Phytochemistry, 1981, Vol. 20, pp. 473–480. © Pergamon Press Ltd. Printed in England. 0031-9422/81/030473-08 $02.00/0

ALLENIC GERMACRANOLIDES, BOURBONENE DERIVED LACTONES AND OTHER CONSTITUENTS FROM *VERNONIA* SPECIES*

Ferdinand Bohlmann,† Jasmin Jakupovic,† Rajinder K. Gupta,† Robert M. King† and Harold Robinson‡

† Institute for Organic Chemistry, Technical University Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, W. Germany; ‡ Smithsonian Institution, Washington, DC 20560, U.S.A.

(*Revised received* 19 *May* 1980)

Key Word Index—*Vernonia* species; Compositae; sesquiterpene lactones; allenic germacranolides; bourbonene derived lactones; new glaucolides; furansesquiterpenes; nerolidol derivatives; eudesmanes.

Abstract—An investigation of seven *Vernonia* species, mainly from northern Brazil, afforded in addition to known compounds three new unusual sesquiterpene lactones with an allenic group. Intensive NMR studies fully established the structures. Furthermore, two lactones derived from bourbonene, two new glaucolides, a new furansesquiterpene, a nerolidol derivative and two other sesquiterpenes derived from eudesmane were isolated. The biogenetic relationships of the sesquiterpene lactones present in *Veronia* species as well as the chemotaxonomic aspects are discussed.

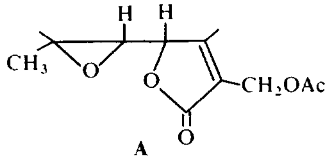
INTRODUCTION

The extremely large genus *Vernonia* (Vernonieae; Compositae) has been extensively investigated chemically [1], In addition to the widespread occurrence of triterpenes, highly oxygenated germacranolides are typical for many species of this genus. Lactones without a 11,13-exo-methylene group, as found in the glaucolides and hirsutinolides, are very common. So far, sesquiterpene lactones have been isolated from 65 species. We have now investigated seven further species, most of them native in Brazil and report the results below.

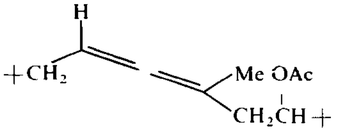
RESULTS AND DISCUSSION

The aerial parts of *Vernonia lilacina* Mart. contain germacrene D, α-humulene, caryophyllene, lupeyl acetate and three sesquiterpene lactones, one being identical with the known allenic lactone, vernonallenolide (**15**), which we isolated earlier in minute amounts from *V. cotoneaster* [2]. Though the amount of material was not sufficient to establish the structure rigorously, the NMR data showed the allenic structure.

The two other lactones were isomers and from the data obviously are the allenic germacranolides **16** and **17**; the IR-band at 1965 cm^{-1} supports their allenic nature. The ^{1}H NMR data of **16** (see Table 1) are very similar to those of **15**, but the olefinic signal at 4.69 ppm is replaced by a doublet at 2.65 which is coupled with a broadened doublet at 4.93. Irradiation of this signal collapses the double doublet at 4.84 (13-H) to a doublet and therefore must be assigned to 6-H. Consequently the 2.65 signal is assigned to 5-H and therefore a 4,5-epoxide must be present. Further double resonance experiments show that the allenic proton is coupled with signals at 2.24 (*dd*), 1.95 (*dd*), 2.96 (*ddd*) and 1.61 (*d*). The signal at 2.96 further is coupled with double doublets at 2.27 and 5.06. The latter must be assigned to 8-H. Furthermore there is a methyl singlet for a tertiary methyl (1.56) which must be placed on an oxygen-bearing carbon, and there are two acetate methyl signals. The sequences **A** and **B** therefore must be present.



