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GLAUCOLIDES AND OTHER CONSTITUENTS FROM SOUTH AFRICAN *VERNONIA* SPECIES*

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Key Word Index—*Vernonia galpinii*; *V. cinarescens*; *V. natalensis*; *V. stipulacea*; Compositae; sesquiterpene lactones; glaucolides; sesquiterpenes; eudesmanes; daucalane; 5-methyl coumarin.

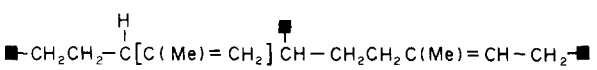
Abstract—The investigation of South African *Vernonia* species afforded, in addition to known compounds, three new glaucolides, two eudesmane derivatives, a daucadiene and a 5-methyl coumarin. The structures were elucidated by spectroscopic methods and chemical transformations. The chemotaxonomic relevance of the new compounds is discussed briefly.

INTRODUCTION

From the large genus *Vernonia* (Compositae, tribe Vernonieae) more than 100 species have been investigated chemically. Most species afforded highly oxygenated germacranolides, especially glaucolides [1], but many other types of compounds have been reported. We have studied the constituents of four South African species and the results are discussed in this paper.

RESULTS AND DISCUSSION

The roots of *Vernonia galpinii* Klatt. afforded tridecapentaynene, trideca-3,5,7,9-tetrayne-1,11-diene, α- and β-bergamotene, β-bisabolene, the 5-methyl coumarins **1** and **2** [2], the bisabolene derivative **5** [3] and the hydrocarbon **6**. The structure of **6** followed from the ^{1}H and ^{13}C NMR spectral data (Table 1). The ^{1}H NMR spectrum showed the presence of two olefinic methyls and one tertiary methyl. An olefinic methylene group was revealed by the typical signals around δ 4.9. Spin decoupling showed that these protons were coupled with one of the olefinic methyls, while the second one was coupled with an additional olefinic proton, which showed further couplings with two vicinal protons and an allylic coupling with a further proton. The latter was coupled with three protons, one of them was the geminal allylic proton. The couplings of a downfield shifted three-fold doublet indicated a four- or a five-membered ring which must be placed α to the isopropenyl group. The latter therefore was α to a secondary carbon. Further spin decoupling led to the sequence **A**:



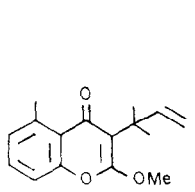
A

Table 1. ^{1}H NMR and ^{13}C NMR spectral data of compound **6**

	^{1}H NMR		^{13}C NMR	
	C_6D_6	$CDCl_3$		
H-1α	1.90 *br d*	1.84 *br d*	C-1	42.2 *t*
H-1β	2.12 *dd*	2.08 *dd*	C-2	123.1 *d*
H-2	5.51 *ddq*	5.38 *ddq*	C-3	138.5 *s*
H-4α	2.01 *br dd*	1.99 *br dd*	C-4	35.5 *t*
H-4β	2.04 *ddd*	2.06 *ddd*	C-5	28.4 *t*
H-5α	1.59 *dddd*	1.51 *m*	C-6	56.9 *d*
H-5β	1.34 *m*	1.37 *m*	C-7	50.5 *d*
H-6	1.70 *m*	1.75 *m*	C-8	23.4 *t*
H-7	2.90 *ddd*	2.95 *ddd*	C-9	42.6 *t*
H-8	1.80 *m*	1.80 *m*	C-10	42.7 *s*
H-9α	1.50 *ddd*	1.51 *m*	C-11	147.7 *s*
H-9β	1.34 *m*	1.26 *m*	C-12	19.4 *q*
H-12	1.71 *br s*	1.71 *br s*	C-13	113.0 *t*
H-13	4.94 *dq*	4.78 *dq*	C-14	27.5 *q*
H-13′	4.86 *dq*	4.71 *dq*	C-15	23.1 *q*
H-14	0.92 *s*	0.81 *s*		
H-15	1.79 *dd*	1.94 *dd*		

J(Hz): 1α, 1β = 14; 1β, 2 = 8.5; 1α, 2 = 3.5; 1α, 4α = 2, 4α = 2, 15 ~ 1.5; 4α, 4β = 15; 4β, 5α = 4β, 5β = 4; 4α, 5β = 12; 4α, 5α ~ 3; 5α, 5β = 13; 5α, 6 ~ 3; 6, 7 = 10; 7, 8 = 10; 7, 8′ = 9; 8, 9α = 6; 8, 9β = 2; 9, 9′ = 12; 12, 13 = 1.5; 12, 13′ = 1; 13, 13′ = 1.7.

