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NEW FURANOSESQUITERPENES FROM *EUMORPHIA* SPECIES*

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Key Word Index—*Eumorphia sericea*; *E. prostata*; *Gymnopentzia bifurcata*; Compositae; new furanosesquiterpenes; new triterpene.

Abstract—*Eumorphia sericea* and *E. prostata* contained several new furanosesquiterpenes and a new triterpene aldehyde. Structures were elucidated mainly by spectroscopic methods and by some chemical reactions. Structures of three compounds however could not be established with certainty and are partially based on biogenetic considerations. *Gymnopentzia bifurcata* also contained known furanosesquiterpenes. The number of South African genera from the tribe Anthemideae, where these furanosesquiterpenes are characteristic, has now increased to eight. The importance of these observations for the botanical position of these genera is still not clear.

INTRODUCTION

The South African genus *Eumorphia* belongs to a group of genera in the tribe Anthemideae, whose position in the tribe is problematic [1]. Only *E. dregeana* DC has been investigated chemically [2]; this species contains no acetylenes, but characteristic furanosesquiterpenes (**2–4**) which are also present in *Lasiospermum*, *Ursinia*, *Athanasia*, *Phymaspermum*, *Stilpnophytum* and *Peyrousia* species [3–9]. We have now investigated two further *Eumorphia* species and *Gymnopentzia bifurcata*, which also belongs to the woody South African Anthemideae.

RESULTS AND DISCUSSION

The roots of *Eumorphia sericea* contained the furanosesquiterpenes **1** and **2** [8], while the aerial parts afforded the hydrocarbons **19**, **21** and **22**, the furans **1–4** [3, 8], **6** [10], **7** and **10** [9] together with the aromatic compounds **23**, **24** and two further furanosesquiterpenes both having the molecular formula $C_{15}H_{20}O_4$. While the more polar substance was a β-ketofuran (IR: 1690, 1570, 880 cm^{-1}; ^1H NMR: δ 8.05 *dd*, 7.45 *dd* and 6.77 *dd*),

* Part 137 in the series: "Naturally Occurring Terpene Derivatives"; for part 136 see: Bohlmann, F., Suwita, A. and Mabry, T. J. (1978) *Phytochemistry* **17**, 763.

Table 1. ^1H-NMR data of compounds **8**, **9**, **11** and **12** (δ-values, TMS as internal standard, 270 MHz, $CDCl_3$)

	8	9	11	12
1-H	1.25 *s*	1.27 *s*	—	—
3-H	3.55 *s*	3.88 *s*	—	—
5-H	2.85 *d*	2.55 *dd*	2.40 *dd*	2.36 *dd*
5'-H	2.73 *d*	2.40 *dd*	2.25 *dd*	2.21 *dd*
6-H	—	2.15 *ddddq*	2.05 *ddddq*	2.05 *ddddq*
7-H	2.22 *m*	1.76, 1.63 *m*	1.81, 1.65 *m*	1.78, 1.63 *m*
8-H	1.82 *m*	2.77 *m*	2.78 *m*	2.77 *m*
9-H	4.93 *dd*	—	—	—
11-H	6.41 *s(br)*	6.77 *dd*	6.77 *dd*	6.77 *dd*
12-H	7.38 *dd*	7.45 *dd*	7.45 *dd*	7.44 *dd*
13-H	7.41 *s(br)*	8.05 *dd*	8.04 *dd*	8.03 *dd*
14-H	1.34 *s*	0.98 *d*	1.04 *d*	1.01 *d*
15-H	1.35 *s*	1.44 *s*	—	—

J (Hz): 5,5' = 17; 5,6 = 5.5; 5',6 = 7.5; 6,7 = 7; 6,14 = 7; 11,12 = 1.6; 11,13 = 0.7; 12,13 = 1.6.

