13 = 7; 1′, 2′ = 8; 2′, 3′ = 3′, 4′ = 4′, 5′ = 9.5; 5′, 6′ = 6.5.

Table 2. ^{1}H NMR spectral data of compounds **27** and **29** (400 MHz, $CDCl_3$, TMS as int. standard)

	27	**29**
H-3	8.41 *d*	7.82 *d*
H-5	8.17 *dd*	7.58 *dd*
H-6	7.12 *d*	7.02 *d*
H-7	—	4.90 *q*
H-8	2.60 *s*	1.47 *d*
H-9	10.54 *s*	10.51 *s*
H-1′	6.32 *qq*	6.25 *qq*
H-3′	1.73 *d*	1.71 *d*
H-4′	1.76 *d*	1.73 *d*

J (Hz): 3, 5 = 2; 5, 6 = 9; 1′, 3′ = 1′, 4′ = 1.5 (compound **29**: 7, 8 = 6.5).

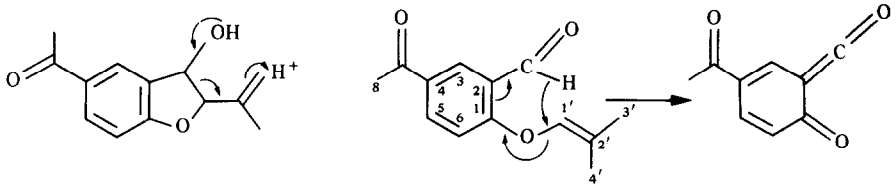
Table 3. ^{1}H NMR spectral data of compounds **23–25** (400 MHz, $CDCl_3$, TMS as int. standard)

	23	**24**	**25**
H-1 H-1′	3.25 *d*	1.11 *m* 3.34 *ddd*	3.27 *d*
H-2	3.74 *ddd*	3.90 *dddd*	3.74 *ddd*
H-3	1.32 *dd*	1.11 *m*	1.32 *dd*
H-3′	1.75 *ddd*	1.79 *ddd*	1.75 *ddd*
H-5	0.97 *dd*	0.87 *dd*	0.97 *dd*
H-6	—	1.3 *m*	—
H-6′	—	1.71 *m*	—
H-7	—		—
H-7′	—	1.50 *dddd*	—
H-8	—	2.21 *dddd*	2.2 *m*
H-9	—	1.94 *d*	1.75 *m*
H-12	5.82 *br s*	5.74 *br s*	5.90 *br s*
H-14	—	2.59 *dq*	2.63 *dq*
H-15	2.25 *m*	6.34 *dd*	6.38 *dd*
H-16 H-16′	1.09 *t*	5.47 *d* 5.66 *d*	5.57 *d* 5.74 *d*
H-17	1.03 *d*	1.07 *d*	1.07 *d*
H-18 H-19 H-20	0.88 *s* 0.94 *s* 0.95 *s*	0.86 *s* 0.94 *s* 0.97 *s*	0.88 *s* 0.94 *s* 0.96 *s*

J (Hz): Compound **24**: 1, 1′ = 1, 2′ = 2′, 3 = 3, 3′ = 12.5; 1′, 2′ = 2′, 3′ = 4; 1′, 3′ = 2.5; 5, 6 = 12; 5, 6′ = 2.5; 6′, 7′ = 4; 6, 7′ = 7′, 8 = 7, 7′ = 13; 8, 9 = 13; 7, 8 = 8, 14 = 4; 14, 17 = 7; 15, 16 = 11; 15, 16′ = 18 (couplings of **23** and **25** nearly the same, except for **23** and **25**: 1, 2′ = 2′, 3 = 9; and for **23**: 15, 16 = 7.5).