*Part 452 in the series "Naturally Occurring Terpene Derivatives". For Part 451 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21** (in press).



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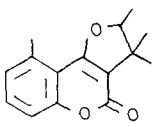

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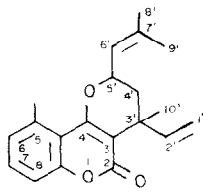

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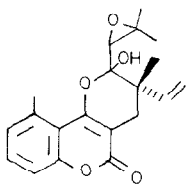

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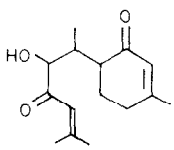

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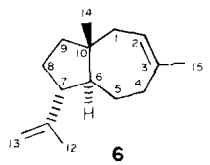

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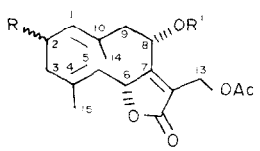
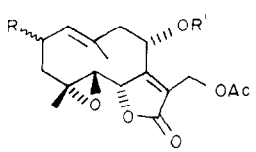
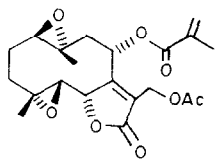


7 R = α-OAc, R' = Meacr
8 R = β-OAc, R' = Ac



9 R = α-OAc, R'= Meacr
10 R = β-OAc, R'= Ac



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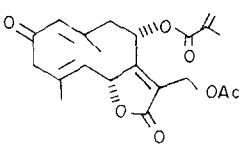

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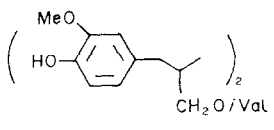

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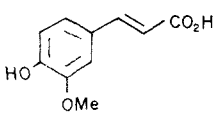

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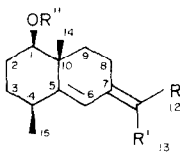
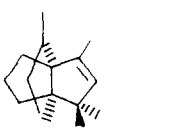


	15	16	17	18
R	Me	CHO	CHO	Me
R'	CHO	Me	Me	CH_2OH
R''	H	H	Ac	H



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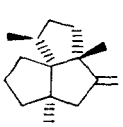

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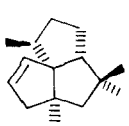

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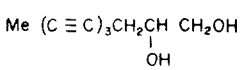


22

The presence of an additional tertiary methyl group consequently led to the structure **6**. The stereochemistry followed from the couplings. The ^{13}C NMR signals were in good agreement with this proposal. The absolute configuration of **6** is not known. Therefore compound **6** was a daucalane derivative, which are rare in Compositae. So far only one derivative has been reported [4]. The aerial parts of the plant gave tridecapentaynene, germacrene D, bicyclogermacrene, lupeyl acetate and again the 5-methyl coumarins **1** and **2**.

The roots of *V. cinarescens* Sch. Bip. afforded tridecapentaynene, α-humulene, lupeol and its acetate as well as the 5-methyl coumarin **4** [5] and the coumarin diene **3**, which obviously was the precursor of **4**. The structure of compound **3** followed from the ^1H

NMR spectral data (Table 2), which were close to those of related compounds. Irradiation of a partly overlapped three-fold doublet at δ 5.07 collapsed the signal at 5.35 to a broadened singlet and the double doublets at 1.95 and 1.66 collapsed to doublets, clearly indicating the nature of the side chain. However, the relative stereochemistry at C-3′ and C-5′ could not be assigned with certainty. We have named compound **3** preethulia coumarin. The aerial parts of this plant gave tridecapentaynene, lupeol and its acetate together with their Δ^{12}-isomers and traces of a sesquiterpene, which could not be identified.

