petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). The less polar fractions afforded 500 mg γ-humulene and 200 mg **1**, while the polar fractions (Et_2O–MeOH, 20:1) gave 200 mg **3a**, 5 mg **3c–3f**, 5 mg **4a** as well as 3 mg **4b** and **4c**. Separation of the lactones was achieved by TLC (C_6H_6–CH_2Cl_2–Et_2O, 10:10:1, several times). However, **3c–3f** and **4b/4c** could not be separated.

6α - *Hydroxy* - 9 - *desacylineupatorolide* - 9 - O - (3 - *methyl* - *pent* - 3c - *enoate*) (**3a**). Colourless crystals, mp 191–192° (Et_2O-petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1720, 1650 (C=CCO$_2$R, C=O); MS *m/z* (rel. int.): 394.199 $[M]^+$ (0.5) ($C_{21}H_{30}O_7$), 376 $[M-H_2O]^+$ (2.5), 97 $[C_5H_9CO]^+$ (100), 69 $[97-CO]^+$ (11).

10 mg **3a** was heated for 1 hr with 0.1 ml Ac_2O at 70°. Usual work-up afforded 8 mg **3b**, colourless crystals, mp 168–169° (Et_2O-petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1730 (OAc, C=O, C=CCO$_2$R); MS *m/z* (rel. int.): 436.210 $[M]^+$ (0.5) ($C_{23}H_{32}O_8$), 418 $[M-H_2O]^+$ (3), 358 $[418-HOAc]^+$ (1), 245 $[358-OCOR]^+$ (1), 97 $[C_5H_9CO]^+$ (100), 69 $[97-CO]^+$ (9);

$$[\alpha]_{24°}^{\lambda} = \frac{589}{+44} \quad \frac{578}{+46} \quad \frac{546}{+56} \quad \frac{436\ nm}{+146} \ (CHCl_3;\ c = 0.5).$$

The mixture of **3c–3f** was a colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1730 (CO$_2$R, C=CCO$_2$R, C=O); MS *m/z* (rel. int.): 382, 380, 368 $[M]^+$ (0.1, 0.2, 0.1), 280 $[M-RCO_2H]^+$ (1), 85 $[C_4H_9CO]^+$ (40), 83 $[C_4H_7CO]^+$ (60), 71 $[C_3H_7CO]^+$ (33), 57 $[85-CO]^+$ (100), 55 $[83-CO]^+$ (61).

Dittrichiolide-isobutyrate (**4a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone 1720 (C=CCO$_2$R); MS *m/z* (rel. int.): 336.294 $[M]^+$ (0.5) ($C_{19}H_{28}O_5$), 248 $[M-RCO_2H]^+$ (18), 71 $[C_3H_7CO]^+$ (100); CD (MeCN) $\Delta\epsilon_{256}-1.4$.

Dittrichiolide-isovalerate and (*2-methylbutyrate*) (**4b** and **4c**). Colourless gum, not free from **4a**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1730 (CO$_2$R); MS *m/z* (rel. int.): 350 $[M]^+$ ($C_{20}H_{30}O_5$), 248 $[M-RCO_2H]^+$ (20), 85 $[C_4H_9CO]^+$ (95), 57 $[85-CO]^+$ (100).

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REFERENCES

1. Merxmüller, H., Leins, P. and Rössler, H. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.), p. 585. Academic Press, London.
2. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 43.
3. Baruah, R. N., Sharma, R. P., Thyagarajan, G., Herz, W., Govindan, S. V. and Blount, J. F. (1980) *J. Org. Chem.* **45**, 4838.
4. Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 157.

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GLAUCOLIDE FROM *VERNONIA STAEHELINOIDES**

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Key Word Index—*Vernonia staehelinoides*; Compositae; sesquiterpene lactone; glaucolide.

Abstract—*Vernonia staehelinoides* afforded a new glaucolide.

In a continuation of our investigations of representatives of the tribe Vernonieae, we now have studied the constituents of the South African *Vernonia* species, *V. staehelinoides* Harv. The roots afforded squalene, stigmasterol and sitosterol, while the aerial parts gave caryophyllene, α-humulene, germacrene D and the glaucolide **1**. Acetylation of **1** gave the acetate **2**, while treatment with slightly acidic Si gel afforded **3**. The structures were elucidated by ^1H and ^{13}C NMR spectroscopy (Table 1). The nature of the ester group followed from the ^1H NMR signals. A triplet quartet was coupled with broadened singlets at δ 1.94 and 5.14. The chemical shifts of these signals indicated an acetoxy derivative of a senecioate, where the CH_2OAc group was *cis* to the carbonyl group. The typical pair of doublets around δ 4.9 were assigned to H-13 and the double doublet at δ 4.79 to H-8 as spin decoupling showed that the latter was coupled with

*Part 436 in the series "Naturally Occurring Terpene Derivatives". For Part 435 see Bohlmann, F., Wallmeyer, M. and Jakupovic, J. (1982) *Phytochemistry* **21** (in press).