Table 2. ^1H-NMR data of compound **28**

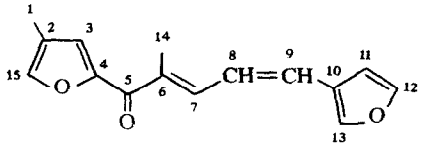
	C_6D_6	+ Eu(fod)$_3$	$CDCl_3$
1-H	1.87 *m*	2.55 *m*	
1'-H		2.73 *m*	
2-H	2.14 *m*	3.58 *dddd*	2.38 *dddd*
2'-H		3.74 *dddd*	2.16 *dddd*
3-H	9.43 *t*	11.64 *s(br)*	9.69 *t*
5-H	5.21 *d(br)*	5.64 *d(br)*	5.16 *d(br)*
6-H	2.94 *ddd*	3.40 *ddd*	2.90 *ddd*
21-H	5.28 *t(br)*	5.30 *t(br)*	5.10 *t(br)*
23-H	1.63 *s(br)*	1.64 *s(br)*	1.62 *s(br)*
24-H	1.72 *s(br)*	1.73 *s(br)*	1.68 *s(br)*
25-H	1.00 *d*	1.03 *d*	0.91 *d*
26-H	0.79 *s*	0.88 *s*	0.800 *s*
27-H	0.87 *s*	1.09 *s*	0.84 *s*
28-H	0.87 *s*	1.14 *s*	0.90 *s*
29-H	1.54 *s(br)*	1.84 *s(br)*	1.60 *s(br)*
30-H	1.63 *s(br)*	1.84 *s(br)*	1.68 *s(br)*

J(Hz): 1,2 = 7.5; 1,2' = 6; 2,2' = 16; 2,3 = 1.5; 5,6 = 10; 6,7 = 7; 18,25 = 7; 29,21 = 7.

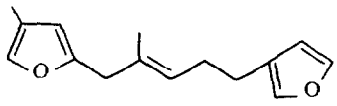
Table 3. ^1H-NMR data of compound **5**

1-H	1.98 *d*	8-H	2.73 *m*
3-H	5.88 *s(br)*	11-H	6.76 *dd*
5-H	2.57 *d*	12-H	7.43 *dd*
5'-H	2.46 *d*	13-H	8.00 *dd*
6-H	1.87 *ttq*	14-H	0.95 *d*
7-H	1.75 *m*	15-H	7.06 *dd*

J (Hz): 1,15 = 3,15 = 1; 5,5' = 15; 5,6 = 6.5; 5,6' = 6,7 = 6,14 = 7; 11,12 = 1.5; 11,13 = 12,13 = 1.



1: *cis*[*13]
2: *trans*



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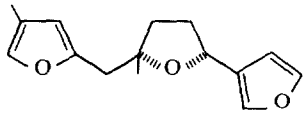

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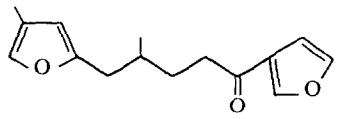

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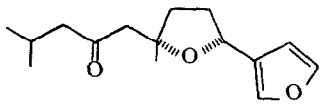

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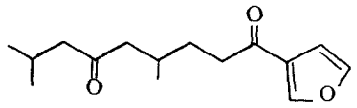

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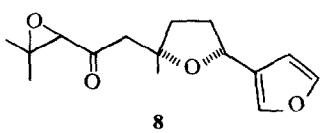

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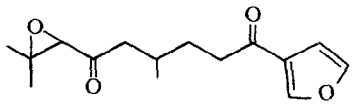

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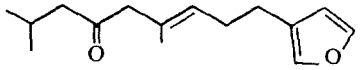

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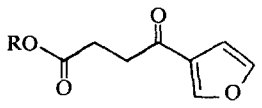
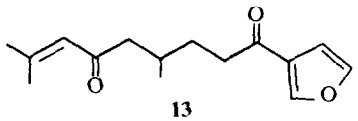