162, which itself was the result of a McLafferty fragmentation leading to **28** (Scheme 1). The ^{1}H NMR spectral data (Table 2) showed that the aromatic ring was substituted by two carbonyl groups, their nature followed from the corresponding signals. The nature of the third substituent was indicated by the quartet quartet at δ 6.32 and the narrowly split methyl doublets at 1.76 and 1.73. Most probably, **27** was formed in the plant by proton attack of toxol (**26**) as shown in Scheme 1. A second aromatic compound was the corresponding carbinol, **29**, whose ^{1}H NMR spectrum (Table 2) showed the typical upfield shifts of the aromatic protons, while a quartet at δ 4.90 and a doublet at 1.47 indicated the nature of the side chain.

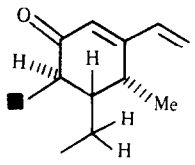
The spectral data of **23–25** (Table 3) showed that these compounds had the same carbon skeleton, which only differed in the number of hydroxy groups and the nature of the side chain, respectively. The ^{1}H NMR spectrum of **24** showed the presence of a dienone with a vinyl end group. The allylic nature of a proton which displayed a double quartet at δ 2.59 followed from the chemical shift. Spin decoupling of the latter indicated that this proton was coupled with a secondary methyl and with a proton which gave rise to a four-fold doublet at δ 2.21. One of the



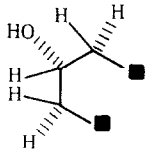
26 **27** *m/z* 162 **28**

Scheme 1.

neighbours of the latter was a doublet with a large coupling indicating a *trans*-diaxial orientation of these two protons. This led to the partial structure **A** as $J_{8,14}$ was small.



A



B

As the four-fold doublet at δ 3.90 was the signal of the proton under the hydroxy group which was coupled with a pair of three-fold doublets and two multiplets, the sequence **B** was also present. The remaining signals, which could be assigned by spin decoupling, led to the structure **24**. The stereochemistry at C-2, C-5 and C-10 followed from the couplings observed. Comparison of the ^{1}H NMR spectral data of **24** with those of **25** revealed that an additional hydroxy group had to be placed at C-1 or C-3 in the ketone, **25**. However, the lowfield signal of H-1β in the spectrum of **24** was missing in that of **25** indicating that a 1β-hydroxyl group was present. Accordingly, the axial orientation of H-1 and H-2 caused a large coupling, $J_{1,2}$. The unusual large downfield shift of H-1β in the spectrum of **24** can be explained by a strong deshielding effect of the 11-keto group. Compound **23**, which could not be obtained free from **25**, was the 15,16-dihydro derivative of **25**. The ^{1}H NMR signals of the vinyl protons were replaced by those of an ethyl group. All the other signals were nearly identical with those of **25**. 2-Desoxy-**24** has been named osteomuricone. The absolute configurations of **23**–**25** could not be determined. The aerial parts of the plant gave phytodiene, phytol, squalene, bicyclogermacrene, caryophyllene, cycloartenol, eudesmol and hinesol (**13**).

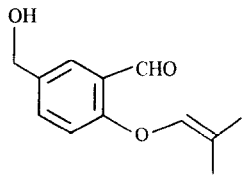
The roots of *O. barberiae* afforded phytodiene, α-humulene, **1**–**5**, **8**, caryophyllenepoxide (**9**), the epimers **10** and **11**, **16**, the diterpenes **21** and **22** and the thymol derivative, **30**. The structure of the latter compound followed from the molecular formula and the ^{1}H NMR spectrum (see Experimental) which showed that the methoxy groups were at C-2 and C-6. The structure of **10** was deduced from the ^{1}H NMR spectral data (see Experimental) which were similar to those of the known epimer, **11**. However, the H-9 signal was shifted downfield in the spectrum of **10** due to a changed conformation.

The structures of **21** and **22** followed from the molecular formulae and the ^{1}H NMR spectra (Table 4) which were close to that of **16**. However, one of the methyl singlets was missing in both spectra. In the spectrum of **21** this methyl was replaced by a pair of doublets at δ 3.97 and 3.61, and in the spectrum of **22** an additional lowfield doublet at 5.44 was present which collapsed to a singlet on irradiation of a doublet at 2.64 indicating a coupling with a hydroxyl proton. Compound **21** on acetylation afforded the monoacetate **21a**, its ^{1}H NMR spectrum and the ^{13}C NMR spectrum of **21** (Table 4) further supported the proposed structure. The position of the hydroxymethylene group was deduced from the chemical shifts of H-20 and from biogenetic considerations since in **21** only a hemiacetal at C-20 was possible. Finally, oxidation of **21** led to **22** which excluded any other position of the hydroxy-methylene group. The aerial part of the plant gave phytodiene, squalene and **16**.