Table 2. ^{1}H NMR spectral data of compound **3** (400 MHz, $CDCl_3$, TMS as internal standard)

H-6	7.05 *br d*	H-4′$_1$	1.95 *br dd*
H-7	7.38 *dd*	H-4′$_2$	1.66 *dd*
H-8	7.16 *br d*	H-5′	5.07 *ddd*
H-9	2.83 *br s*	H-6′	5.35 *dqq*
H-1 *t′*	5.13 *d*	H-8′	1.83 *d*
H-1 *c′*	5.09 *d*	H-9′	1.80 *d*
H-2′	6.18 *dd*	H-10′	1.62 *s*

J(Hz): 6, 7 = 7; 7, 8.5; 1*t*′, 2′ = 17.5; 1*c*′, 2′ = 10.5; 4′$_1$, 4′$_2$ = 14; 4′$_1$, 5′ = 11.5; 4′$_2$, 5′ = 1.8; 5′, 6′ = 8.5; 6′, 8′ = 6′, 9′ = 1.3.

The aerial parts of *V. natalensis* Sch. Bip. afforded germacrene D, bicyclogermacrene, lupeol and its acetate together with their Δ^{12}-isomers, β-amyrin acetate, lupenone, stigmasterol, spathulenol and the glaucolides **7**, **9** [6], **11** and **12**. The structure of compound **7** followed from the molecular formula and the ^{1}H NMR spectrum (Table 3). The presence of a glaucolide with two acetate residues and a methacrylate residue clearly followed from the corresponding ^{1}H NMR signals and the fragmentation pattern in the mass spectrum. Furthermore, the positions of three double bonds were deduced from the signals of two olefinic protons, which were coupled with olefinic methyl groups, the typical doublets of H-13 and the absence of a H-7 signal. The position of the ester groups followed from decoupling experiments. Though the relative position could not be established with certainty, an 8α-methacryloyloxy group was likely from biogenetic considerations. Accordingly, compound **7** was the precursor of glaucolide E (**9**), with the established stereochemistry [7]. However, this conclusion indicated that a reinvestigation was required of the configuration of a triacetate isolated from *V. cotoneaster* [8] and of the corresponding 4, 5-epoxide from *V. lilacina* [9], where 2α,8α-diacetoxy derivatives were assumed. Most probably the configuration at C-2 of these lactones must be changed to that shown in **8** and **10** respectively. NOE experiments clearly confirmed this assumption; H-8 showed a NOE with H-1 and H-6, while H-14 showed a NOE with H-2 and H-5 and H-15 with H-6. Ac-

Table 3. ^{1}H NMR spectral data of compounds **7**, **9**, **11** and **12** (400 MHz, $CDCl_3$, TMS as internal standard)

	7	**7** C_6D_6	**9** C_6D_6	**11** C_6D_6	**12**
H-1	4.93 *br d*	4.63 *br d*	4.86 *br d*	2.05 *br d*	5.70 *br s**
H-2	5.64 *ddd*	5.55 *ddd*	5.45 *ddd*	0.77 *m*	—
H-3	2.64 *dd*	2.28 *dd*	1.10 *dd*	1.49 *m*	3.31 *dd*
	2.20 *dd*	1.90 *dd*	2.30 *dd*	0.63 *ddd*	2.88 *d*
H-5	4.51 *br d*	4.07 *br d*	2.08 *d*	1.65 *m*	4.69 *br d*
H-6	5.72 *d*	5.32 *d*	4.53 *d*	1.87 *d*	5.98 *d*
H-8	5.13 *d*	5.06 *d*	4.95 *br d*	4.55 *dt*	5.13 *dd*
H-9	2.90 *dd*	2.62 *dd*	2.74 *dd*	5.07 *br d*	2.94 *m**
H-9′	2.67 *br d*	2.35 *br d*	2.34 *br d*	2.40 *br d*	2.66 *m**
H-13	4.94 *br d*	5.20 *br d*	5.18 *br d*	1.75 *dd*	4.98 *d*
H-13′	4.83 *d*	4.99 *d*	4.95 *br d*	5.00 *dd*	4.85 *d*
H-14	1.88 *br s*	1.62 *br s*	1.78 *br s*	4.78 *dd*	2.03 *br s*
H-15	1.80 *d*	1.13 *d*	0.95 *s*	0.81 *s*	1.70 *br s*
OCOR	6.13 *br s*	6.10 *br s*	6.05 *br s*	0.95 *s*	6.14 *br s*
	5.68 *dq*	5.23 *dq*	5.27 *dq*	6.02 *dq*	5.70 *br s*
	1.94 *dd*	1.80 *dd*	1.78 *br s*	5.16 *dq*	1.95 *dd*
OAc	2.06 *s*	1.73 *s*		1.70 *dd*	2.08 *s*
	2.05 *s*	1.72 *s*		1.65 *s*	

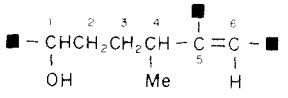
*In C_6D_6 H-1 5.60 *ddq*; H-9 2.47 *dd* and 2.37 *dd*.