A



B

The combination of these fragments leads to the structure **16**, assuming a normal carbon skeleton is present, and this is supported by the chemical shifts of the methylene protons, which are coupled with that from the allenic group. A position between two unsaturated groups would result in a reversed combination which should be accompanied with a downfield shift. The ^{13}C NMR spectrum also clearly establishes the proposed structure. A gated decoupled spectrum allows estimation of all couplings (see Table 1), which are in good agreement with those expected [3]. Also the chemical shifts agree with those of model compounds [3]. Only the signals for C-3 and C-9 could not be assigned with certainty. The upfield shifts of the C-8 and C-13 signals are surely due to a large γ-effect. Dreiding-models show that the observed

---

* Part 296 in the series 'Naturally Occurring Terpene Derivatives'. For Part 295 see: Bohlmann, F. and Ziesche, J. (1980) *Phytochemistry* **19**, 2681.

Table 1. NMR data of **15–17** [270 respectively 67.9 (^{13}C) MHz, TMS as internal standard]

	15	**16** ($CDCl_3$)	$CDCl_3/C_6D_6$, 77°	**17** ($CDCl_3$)	**16** (^{13}C, $CDCl_3$)		*J* (Hz)	**17** (^{13}C, $CDCl_3$)
2-H	5.38 *m*	5.31 *dddq*	5.12 *dddq*	5.43 *m*	C-1	204.0 *m*		200.2 *s*
3α-H	2.29 *dd*	1.95 *dd* (*br.*)	1.83 *dd* (*br.*)	2.05 *dd*	C-2	88.5 *dd*	168, 6.5, 6.5	87.8 *d*
3β-H	2.90 *dd*	2.24 *dd*	2.04 *dd*	2.67 *dd*	C-3	35.2**t* (*br.*)*	133	40.7 *t*
5-H	4.69 *d* (*br.*)	2.65 *d*	2.57 *d*	6.39 *s*	C-4	61.6 *tq*	6, 6	73.7 *s*
6-H	5.92 *d* (*br.*)	4.93 *d* (*br.*)	4.90 *d* (*br.*)	—	C-5	61.2 *dtq*	178, 4, 4	131.0 *d*
8β-H	4.97 *dd*	5.06 *dd*	5.08 *dd*	5.99 *dd*	C-6	82.8 *d*	156	146.4 *s*
9α-H	2.19 *dd*	2.27 *dd*	2.20 *dd*	2.24 *ss* (*br.*)	C-7	163.5 *ddt*	~10, 6, 6	152.4 *s*
9β-H	2.92 *d* (*br.*)	2.96 *ddd*	2.77 *ddd*	3.00 *ddd*	C-8	67.5 *dt*	152, 7	68.1 *d*
13-H	4.98 *d*	4.98 *d*	4.90 *d*	5.11 *d*	C-9	36.5 *t* (*br.*)*	133	37.7 *t*
13′-H	4.87 *dd*	4.84 *dd*	5.00 *dd*	5.00 *dd*	C-10	95.3 *tq*	~4, 6	94.5 *s*
14-H	1.65 *d*	1.61 *d* (*br.*)	1.50 *dd*	1.64 *d* (*br.*)	C-11	127.5 *ddt*	~7, 7, 7	128.2 *s*
15-H	1.99 *d*	1.56 *s*	1.49 *s*	1.85 *s*	C-12	171.1 *t*	5	169.3 *s*†
OAc	2.11 *s*	2.05 *s*	1.88 *s*	2.11 *s*	C-13	55.0 *t*	150	55.6 *t*
	2.05 *s*	1.99 *s*	1.78 *s*	2.09 *s*	C-14	18.2 *qtt*	128, 4, 2.5	19.5 *q*†
					C-15	21.3 *q* (*br.*)	129	27.3 *q*
					OAc	169.9 *q*	7	169.3 *s*†
						20.3 *q*	129	20.3 *q*†
						170.1 *q*	7	170.1 *s*†
						20.6 *q*	129	20.6 *q*†

* May be interchangeable.

† Uncertain assignments.

J (Hz): **16**: 2, 3β = 8 (in $CDCl_3$: 4), 2, 3α = 3.5; 2, 9β = 4; 2, 14 = 3; 3α, 3β = 14.5; 5, 6 = 9; 6, 13′ = 1; 8, 9α = 12; 8, 9β = 4; 9α, 9β = 14; 13, 13′ = 12; **17**: 2, 3α = 6; 2, 3β = 7; 2, 9β = 4; 2, 14 = 3; 3α, 3β ~ 14; 8, 9α = 12; 8, 9β = 4; 9α, 9β = 14.5; 13, 13′ = 12.