The roots of *O. scariosum* var. *scariosum* afforded **11** and **17**, while the aerial parts gave squalene, eugenol and a further glycoside the caryophyllene derivative **15**. The high resolution mass spectrum led to the molecular formula $C_{28}H_{42}O_7$. Elimination of the sesquiterpene part gave a fragment at *m/z* 271 followed by loss of angelic acid which led to *m/z* 171. Further elimination of acetic acid gave *m/z* 111, a methylhydroxypyrrylium ion. The ^{1}H NMR signals of **15** in deuteriobenzene (Table 5) could be fully assigned by spin decoupling. The similarity of the signals of the sesquiterpene moiety with those of caryophyllene derivatives showed that the oxygen function was at C-13. The nature of the sugar part also followed from the ^{1}H NMR spectrum, while the relative position of the ester groups was deduced from biogenetic considerations as the angelate residue in **14** was at C-4'. Due to the small amount of material this assignment could not be confirmed by chemical transformations.

The roots of *O. jucundum* afforded **1** and **16**–**18**, while the aerial parts gave squalene, α-humulene, **16** and **17**. The roots of *O. ciliatum* also afforded **1** and **16**–**18**, while the aerial parts gave squalene and lupeyl acetate. The roots of *O. thodei* afforded β-bisabolene **1**, **17** and **18**, while the aerial parts gave germacrene D. The roots of *O. imbricatum* subsp. *nervatum* afforded large amounts of the palmitates of lupeol, taraxasterol, dammarenediol, lupenone and small quantities of the aromatic compounds **31** [6] and **32**. The structures of the palmitates were elucidated by reduction with lithium aluminium hydride which gave the corresponding triterpenes and palmityl alcohol. The aerial parts only gave squalene, lupeol and dammarenediol 3-*O*-palmitate.

For the genus *Osteospermum* the presence of sandaracopimarene derivatives and of tridecapentaynene seems to be characteristic. So far we have investigated 16 species (Table 6). Only *O. imbricatum* afforded no diterpenes, which were also absent in *Tripteris* species belonging to a subgenus of *Osteospermum*. So far, only **1** was



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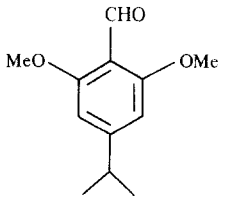

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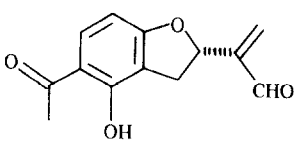

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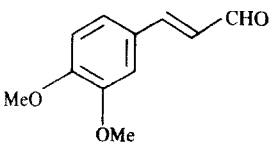

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Table 4. ^{1}H NMR spectral data of compounds **21**, **21a** and **22** (400 MHz, $CDCl_3$, TMS as int. standard)