J(Hz): Compound **7**: 1, 2 = 2, 3′ = 10; 2, 3 = 6; 3, 3′ = 12.5; 5, 6 = 10; 8, 9 = 10; 9, 9′ = 13, 13′ = 12.5; compound **9**: 1, 2 = 2, 3 = 10; 2, 3′ = 6.5,; 3, 3′ = 12.5; 5, 6 = 9; 8, 9 = 10; 9, 9′ = 12.5; 13, 13′ = 13; compound **11**: 1, 2 = 12; 2, 3 = 6; 2′, 3 = 5; 3, 3′ = 15; 5, 6 = 10; 6, 13 = 1; 8, 9′ = 11; 9, 9′ = 16; 13, 13′ = 15; compound **12**: 1, 14 = 1.5; 1, 3 = 1; 3, 3′ = 17; 5, 6 = 10; 8, 9 = 11; 8, 9′ = 5; 13, 13′ = 12; OCOR: 3′, 4′$_1$ = 1; 3′, 4′$_2$ = 1.5; 4′$_1$, 4′$_2$ = 1.5.

cordingly, **8** and **10** were 2β, 8α-diacetoxy derivatives with a conformation in which the 4-methyl group was above and the 10-methyl group was below the plane. Similar NOE-experiments with compound **9** showed that this lactone had the usual conformation with both methyls above the plane thus explaining the differences in the ^{1}H NMR spectra (Table 3). The ^{1}H NMR spectrum of **11** (Table 3) indicated the presence of a diepoxide. Spin decoupling allowed the assignment of all signals, while the couplings supported the proposed stereochemistry. We have named compound **11** vernonataloide.

The lactone **12** was isolated only in very minute amounts. The molecular formula was $C_{21}H_{24}O_7$ and the ^{1}H NMR spectrum (Table 3) indicated the presence of a flexible system. At elevated temperatures most signals were sharpened and spin decoupling showed that the proposed structure was very likely. We have named compound **12** natalensolide.

The roots of *V. stipulacea* Klatt. afforded tridecapentaynene, α-humulene, caryophyllene, linolenic acid, lupeol, stigmasterol, the dimeric isovalerate **13** [10], ferulic acid (**14**), the hydrocarbons **19–21**, the triacetylene **22** [11] and two isomeric sesquiterpene aldehydes **15** and **16**. Sodium boranate reduction of **15** afforded **18**, while acetylation of **16** gave **17**. The ^{1}H NMR spectral data (Table 4) showed that **15** and **16** were isomeric eudesma-4,7(11)-dienes with an aldehyde group at C-11 and a hydroxy group at C-1. The position of the latter followed from the results of spin decoupling, which led to the sequence **B**. As the chemical shift of H-6 was typically different in the spectra of **15** and **16**, the relative position of the aldehyde group could be assigned in the two isomers. The couplings of H-1 showed that an equatorial hydroxy group was present in both isomers, while the couplings of H-4 indicated a β-orientated methyl group. Although the absolute stereochemistry could not be determined, the proposed one was very likely, as all known eudesmane derivatives from the Compositae have this configuration. Compounds **15** and **16** have been named vernostipulal A and B respectively. The aerial parts of this plant gave lupeyl acetate and its Δ^{12}-isomer, linolenic acid and compound **22**. The latter was isolated previously from *V. appendiculata* from Malagasy [9], but it may be more widespread as detection is difficult due to its instability and the low intensity of the UV maxima. The results again show the diversity of this large genus. Probably the degree of evolution may be an explanation for the pronounced differences in the chemistry of those species so far investigated. The isolation of 5-methyl coumarins from two species may be an indication of a relationship of parts of the genus to *Ethulia*, *Erlangea* and *Bothriocline*.



B

EXPERIMENTAL

The air-dried plant material, collected in February 1981 in Transvaal (voucher deposited in the Botanic Research Institute, Pretoria) 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 comparing the ^{1}H NMR spectra with those of authentic material.