11: R = H 12: R = CH_3

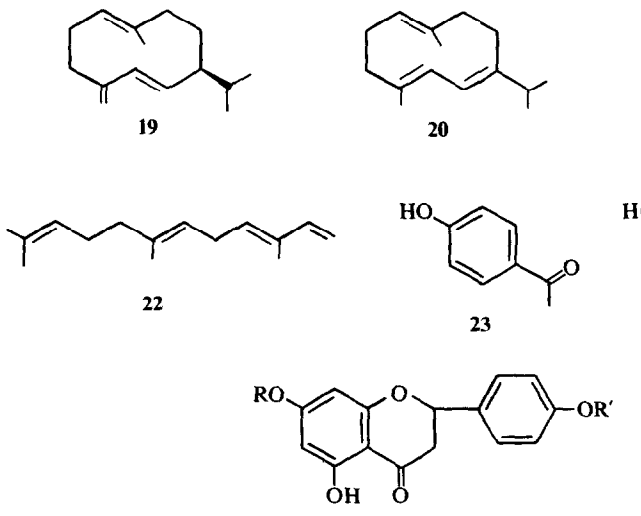


13

the less polar one was closely related to **6** as most of the NMR signals were very similar in both compounds (Table 1). However, instead of the two methyl doublets, two singlets were observed. The same was true for the more polar compound, its NMR spectrum was similar to that of **7**. Singlets at δ3.38 and 3.55 respectively indicated an epoxide. Therefore the structures of the two furanes were most probably **8** and **9**. By acid hydrolysis and periodate cleavage **9** was transformed into the acid **11**, which established this assumption. We have named compound **9** eumorphinone and compound **8** cyclo-eumorphinone. A small amount of a triterpene aldehyde was also isolated, both from the roots and the aerial parts, with the molecular formula $C_{30}H_{50}O$. The spectroscopic data (Table 2) and biogenetic considerations are in agreement with structure **28**. A possible pathway to **28** could be the rearrangement of **25** (Scheme 1). However, the amount of material was not sufficient to establish the proposed structure.

The aerial parts of *Eumorphia prostata* contain germacrene C (**20**), **7**, **13** [8, 9] and a further ketone with the molecular formula $C_{15}H_{18}O_3$. The NMR spectrum (Table 3) was in agreement only with structure **5**. The polar fractions afforded a hydroxy ketone as shown by the IR spectrum. In the MS no molecular ion was detectable. The observed fragments however were in agreement with the molecular formula $C_{15}H_{20}O_3$. Intensive NMR studies finally led to structure **16** (Table 4). Decoupling experiments and shift reagents clearly showed that the compound was a trisubstituted cyclohexene derivative. The two protons at C-2 showed allylic coupling with 4-H and a vicinal one with 1-H, which is the coupling partner of the secondary methyl group. Furthermore 4-H showed a small coupling with 5-H. Dreiding-models show that the angle is nearly 90°,

* The stereochemistry of **5**, **7**, **8–10**, **13** and **16–18** has not been elucidated.



	R	*R'*
29:	H	Me
30:	Me	H

Table 4. ^{1}H-NMR data of compound **16**

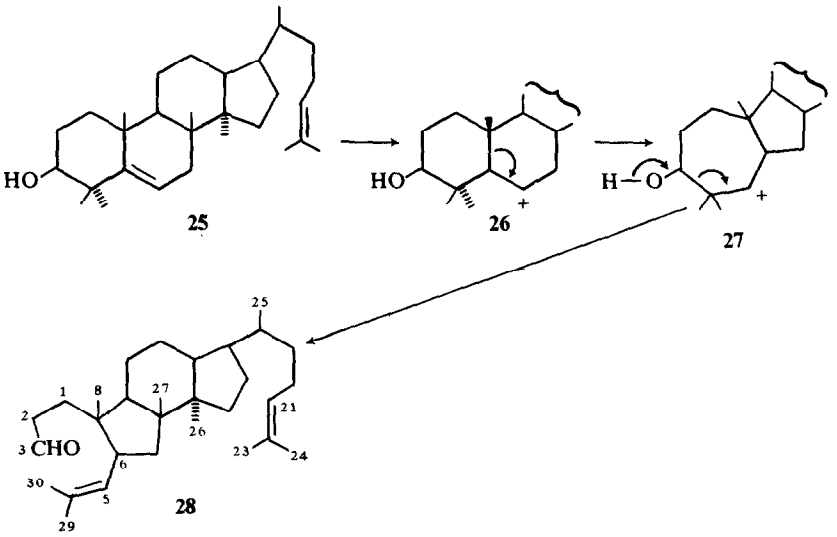
	C_6D_6	+ Eu(fod)$_3$	$CDCl_3$
1-H	1.77*m*	2.14 *ddddq*	1.63 *m*
2α-H	2.98 *dd(br)*	3.50 *dd(br)*	2.98 *m*
2β-H	2.04 *dd(br)*	2.58 *dd(br)*	2.05 *m*
4-H	5.29 *ddd*	6.48 *s(br)*	5.27 *ddd*
5-H	3.64 *dd(br)*	4.50 *dd(br)*	3.92 *dd(br)*
6-H	1.77 *m*	2.30 *m*	2.05 *m* 1.63 *m*
7-H	0.98 *d*	1.07 *d*	1.13 *d*
9-H	1.18 *s*	1.78 *s*	1.31 *s*
10-H	1.13 *s*	1.72 *s*	1.29 *s*
13-H	6.72 *dd*	7.05 *s(br)*	6.79 *dd*
14-H	6.84 *dd*	7.09 *s(br)*	7.46 *dd*
15-H	7.51 *s(br)*	8.03 *s(br)*	8.03 *s(br)*

J(Hz): 1,2α = 6; 1,2β = 10; 1,7 = 7; 2α,2β = 16; 2α.4 = 2β,4 = 4,5 = 1.5; 5,6 = 7.5; 13,14 = 1.5; 13,15 = 0.7; 14.15 = 1.