	21	**21a***	**22**†	**21** (^{13}C NMR)‡	
H-3	0.75 *ddd*	0.75 *ddd*	—	C-1	37.1 *t*
H-3′	1.61 *m*	2.0 *m*	—	C-2	18.5 *t*
H-5	0.98 *dd*	0.97 *dd*	1.17 *m*	C-3	38.6 *t*
H-6	—	1.56 *m*	—	C-4	33.4 *s*
H-6′	—	1.79 *dddd*	—	C-5	56.5 *d*
H-7	—	1.23 *ddd*	—	C-6	17.5 *t*
H-7′	—	1.59 *m*	—	C-7	42.3 *t*
H-9	0.98 *d*	1.01 *dd*	1.21 *m*	C-8	71.6 *s*
H-11	—	1.55 *m*	—	C-9	57.9 *d*
H-11′	—	1.61 *m*	—	C-10	41.0 *s*
H-12	—	1.45 *m*	—	C-11	19.5 *t*
H-12′	—	1.74 *m*	—	C-12	43.5 *t*
H-14	1.39 *d*	1.32 *d*	1.29 *d*	C-13	36.5 *s*
H-14′	1.47 *d*	1.41 *d*	1.45 *d*	C-14	50.9 *t*
H-15	5.73 *dd*	5.72 *dd*	5.76 *dd*	C-15	151.6 *d*
H-16	4.83 *dd*	4.81 *dd*	4.83 *dd*	C-16	108.7 *t*
H-16′	4.88 *dd*	4.86 *dd*	4.90 *dd*	C-17	24.4 *q*
H-17	1.23 *s*	1.20 *s*	1.19 *s*	C-18	21.6 *q*
H-18	0.88 *s*	0.83 *s*	0.85 *s*	C-19	33.6 *q*
H-19	0.98 *s*	0.87 *s*	0.87 *s*	C-20	64.1 *t*
H-20	3.61 *d*	4.34 *d*	5.44 *d*		
H-20′	3.97 *d*	4.75 *d*			

*OAc 2.08 *s*.
†OH 2.64 *d*.
‡Some signals may be interchangeable.
J (Hz): Compound **21a**: 2, 3 = 13; 2′, 3 = 3.5; 3, 3′ = 13; 5, 6 = 12; 5, 6′ = 3; 6, 6′ = 14; 6, 7 = 6, 7′ = 3; 6′, 7 = 7, 7′ = 12; 9, 11 = 12; 9, 11′ = 2.5; 14, 14′ = 14; 15, 16 = 11; 15, 16′ = 18; 16, 16′ = 1; 20, 20′ = 12 (couplings of **21** and **22** very similar except 20, OH = 3.5 for **22**).

Table 5. ^{1}H NMR spectral data of compound **15** (400 MHz, $CDCl_3$, TMS as int. standard)

	C_6D_6	$CDCl_3$		C_6D_6	$CDCl_3$
H-1	1.85 *br t*	—	H-1′	4.17 *d*	4.36 *d*
H-2	1.68 *m*	—	H-2′	3.65 *dd*	3.62 *dd*
H-2′	2.24 *m*	—	H-3′	5.50 *dd*	5.48 *dd*
H-5	5.4 *br dd*	5.29 *br dd*	H-4′	5.08 *dd*	5.16 *dd*
H-9	2.39 *br ddd*	2.33 *br ddd*	H-5′	3.39 *dq*	3.57 *dq*
H-10	1.74 *dd*	—	H-6′	1.20 *d*	1.23 *d*
H-10′	2.15 *dd*	—	OAc	1.74 *s*	2.04 *s*
H-12	1.15 *s*	1.08 *s*	OAng	5.77 *qq*	6.11 *qq*
H-13	3.30 *d*	3.45 *d*		2.01 *dq*	1.98 *dq*
H-13′	3.97 *d*	3.93 *d*		1.95 *dq*	1.87 *dq*
H-14	4.93 *br s*	4.84 *br s*			
H-14′	5.12 *br s*	4.97 *br s*			
H-15	1.61 *br s*	1.59 *br s*			

J (Hz): 1, 2 = 1, 9 = 13, 13′ = 9.5; 5, 6 ~ 12; 5, 6′ ~ 4; 9, 10 = 9, 10′ = 9; 1′, 2′ = 8; 2′, 3′ = 3′, 4′ = 3′, 5′ = 7.5; 5′, 6′ = 7.

isolated, which is present in all genera belonging to the Calendulaceae. Sandaracopimarene derivatives are also present in *Chrysanthemoides* [7] and *Garuleum* [2, 8], while *Dimorphotheca* [9, 10] contains different diterpenes though sandaracopimarenes are present although these are of a different type. So far no diterpenes have been isolated from *Calendula*.