V. galpinii (*voucher* 81/69). The roots (400 g) gave 4 mg tridecapentaynene, 1 mg trideca-3,5,7,9-tetrayne-1,11-diene, 25 mg α-bergamotene, 25 mg β-bergamotene, 20 mg bisabolene, 200 mg **1**, 300 mg **2**, 10 mg **5** and 20 mg **6** ($AgNO_3$-coated Si gel; Et_2O–petrol, 1:20). The aerial parts

Table 4. ^{1}H NMR spectral data of compounds **15–18** (400 MHz, $CDCl_3$, TMS as internal standard)

	15	**16** $CDCl_3$–C_6D_6 (2:1)		**17**	**18**
H-1	3.40 *dd*	3.40 *dd*	3.18 *dd*	4.64 *dd*	3.33 *dd*
H-2α	—	1.85 *m*	1.56 *m*	1.87 *m*	—
H-2β	—	1.76 *dddd*	1.48 *dddd*	1.78 *m*	—
H-3	—	1.85 *m*	1.60 *m*	1.58 *m*	—
H-3′	—	1.12 *m*	0.88 *m*	1.15 *m*	—
H-4	—	2.39 *br ddq*	2.11 *br ddq*	2.41 *br ddq*	2.30 *m*
H-6	6.99 *d*	6.35 *d*	6.18 *d*	6.36 *d*	6.26 *br s*
H-8α	—	3.20 *ddd*	2.99 *ddd*	3.13 *ddd*	2.46 *ddd*
H-8β	—	2.53 *dddq*	2.23 *dddq*	2.53 *dddq*	2.30 *m*
H-9α	—	1.62 *ddd*	1.35 *ddd*	1.58 *m*	—
H-9β	—	1.99 *ddd*	1.72 *ddd*	1.88 *m*	—
H-12	1.83 *br s*	10.21 *s*	10.08 *s*	10.20 *s*	1.85 *br s*
H-13	10.38 *s*	1.85 *d*	1.79 *d*	1.85 *br s*	4.35 *d* 4.23 *d*
H-14	1.13 *s*	1.15 *s*	0.92 *s*	1.20 *s*	1.07 *s*
H-15	1.11 *d*	1.13 *d*	0.93 *d*	1.13 *d*	1.07 *d*

J(Hz): 1, 2α = 4.5; 1, 2β = 11; 2α, 2β = 13; 2β, 3α = 4; 2β, 3α ~ 12; 2β, 3β = 4; 3α, 4α ~ 5; 3β, 4α ~ 12; 4α, 6 = 1.5; 4α, 15 = 6.5; 8α, 8β = 15; 8α, 9α = 4; 8α, 9β = 5; 8β, 9α = 12; 9β, 9β = 4; 8β, 13 = 1.5; 9α, 9β = 13.

(380 g) afforded 1 mg tridecapentaynene, 10 mg germacrene D, 2 mg bicyclogermacrene, 20 mg lupeyl acetate, 4 mg **1**, and 4 mg **2**.

V. cinarescens (*voucher* 81/45). The roots (70 g) gave traces of tridecapentaynene, 2 mg α-humulene, 15 mg lupeol, 50 mg lupeyl acetate, 10 mg **3** (Et_2O–petrol, 1:10) and 15 mg **4**. The aerial parts (190 g) afforded traces of tridecapentaynene, 100 mg lupeol, 10 mg lupeyl acetate together with the Δ^{12}-isomers (*ca* 2:1) and traces of a sesquiterpene lactone, which could not be identified.

V. natalensis (*voucher* 81/243). The aerial parts (220 g) gave 10 mg germacrene D, 6 mg bicyclogermacrene, 150 mg lupeol, 50 mg lupeyl acetate together with the Δ^{12}-isomers (*ca* 5:1), 10 mg β-amyrin acetate, 5 mg lupenone, 4 mg stigmasterol, 5 mg spathulenol, 5 mg **7**, 3 mg **9**, 2 mg **11** and 1 mg **12** (lactones separated by repeated TLC; Et_2O–petrol, 3:1 and 1:1).

V. stipulacea (*voucher* 81/88). The roots (100 g) afforded 2 mg tridecapentaynene, 5 mg linolenic acid, 2 mg α-humulene, 10 mg lupeol, 2 mg stigmasterol, 3 mg caryophyllene, 3 mg **13**, 2 mg **14**, 1 mg **15** and 3 mg **16** (Et_2O–petrol, 1:1), 2 mg **19**, 2 mg **20**, 2 mg **21** and 3 mg **22**. The aerial parts (400 g) gave 50 mg lupeyl acetate and 20 mg of its Δ^{12}-isomer, 20 mg linolenic acid and 6 mg **22**.

