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FURANOSESQUITERPENES FROM *BRACHYMERIS MONTANA*[*]

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Key Word Index—*Brachymeris montana*; Compositae; sesquiterpenes; furanosesquiterpenes; chemotaxonomy.

Abstract—*Brachymeris montana* afforded several furanosesquiterpenes two of them not being isolated previously. The structures were elucidated by highfield ^{1}H NMR spectroscopy. The present isolation of these characteristic sesquiterpenes from one of the woody South African genera of the Anthemideae is of chemotaxonomic interest.

INTRODUCTION

The small South African genus *Brachymeris* (Compositae) has not been investigated chemically. It belongs to the group of woody genera of the tribe Anthemideae, though their placement still seems to be in doubt [1]. Since, however, the chemistry of all these genera is very similar, it was of interest to see whether these compounds are also present in *Brachymeris*. We therefore have studied the constituents of *B. montana* Hutch. The results will be discussed in this paper.

RESULTS AND DISCUSSION

The roots of *Brachymeris montana* afforded α-pinene, eugenol methyl ether, sitosterol, stigmasterol, the furanosesquiterpenes **1** [2], **3** [2], **4** [2] and **5** [2] as well as **6** and **8**. The structure of **6** clearly followed from the ^{1}H NMR spectrum, which was identical with a synthetic sample [Bornowski, H., unpublished]. The aldehyde **8**, molecular formula $C_{15}H_{16}O_4$, showed a UV maximum at 264 nm, while the IR spectrum indicated, in addition to a band of an unsaturated aldehyde (1695 cm^{-1}), the presence of a hydroxy group and of a β-substituted furan (880 cm^{-1}). The mass spectrum showed the fragments *m/z* 95 and 81 typical for alkyl substituted furans as well as *m/z* 82, obviously formed by a McLafferty fragmentation leading to methyl furan. The ^{1}H NMR spectrum (Table 1) showed signals for five furan protons, one of them being drastically shifted downfield (δ 8.02), indicating that the aldehyde group was in a β-position in the furan moiety. As already followed from the UV spectrum a further conjugation had to be assumed. Accordingly, one of the lowfield signals (δ 6.17) showed couplings with a broadened singlet at δ 4.47 (2H), the broadened triplet at 2.38 and the narrowly split double doublet at 8.02, clearly indicating the conjugation of the furan aldehyde with an olefinic

Table 1. ^{1}H NMR spectral data of compounds **6–8** (400 MHz, $CDCl_3$ TMS as int. standard)

	6	**7**	**8**
H-1	7.32 *dd*	5.62 *d*	7.38 *dd*
H-2	6.45 *s br*	3.84 *dd*	6.31 *dd*
H-3	—	2.85 *ddd*	—
H-4	6.25 *d br*	2.56*q*[*]	2.51 *t br*
H-5	5.87 *dt*		1.84 *tt*
H-6	2.62 *dddd* 2.28 *dddd*	6.56 *tq*	2.38 *t br*
H-7	3.32 *ddq*	—	—
H-8	—	—	6.17 *dtt*
H-10	7.05 *s br*	6.98 *s br*	6.62 *s br*
H-12	2.08 *d*	2.08 *d*	9.91 *s*
H-13	7.36 *s br*	7.39 *s br*	8.02 *dd*
H-14	1.20 *d*	1.97 *s br*	4.47 *s br*
H-15	7.33 *s br*	—	7.25 *s br*

[*]Not first order.

J(Hz): compound **6**: 1,2 = 1,15 = 1.5; 4,5 = 16; 4,6 = 1.3; 4,6′ = 1; 5,6 = 5,6′ = 6,7 = 6′, 7 = 7,14 = 7; 6,6′ = 14; 12,13 = 1; compound **7**: 1,2 = 2,3 = 2.3; 3,4 = 9; 3,4′ = 5; 5,6 = 7; 5,14 = 1.5; compound **8**: 1,2 = 1, 15 = 1.7; 2,15 ~ 1; 1,2 = 1, 15 = 1.7; 2,4 = 1; 4,5 = 7.5; 5,6 = 8; 6,8 ~ 1; 6, 14 = 8,10, 13 ~ 1; 8,14 = 1.

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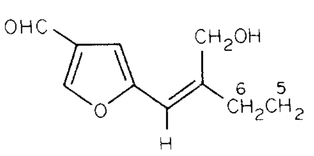
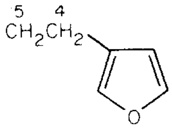
[*]Part 442 in the series "Naturally Occurring Terpene Derivatives". For Part 441 see Bohlmann, F., Mathur, R., Gupta, R. K., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2045.

double bond. As the signal at 4.47 obviously was that of an allylic CH_2OH group the sequence **A** was established:



A



B

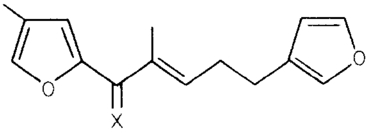
Further spin decoupling showed that the remaining signals led to the sequence B, thus leading to structure **8**. The stereochemistry of the 7, 8-double bond was deduced by comparison of the chemical shifts with those of similar compounds. Compound **8** we have named brachymeral. The aerial parts gave *cis*- and *trans*-ocimene, germacrene D, bicyclogermacrene, lupeyl acetate, eugenol methyl ether, the furanosesquiterpenes **1** [2], **2** [Bornowski, H., unpublished] and **3** as well as a further one, the epoxy lactone **7**. The molecular formula of $C_{15}H_{16}O_5$ immediately indicated a highly oxygenated furanosesquiterpene. From the IR spectrum followed a cross-conjugated keto group and an epoxy - γ - lactone as the corresponding band was at 1815 cm^{-1}. The ^1H NMR spectrum (Table 1) was in part close to a corresponding 8 - desoxo compound which was isolated from an *Ursinia* species [3]. All signals and the result of spin decoupling therefore agreed nicely with the proposed structure. The relative stereochemistry at C-2 and C-3 could not be assigned with certainty. However, a *cis*-position of H-2 and H-3 seemed to be more likely [3]. Surprisingly, in the mass spectrum of **7**, which we have named brachymerolide, the base peak was *m/z* 109, obviously the acyl cation formed by splitting the 7, 8-bond.

The present isolation of characteristic furanosesquiterpenes from one of the woody South African genera placed in the tribe Anthemideae surely further supports that these genera, including the problematic genus *Ursinia*, are closely related. So far this type of sesquiterpene has been isolated from *Athanasia* [4–6], *Ursinia* [Bornowski, unpublished; 3, 7, 8] *Lasiospermum* [Bornowski, unpublished; 9], *Asaemia* [10], *Eumorphia* [2, 10], *Phymaspermum* [11], *Stilpnophytum* [10] and *Gymnopentzia* [11]. However, *Pentzia* [6, 12, 13], obviously close to *Athanasia*, which in part also contains compounds like *Pentzia* [6], so far only gave compounds typical for the tribe Anthemideae and from *Ursinia* [7, 8, 14] several sesquiterpene lactones are reported too. All these genera, however, except *Pentzia*, do not contain the typical acetylenes widespread in the Anthemideae. These genera therefore may be best placed in a subtribe of Anthemideae, *Pentzia* being a link to the other parts of the tribe.

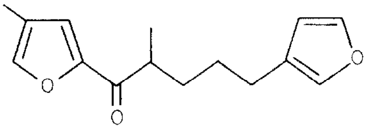
EXPERIMENTAL

The air-dried plant material, collected in Transvaal in February 1981 (voucher 81/76, deposited in the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol, 1:2, and the resulting extracts were separated by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. The roots (150 g) afforded 4 mg sitosterol, 1 mg stigmasterol, 10 mg α-pinene, 5 mg eugenol methyl ether, 12 mg **1**, 5 mg **3**, 25 mg **4**, 10 mg **5**, 2 mg **6** (Et_2O–petrol, 1:3) and 6 mg **8** (Et_2O–petrol, 1:1), while the aerial parts (70 g) gave 5 mg germacrene D, 2 mg bicyclogermacrene, 3 mg lupeyl acetate, 50 mg eugenol methyl ether, 2 mg *cis*-ocimene and 2 mg *trans*-ocimene, 1 mg **1**, 20 mg **2**, 7 mg **3** and 2 mg **7** (Et_2O–petrol, 4:1).

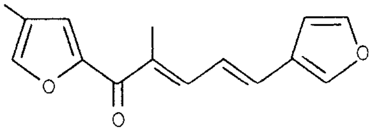
Brachymerolide (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1815 (γ-lactone), 1650 (C=CC=O); MS *m/z* (rel. int.): 276.100 $[M]^+$



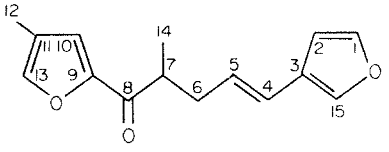
1 X = H_2
2 X = O



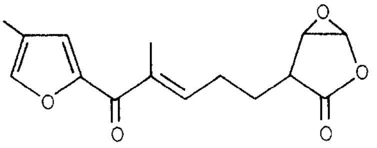
3



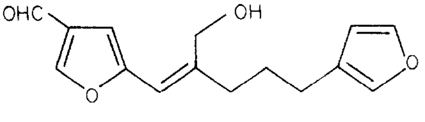
4 *trans*
5 *cis*



6



7



8

(16) ($C_{15}H_{16}O_5$), 247 $[M - {}^{\cdot}CHO]^+$ (3), 109 $[C_5H_5CO]^+$ (100), 81 $[109 - CO]^+$ (25).

Brachymeral (**8**). Colourless gum, UV (Et_2O) 264 nm, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 2720, 1695 (CHO), 880 (β-subst. furan); MS m/z (rel. int.): 260.105 $[M]^+$ (12) ($C_{15}H_{16}O_4$), 242 $[M - H_2O]^+$ (35), 229 $[M - CH_2OH]^+$ (10), 214 $[242 - CO]^+$ (5), 95 $[C_6H_7O]^+$ (94), 82 $[C_5H_6O]^+$ (100) (McLafferty), 81 $[C_5H_5O]^+$ (78).

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