EXPERIMENTAL

The air-dried plant material collected in Transvaal and Natal, respectively, was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by direct comparison with authentic material (^{1}H NMR, MS, IR and TLC).

Table 6. Constituents of *Osteospermum* species

	Sandaraco pimarenes	Diterpenes of type **24**	Me ≡ $_5$ =	Others
O. auriculatum	+	+	+	Cubebol glyc.
O. ciliatum	+	–	+	
O. corymbosum [3]	+	–	+	
O. ecklonis [3]	+	–	+	
O. fruticosum [2]	+	–	+	
O. jucundum	+	–	+	
O. junceum [2]	+	–	+	
O. muricatum subsp. *muricatum*	+	–	+	Hydroxyacetophenones
O. oppoisitifolium [2]	+		+	
O. rotundifolium [3]	+	–	+	
O. polygalioides [3]	+	–	+	
O. subulatum [3]	+	–	+	
O. thodei	+	–	+	
O. imbricatum subsp. *nervatum*	–	–	+	*p*-Hydroxyacetophenones
O. barberiae	+	–	+	
O. scariosum var. *scariosum*	+	–	+	Caryophyllene glyc.

Osteospermum auriculatum (*S. Moore*) *Norl.* (*voucher* 81/40). The roots (220 g) afforded a petrol fraction, which gave 20 mg caryophyllene, 5 mg bicyclogermacrene, 10 mg heptadec-1-ene, 5 mg **1**, 15 mg **5**, 10 mg **6** and 5 mg **7**. The more polar fractions finally afforded 10 mg **16**, 100 mg **17**, 140 mg **18**, 40 mg **19** and 30 mg **20**. The aerial parts (130 g) gave 15 mg amyrone, 10 mg **16**, 5 mg **17** and 25 mg **14** (which were purified by TLC, Et_2O–petrol, 3:1).

Cubebol-(β-6′-desoxyglucopyranoside-4′-O-angelate) (**14**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 229 (15) ($C_{11}H_{17}O_5$), 205 (92) ($C_{15}H_{25}$), 204 (25) ($C_{15}H_{24}$), 161 (51) $[204 - CHMe_2]^+$, 83 (100) $[C_4H_7CO]^+$, 55 (78) $[83 - CO]^+$.

$$[\alpha]_{24}^{\lambda} = \frac{589}{+67} \quad \frac{576}{+80} \quad \frac{546}{-90} \quad \frac{436\,nm}{+285} \text{ (CHCl}_3\text{; c 0.6).}$$

Osteospermum muricatum *E. Mey ex. DC. subsp.* muricatum (*voucher* 81/7). The roots (120 g) afforded 3 mg **11**, 1 mg **13**, 2 mg **16**, 2 mg **17**, 2 mg **23**, 1 mg **24** and 3 mg **25** (separated by TLC (using Et_2O–petrol, 3:1) as well as 4 mg **27** (Et_2O–petrol, 1:3) and 4 mg **29** (Et_2O–petrol, 1:1). The aerial parts (130 g) gave 10 mg phytodiene, 1 mg phytol, 5 mg caryophyllene, 1 mg bicyclogermacrene, 10 mg squalene, 70 mg cycloartenol, 40 mg cudesmol (**12**) and 60 mg hinesol (**13**).

1β,2α-Dihydroxy-15,16-dihydroosteomuricone (**23**). Colourless gum, not free from **25**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3660 (OH), 1680 C=CC=O); MS *m/z* (rel. int.): 320 $[M]^+$ (2) ($C_{20}H_{32}O_3$), 302 $[M - H_2O]^+$ (100), 287 $(302 - Me]^+$ (45), 150 $[C_{10}H_{14}O]^+$ (95).

2α-Hydroxyosteomuricone (**24**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1650 (C=CC=O); MS *m/z* (rel. int.): 302.227 $[M]^+$ (6), 284 $[M - H_2O]^+$ (22), 148 $[C_{10}H_{12}O]^+$ (100).