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

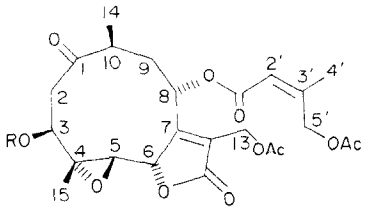
	1	**2**	**3**(acetone-d_6)	**1**(acetone-d_6)‡		**2**($CDCl_3$)
H-2α	2.53 *dd*	2.43 *dd*	2.05 *m*	C-1	211.9 *s*	209.2
H-2β	3.29 *dd*	3.52 *dd*		C-2	48.6 *t*	45.2
H-3	3.77 *dd*	4.73 *dd*	4.63 *dd*	C-3	72.9 *d*	73.9
H-5	2.77 *d*	2.80 *d*	6.01 *s*	C-4	55.8 *s*	55.3
H-6	4.98 *d*	4.95 *d*	—	C-5	64.0 *d*	64.0
H-8	4.79 *dd*	4.79 *dd*	6.42 *dd*	C-6	81.2 *d*	81.2
H-9α	2.10 *ddd*	2.14 *m*†	1.83 *dd*	C-7	164.8 *s*	163.5
H-9β	2.57 *m**	2.53 *ddd*	2.28 *m*	C-8	67.6 *d*	66.4
H-10		2.61 *ddq*		C-9	37.9 *t*	36.9
H-13	4.83 *d*(*br*)	4.83 *d*(*br*)	5.06 *d*	C-10	4.19 *d*	42.1
H-13′	4.93 *d*	4.93 *d*	4.19 *d*	C-11	127.9 *s*	169.7
H-14	1.20 *d*	1.22 *d*	0.99 *d*	C-12	167.8 *s*	127.7
H-15	1.50 *s*	1.54 *s*	1.52 *s*	C-13	62.6 *t*	59.4
H-2′	5.73 *tq*	5.73 *tq*	5.83 *tq*	C-14	12.0 *q*	13.1
H-4′	5.14 *s*(*br*)	5.19 *s*(*br*)	5.33 *d*(*br*)	C-15	21.3 *q*	21.5
			5.21 *d*(*br*)			
H-5′	1.94 *s* (*br*)	1.94 *s*(*br*)	1.93 *d*			
OAc	2.10 *s*	2.09 *s*	2.06 *s*			
	2.07 *s*	2.14 *s*	2.01 *s*			
		2.07 *s*				
OH	4.70 *s*(*br*)					

*,†In acetone-d_6 H-9α 2.21 *ddd*, H-9β 2.43 *ddd*, H-10 2.92 *ddq*;.
‡OCOR: 167.8 *s*, 116.9 *d*, 157.8 *s*, 63.8 *t*, 20.4 *q*, OAc: 170.4 *s*, 170.7 *s*, 20.3 *q*, 20.4 *q*; J(Hz): 2α, 2β = 14; 2α, 3α = 2α, 3α = 8.5; 5, 6 = 9.5; 8, 9α = 3; 8, 9β = 12; 9α, 9β = 12; 9α, 10 = 12; 9β, 10 = 3; 10, 14 = 7; 13, 13′ = 13; 2′, 4′ = 2′, 5′ = 1.5; 4, 4′ = 15; compound **3**: 8, 9α = 1.5; 8, 9β = 10; 9α, 9β = 13.

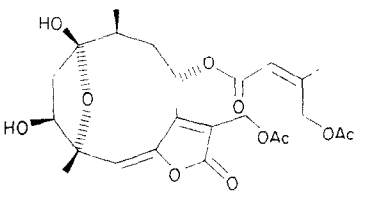
two three-fold doublets (in acetone-d_6), which were further coupled with *ddq* δ 2.92, obviously the signal of H-10. Accordingly irradiation of this signal collapsed the methyl doublet at δ 1.20 to a singlet. A further downfield double doublet (δ 3.77), which was shifted to δ 4.73 on acetylation, was coupled with a pair of double doublets. The chemical shifts indicated a neighbouring keto group, which must be placed at C-1 to explain the downfield shift of H-10. Consequently, a hydroxyl group was at C-3. A singlet at δ 1.50 and a doublet at 2.77 indicated the presence of a 4, 5-epoxide as the coupling showed that the latter signal collapsed to a singlet on irradiation of a doublet at δ 4.98, which was assigned provisionally to H-6. Inspection of models indicated, in agreement with the couplings, that most probably the ester group at C-8 was α-orientated as in all other known glaucolides. The stereochemistry at C-3 was supported by the chemical shifts and the couplings of H-2 and the presence of a hydrogen bridge with the epoxide oxygen (IR spectrum). In this conformation, H-2β would be deshielded by the keto and the hydroxyl group, which explained the shift differences of H-2. A hydrogen bridge with the keto group had to be excluded, as the couplings of H-2 would not agree with both an α or a β-orientated hydroxyl. The coupling $J_{5,6}$ showed that H-5 was α-orientated, while the couplings $J_{9,10}$ led to the stereochemistry at C-10. The ^{13}C NMR spectra of **1** and **2** were also in good agreement with the proposed structures.