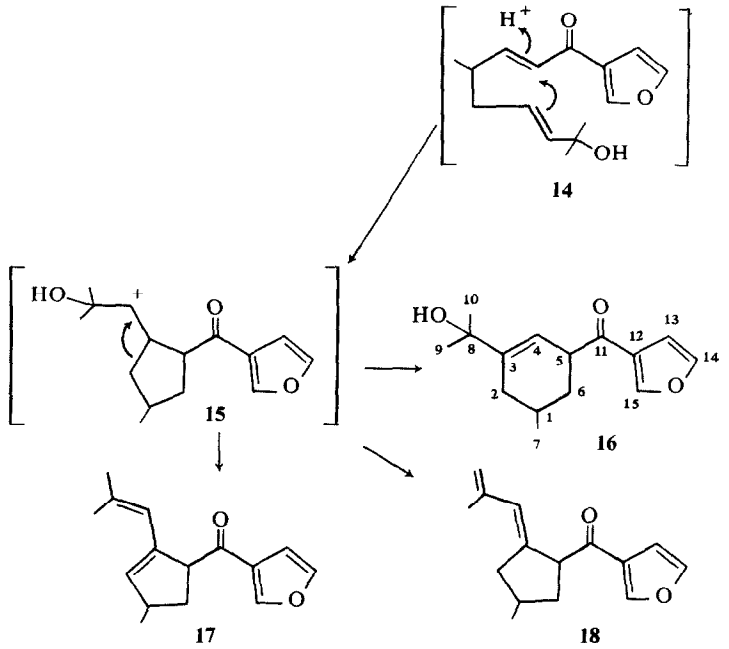
which would be in agreement with the coupling observed. The two remaining substituents can only be placed as shown in **16**, as the double bond was not conjugated with the carbonyl group. The abnormal carbon skeleton of **16** may be formed by rearrangement of a precursor such as **14** (Scheme 2). We have named compound **16** eumorphistonol. Two isomeric ketones, which may be related to the intermediate **15** were isolated in minute quantities. All spectroscopic data showed that they might possess structures **17** and **18**. However, the amount of material was too small to establish these structures. We therefore have started a synthesis of **17**.

The roots of *Gymnopentzia bifurcata*, which also belongs to the endemic South African genera of the tribe Anthemideae, again contained **1** and **2** together with the dihydroflavone **30**, while the aerial parts afforded **23**, the flavones **29** and **30** [11, 12] as well as ngaione (**6**).

Summarizing the results it is of chemotaxonomical



Scheme 1.



Scheme 2.

Table 5. ^{1}H-NMR data of compounds **17** and **18**

	17	18
2-H	5.53 *d(br)*	2.31 *m*
4-H	2.92 *m*	2.90 *m*
6-H	5.69 *s(br)*	5.67 *s(br)*
9-H	1.73 *s(br)*	4.20 *s(br)* 4.77 *s(br)*
10-H	1.78 *s(br)*	1.87 *s(br)*
13-H	6.81 *s(br)*	6.80 *s(br)*
14-H	7.44 *dd*	7.46 *dd*
15-H	8.06 *s(br)*	8.03 *s(br)*

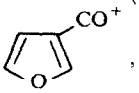
J(Hz): 2,3 = 9; 13,14 = 14,15 = 1.5.

interest that so many South African genera are characterized by the occurrence of furanosesquiterpenes. Morphological investigations are desirable to find out whether this is in agreement with anatomical features.

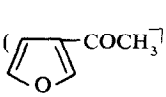
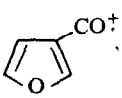
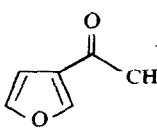
EXPERIMENTAL

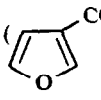
IR spectra were measured in CCl_4; ^{1}H NMR: all assignments were established by decoupling experiments. MS were determined at 70 eV; optical rotations were measured in $CHCl_3$. The airdried plant material, collected in Natal, was extracted with Et_2O—petrol (1:2) and the resulting extracts were first separated by CC (Si gel, act. grade II) and further by TLC (Si gel, GF 254). Known compounds were identified by comparison of their IR and NMR spectra with those of authentic material.