Preethulia coumarin (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1640, 1620, 1610, 1570 (coumarin), 3080, 920 (CH=CH_2); MS *m/z* (rel. int.): 310.157 $[M]^+$ (4) ($C_{20}H_{22}O_3$), 295 $[M-Me]^+$ (7), 228 $[M-H_2C{=}CHCH{=}CMe_2]^+$ (100), 213 $[228-Me]^+$ (11).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+54 \quad +59 \quad +69 \quad +150} \ (CHCl_3;\ c\ 0.53).$$

Dauca-2,11(13)-*diene* (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3075, 1640, 905 (C=CH_2), 1460, 1450, 1395; MS *m/z* (rel. int.): 204.188 $[M]^+$ (70) ($C_{15}H_{24}$), 189 $[M-Me]^+$ (62), 163 (13), 161 (21), 147 (28), 134 (36), 133 (35), 121 (69), 119 (41), 107 (51), 93 (100), 91 (31).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+13 \quad +13 \quad +14 \quad +19} \ (CHCl_3;\ c\ 1.1).$$

1,10-*Desoxidoglaucolide E* (**7**). Colourless crystals, mp 73°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1744, 1240 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 432.178 $[M]^+$ (0.5) ($C_{23}H_{28}O_8$), 390 $[M-ketene]^+$ (2), 372 $[M-HOAc]^+$ (1), 346 $[M-RCO_2H]^+$ (0.3), 312 $[372-HOAc]^+$ (2), 286 $[346-HOAc]^+$ (5), 244 $[286-ketene]^+$ (19), 226 $[286-HOAc]^+$ (52), 211 $[226-Me]^+$ (17), 69 $[C_3H_5CO]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+7 \quad +7 \quad +10 \quad +61} \ (CHCl_3;\ c\ 0.09).$$

Vernonataloide (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750, 1235 (OAc), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 346.142 $[M-HOAc]^+$ (2) ($C_{19}H_{22}O_6$), 320 $[M-RCO_2H]^+$ (4), 260 $[346-RCO_2H]^+$ (22), 245 $[260-Me]^+$ (12), 69 $[C_3H_5CO]^+$ (100).

Natalensolide (**12**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1750, 1230 (OAc), 1720 (C=CCO_2R), 1710 (C=CCO); MS *m/z* (rel. int.): 388.152 $[M]^+$ (0.5) ($C_{21}H_{24}O_7$), 328 $[M-HOAc]^+$ (0.5), 242 $[328-RCO_2H]^+$ (6), 69 $[C_3H_5CO]^+$ (100); CI (*iso*-butane): 389 $[M+1]^+$ (100), 303 $[389-RCO_2H]^+$ (15), 243 $[303-HOAc]^+$ (48).

Vernostipulal A (**15**). Colourless gum, not free from **13**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1660, 1610 (C=CCHO); reduction with $NaBH_4$ in MeOH (room temp. 5 min) afforded **18**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3530 (OH); MS *m/z* (rel. int.): 236.177 $[M]^+$ (41) ($C_{15}H_{24}O_2$), 218 $[M-H_2O]^+$ (53), 203 $[218-Me]^+$ (8), 185 $[203-H_2O]^+$ (31), 133 $[C_{10}H_{13}]^+$ (100).

Vernostipulal B (**16**). Colourless gum, UV $\lambda_{max}^{Et_2O}$ nm: 295, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 2760, 1660, 1612 (C=CCHO); MS *m/z* (rel. int.): 234.162 $[M]^+$ (48) ($C_{15}H_{22}O_2$), 216 $[M-H_2O]^+$ (54), 201 $[216-Me]^+$ (26), 187 $[216-CHO]^+$ (16), 55 (100).

To 3 mg **16** in 1 ml CH_2Cl_2, 0.1 ml Ac_2O and 10 mg 4-pyrrolidino pyridine was added. Usual work-up afforded 2 mg **17**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1660 (C=CCHO), 1740, 1245 (OAc); MS *m/z* (rel. int.): 276.172 $[M]^+$ (16) ($C_{17}H_{24}O_3$), 234 $[M-ketene]^+$ (21), 216 $[M-HOAc]^+$ (100), 201 $[216-Me]^+$ (36), 187 $[216-CHO]^+$ (24).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-103 \quad -109 \quad -132 \quad -372} \ (CHCl_3;\ c\ 0.14).$$

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