The ^{1}H NMR spectral data of **3** indicated that this compound was most probably formed by proton attack of the epoxide. The upfield shift of the H-2 signals indicated the presence of a hemi-ketal. This assumption was further supported by the downfield shift of the H-8 signal. Inspection of a model showed that this proton should be strongly deshielded by the oxygen bridge. **1** was related to stilpnotomentolide-8-*O*-methacrylate[1].

The isolation of a glaucolide from a South African *Vernonia* species supports the close relationship to the South American species, where glaucolides are widespread. Glaucolides have also been isolated from *Stilpnopappus*[1], *Erlangea*[2] and *Disynaphia*[3].



1 R=H
2 R=Ac



3

EXPERIMENTAL

The air-dried plant material, collected in Feb. 1981 in Transvaal (voucher 81/22, 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 repeated TLC (Si gel). The roots (110 g) gave 5 mg stigmasterol and 4 mg sitosterol, while the aerial parts (290 g) afforded 60 mg caryophyllene, 50 mg germacrene D, 20 mg α-humulene and 15 mg **1** (C_6H_6–CH_2Cl_2–Et_2O, 1:1:1).

3β-Hydroxystilpnotomentolide-8-O-(*5-acetoxysenecioate*) (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3520 (OH, hydrogen bonded), 1775 (γ-lactone), 1750 (OAc), 1700 (C=CCO_2R, C=O): MS *m/z* (rel. int.): 494 $[M]^+$ (0.15), 337.129 $[M-O_2CR]^+$ (3) ($C_{17}H_{21}O_7$), 336 $[M-RCO_2H]^+$ (0.5), 276 $[336-HOAc]^+$ (10), 258 $[276-H_2O]^+$ (6), 99 $[HOCH_2C(Me)=CHCO]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-100 \quad -105 \quad -123 \quad -214} \quad (CHCl_3;\ c\ 0.8).$$

A part of **1** during purification was adsorbed on Si gel for 2 hr. After extraction with MeOH 2 mg of **3** were obtained, colourless solid, mp ~ 165° MS *m/z* (rel. int.): 435 $[M-OAc]^+$ (0.5), 337 $[M-O_2CR]^+$ (1), 277 $[377-HOAc]^+$ (8), 99 $[HOCH_2C(Me)=CHCO]^+$ (100).

6 mg **1** on acetylation (Ac_2O, 1 hr, 70°) afforded 6 mg **2**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (γ-lactone), 1750 (OAc), 1720 (C=CCO_2R, C=O); MS *m/z* (rel. int.): 536 $[M]^+$ (0.2), 379 $[M-O_2CR]^+$ (1) 378 $[M-RCO_2H]^+$ (0.5), 99 $[HOCH_2C(Me)=CHCO]^+$ (100).

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REFERENCES

1. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 1045.
2. Bohlmann, F. and Czerson, H. (1978) *Phytochemistry* **17**, 1190.
3. Bohlmann, F., Dhar, A. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1077.

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BESHORNIN AND BESHORNOSIDE, STEROIDAL SAPONINS OF *BESHORNERIA YUCCOIDES*

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Key Word Index—*Beshorneria yuccoides*; spirostanol glycosides; furastanol glycosides; beshornin; beshornoside.

Abstract—Two new saponins beshornin and beshornoside have been isolated from the methanolic extract of *Beshorneria yuccoides* leaves and their structures elucidated. Beshornin is 3-*O*-{[α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1 → 2)-]-[α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranosyl}-(25*R*)-5α-spirostan-3β-ol, whereas beshornoside is 3-*O*-{[α-L-rhamnopyranosyl-(1 → 4)-β-D-glycopyranosyl-(1 → 2)]-[α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl} 26-*O*-[β-D-glucopyranosyl]-(25*R*)-5α-furostan-3β,22α,26-triol.

INTRODUCTION

Previous workers [1] have shown the presence of tigogenin based saponins in *Beshorneria yuccoides*. We now report the structure of two new saponins isolated from this plant.

RESULTS AND DISCUSSION

Beshornin and beshornoside were isolated from the leaves of *B. yuccoides* and purified by chromatography. Hydrolysis of both afforded tigogenin and the sugars galactose, glucose and rhamnose in the ratios 1:3:2 for beshornin and 1:4:2 for beshornoside. The fact that beshornoside gave a positive colour with Ehrlich's reagent [2] and was converted to beshornin by β-glucosidase indicated that it was the 26-*O*-(β-D-glucopyranoside) of the furostanol form of beshornin. This was confirmed by chromium trioxide oxidation of beshornoside peracetate to give tetra-acetyl glucosyl-δ-hydroxy-γ-methyl-*n*-valerate [3–5].

The type of glycosidic linkage in compound **1** was proved by methylation [6]. The methylated products were identified by TLC and GLC as methyl-2,3,4-tri-*O*-methyl-L-rhamnopyranoside (**3**), methyl-2,3,6-tri-*O*-methyl-D-glucopyranoside (**4**), methyl-2,3,6-tri-