Eumorphia sericea Wood et Evans (voucher 77/282). Roots (90 g) afforded 120 mg **1**, 60 mg **2** and 5 mg **28** (Et_2O–petrol, 1:20); 240 g aerial parts yielded 10 mg **19**, 10 mg **22**, 10 mg **28**, 5 mg **21**, 10 mg **3**, 15 mg **4**, 15 mg **10**, 100 mg **6**, 100 mg **7**, 400 mg **1** and **2** (*ca* 2:1), 90 mg **8** (Et_2O–petrol, 1:1), 200 mg **9** (Et_2O–petrol, 1:1), 5 mg **23** and 35 mg **24**.

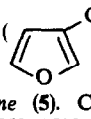
Cycloeumorphinone (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: >C=O 1720; furan 1570, 880. MS *m/e* (rel. int.): 264, 136 (M^+, 2) (calc. for $C_{15}H_{20}O_4$ 264.136); 249 (M^+—·CH_3, 2); 246 (M^+ —H_2O, 2); 231 (246—·CH_3, 1); 193 (246—  , 7); 151 (M^+ —CH_2CO  , 100); 95 ( , 82).

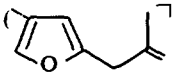
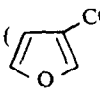
$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-40 \quad -40 \quad -46 \quad -85°} (c = 7.2)$$

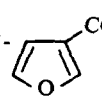
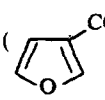
Eumorphinone (**9**). Colourless crystals mp 69.5° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: >C=O 1720; furan ketone 1690, 1570, 1520, 880. MS) *m/e* (rel. int.): 264. 136 (M^+, 0.1) (calc. for $C_{15}H_{20}O_4$ 264. 136); 249(M^+—·CH_3, 2); 246 (M^+—H_2O, 0.4); 231 (246 —·CH_3, 0.4); 193 (246—·  , 8); 147 (246—CO—  , 30); 110 ( , 26) (McLafferty); 95( , 100). 10 mg **9** in 2 ml dioxane were heated with 0.5 ml 2N H_2SO_4 for 5 min. at 70°. After addition of 30 mg HIO_4 the mixture was allowed to stand for 1 hr. The Et_2O extract was shaken with $NaHCO_3$ soln and the acid part was purified by TLC (Et_2O–petrol, 1:3) after esterification with CH_2N_2 3 mg **12** was obtained, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: CO_2R 1740; furan ketone 1687, 1565, 883. MS *m/e* (rel. int.): 224.105 (M^+1) (calc. for $C_{12}H_{16}O_4$ 224.105); 193 (M^+—·OCH_3, 2). 150 (M^+— $H_3CCO_2CH_3$, 17) (McLafferty); 110 ( , 66)

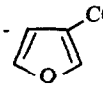
(McLafferty); 95 ( , 100).

Eumorphia prostata Bolus (voucher 77/130): Roots (30 g) afford 2 mg **21** and 15 mg **2**, while 80 g aerial parts yielded 50 mg **20**, 1 mg **17** and 1 mg **18** (Et_2O–petrol, 1:10, $AgNO_3$ coated plate), 10 mg **5** (Et_2O–petrol 1:10), 6 mg **7**, 15 mg **13** and 6 mg **16**.

Eumorphistonol (**16**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH 3620; furanketone 1685, 1570, 878. MS *m/e* (rel. int.): 233.118 (M^+-CH_3, 1) (calc. for $C_{14}H_{17}O_3$ 233.118); 230 (M^+-H_2O, 11); 215 (230-$^{\cdot}CH_3$, 8); 95 ( , 100).

10-*Oxolasiospermane* (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: furan ketone 1680, 1563, 1510, 870. MS *m/e* (rel. int.): 246.126 (M^+, 12) (calc. for $C_{15}H_{18}O_3$ 246.126); 217 (M^+-$^{\cdot}CHO$, 2); 136 ( , 65) (McLafferty); 123 ($C_8H_{11}O^+$, 32); 95 ( , 100).

17. Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: furan ketone 1685, 1570, 875. MS (GC–MS) *m/e* (rel. int.): 230 (M^+, 20); 215 (M^+-$^{\cdot}CH_3$, 14); 135 (M^+-  , 35); 95 ( , 100).

18. Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: furan ketone 1685, 1570, 875. MS (GC–MS) *m/e* (rel. int.): 330 (M^+, 13); 215 (M^+-$^{\cdot}CH_3$, 17); 135 (M^+-  , 15); 95 ( , 100).

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