1β,2α-Dihydroxyosteomuricone (**25**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1660 (C=CC=O); MS *m/z* (rel. int.): 318.219 $[M]^+$ (6) ($C_{20}H_{30}O_3$), 300 $[M - H_2O]^+$ (100), 285 $[300 - Me]^+$ (25), 148 $[C_{10}H_{12}O]^+$ (95).

4-Acetyl-1-O-(2-methylprop-1-en-1-yl)-salicylaldehyde (**27**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695 (C=O), 1620 (C=C); MS *m/z* (rel. int.): 218.094 $[M]^+$ (15) $C_{13}H_{14}O_3$ 203 $[M - Me]^+$ (20), 162 $[M - H_2C{=}CMe_2]^+$ (74) (McLafferty), 147 $[162 - Me]^+$ (100).

4-(1-Hydroxyethyl)-1-O-(2-methylprop-1-en-1-yl)-salicylaldehyde (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1700 (CHO), 1620 (C=C); MS *m/z* (rel. int.): 220.110 $[M]^+$ (10) ($C_{13}H_{16}O_3$), 205 $[M - Me]^+$ (24), 164 $[M - C_4H_8]^+$ (46), 149 $[164 - Me]^+$ (100), 121 $[149 - CO]^+$ (21).

Osteospermum barberiae (*Harv.*) *Norl.* (*voucher* 81/177). The roots (60 g) afforded 2 mg phytodiene, 3 mg α-humulene, 4 mg **1**, 20 mg **2**, 3 mg **3**, 30 mg **4**, 30 mg **5**, 70 mg **8**, 1 mg **9**, 3 mg **10** (Et_2O–petrol, 1:3), 1 mg **11**, 100 mg **16**, 120 mg **21** (Et_2O–petrol, 3:1), 10 mg **22** (Et_2O–petrol, 1:1) and 3 mg **30** (Et_2O–petrol, 1:10), while the aerial parts (110 g) gave 5 mg phytodiene, 5 mg squalene and 2 mg **16**.

2-Hydroxy-9-epicalamenene (**10**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH); MS *m/z* (rel. int.): 218.177 $[M]^+$ (7) ($C_{15}H_{22}O$), 175 $[M - C_3H_7]^+$ (100), 160 $[175 - Me]^+$ (9); ^{1}H NMR ($CDCl_3$): δ 6.56 (*s*, H-1), 6.94 (*s*, H-4), 2.52 (*ddd*, H-6), 2.79 (*ddq*, H-9), 2.20 (*dqq*, H-11), 0.74 (*d*, H-12), 1.00 (*d*, H-13), 1.22 (*d*, H-14), 2.20 (*s*, H-15), 4.46 (*s*, OH), [*J* (Hz): 6, 11 = 11, 12 = 11, 13 ~ 7.5; 6, 7 ~ 7; 8, 9 = 9.14 ~ 6.5].

8β,20-Dihydroxysandaracopimar-15-ene (**21**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1635, 915 (CH=CH$_2$); MS *m/z* (rel. int.): 288.245 $[M - H_2O]^+$ (12) ($C_{20}H_{32}O$), 275 $[M - CH_2OH]^+$ (100), 270 $[288 - H_2O]^+$ (21), 257 $[288 - CH_2OH]^+$ (20), 255 $[270 - Me]^+$ (18); $[\alpha]_D \sim 0°$.

Compound **21** (10 mg) was heated for 1 hr at 70° with 0.1 ml Ac_2O. TLC (Et_2O–petrol, 1:1) afforded 10 mg **21a**, colourless gum, ^{1}H NMR see Table 4.

Compound **21** (10 mg) in 1 ml CH_2Cl_2 was stirred for 15 min with 10 mg pyridine chlorochromate. TLC (Et_2O–petrol, 1:1) afforded 6 mg **22**, identical with the natural compound.

20-Hydroxy-8β,20-oxidosandaracopimar-15-ene (**22**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 3090, 1640, 910 (CH=CH$_2$); MS *m/z* (rel. int.): 304.240 $[M]^+$ (100) ($C_{20}H_{32}O_2$), 286 $[M - H_2O]^+$ (6), 275 $[M - CHO]^+$ (5), 257 $[275 - H_2O]^+$ (17); $[\alpha]_D \sim 0°$.

2,6-Dimethoxy-4-isopropyl benzaldehyde (**30**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1700 (CHO); MS *m/z* (rel. int.): 208 $[M]^+$ (54) ($C_{12}H_{16}O_3$), 193 $[M - Me]^+$ (100), 175 $[193 - H_2O]^+$ (59); ^{1}H NMR ($CDCl_3$): δ 7.06 (*s*, H-3, 5), 3.66 (*qq*, H-7), 1.27 (*d*, H-8, H-9), 9.90 (*s*, H-10), 3.88 (*s*, OMe) [*J* (Hz): 7, 8 = 7, 9 = 7.5].

Osteospermum scariosum (*DC.*) *Norl. var.* scariosum (*voucher* 81/208). The roots (100 g) afforded 3 mg **11** and 8 mg **17**, while the aerial parts (500 g) gave 5 mg squalene, 1 mg eugenol and 5 mg **15** (Et_2O).

13-Hydroxycaryophyllene- (*3'-O-acetyl-β-6-desoxyglucopyranoside-4'-angelate*) (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1760 (OAc), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 490.293 $[M]^+$ (0.2) ($C_{28}H_{42}O_7$), 472 $[M-H_2O]^+$ (0.05), 271 $[M-C_{15}H_{23}O]^+$ (9), 171 $[271-RCO_2H]^+$ (6), 111 $[171-HOAc]^+$ (41), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (42).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-5 \quad -6 \quad -8 \quad -13} \text{ (}CHCl_3\text{; } c \text{ 0.5).}$$

Osteospermum jucundum (*Phill.*) *Norl.* (*voucher* 81/80). The roots (30 g) afforded 1 mg **1**, 5 mg **16**, 40 mg **17** and 5 mg **18**, while the aerial parts (100 g) gave 20 mg squalene, 15 mg α-humulene, 20 mg **16** and 80 mg **17**.

Osteospermum ciliatum *Berg.* (*voucher* 77/289). The roots (25 g) afforded 3 mg **1**, 8 mg **16**, 25 mg **17** and 15 mg **18**, while the aerial parts (300 g) gave 5 mg squalene and 10 mg lupeyl acetate.

Osteospermum thodei *Maikötter* (*voucher* 77/145). The roots (80 g) afforded 25 mg β-bisabolene, 1 mg **1**, 20 mg **17** and 7 mg **18**, while the aerial parts (180 g) gave 20 mg germacrene D.

Osteospermum imbricatum *L. subsp.* nervatum (*voucher* 77/236). The roots (285 g) afforded 500 mg lupeyl palmitate, 750 mg taraxasteryl palmitate, 700 mg dammarendiol-3-O-palmitate, 280 mg lupenone, 33 mg **33** and 33 mg **32**, while the aerial parts (265 g) gave 20 mg squalene, 10 mg lupeol and 15 mg dammarendiol-3-O-palmitate.

Taraxasteryl palmitate. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CCO_2R); MS *m/z* (rel. int.): 664 $[M]^+$ (0.1), 408 $[M-RCO_2H]^+$ (100). Reduction with $LiAlH_4$ in Et_2O afforded taraxasterol and palmityl alcohol, identical with authentic samples.

Lupeyl palmitate. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CCO_2R); MS *m/z* (rel. int.): 664 $[M]^+$ (0.2), 408 $[M-RCO_2H]^+$ (100). Reduction with $LiAlH_4$ afforded lupeol and palmityl alcohol, identical with authentic samples.

Dammaren-3β,20-diol-3-O-palmitate. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 664 $[M-H_2O]^+$ (0.5). The reduction products with $LiAlH_4$ were acetylated (2 hr, 70° with Ac_2O) and the acetates obtained were separated by TLC yielding palmityl acetate and 3β-acetoxydammaren-20-ol, identical with an authentic sample.

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