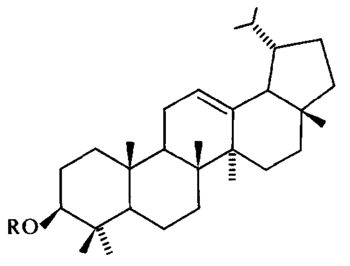
Table 2. NMR data of **18a** and **b** (270 MHz, TMS as internal standard)

	18a ($CDCl_3$)		**18b**	**18a** Δ*	**18a** (C_6D_6)		**18b**	**18a** (^{13}C, $CDCl_3$)			
1-H		2.55 *ddd*		0.22		2.03 *m*		C-1	42.6 *d*	C-11	140.1 *s*
2α-H		2.13 *m*		~0.5		1.38		C-2	24.1 *t*	C-12	168.0 *s*
2β-H		1.79 *dddd*		0.23				C-3	43.5 *t*	C-13	128.0 *t*
3α-H		2.13 *m*		~0.5		2.03		C-4	95.7 *s*	C-14	22.5 *q*
3β-H		1.65 *m*	2.97 *d*	0.28		1.17 *m*		C-5	55.9 *d*	C-15	24.7 *q*
5-H	2.96 *d*			0.52	2.50 *d*		2.49 *d*	C-6	100.1 *s*	C-1′	167.5 *s*
8β-H		4.99 *dd*		3.07	5.04 *dd*		4.95 *dd*	C-7	100.9 *s*	C-2′	128.3 *s*
9α-H		2.14 *dd*		0.58		1.90 *dd*		C-8	79.2 *d*	C-3′	137.9 *d*
9β-H		2.27 *dd*	6.47 *s*	0.73		2.09 *dd*		C-9	40.7 *t*	C-4′	14.4 *q*
13-H	6.44 *s*		6.28 *s*	1.26	6.46 *d*†		6.47 *d*†	C-10	45.6 *s*	C-5′	12.1 *q*
13′-H	6.23 *s*			1.20	6.30 *d*†		6.33 *d*†				
14-H		1.34 *s*		0.49	1.10 *s*		1.09 *s*				
15-H		1.31 *s*	6.22 *s* (*br.*)	0.12	1.09 *s*		1.08 *s*				
OCOR	6.96 *qq*		5.65 *dq*	1.61	7.03 *qq*		6.26 *s* (*br.*)				
	1.84 *dq*		2.00 *dd*	0.32	1.85 *dq*		5.29 *dq*				
	1.89 *dq*			1.05	1.44 *dq*		1.89 *dd*				

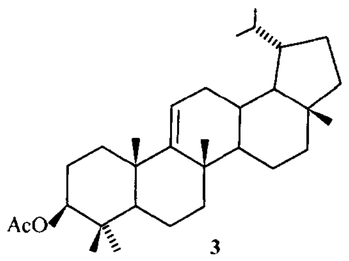
* Δ-values after addition of $Eu(fod)_3$.

† $J = 0.7$ Hz.

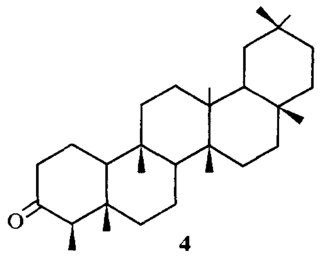
J (Hz): 1, 2α = 4.5; 1, 2β = 10; 1, 5 = 10; 2α, 2β = 13; 8, 9α = 9.5; 8, 9β = 6.5; 9α, 9β = 15.



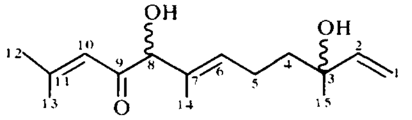
1 R = H
2 R = Ac



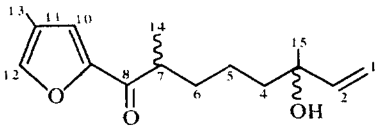
3



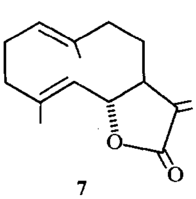
4



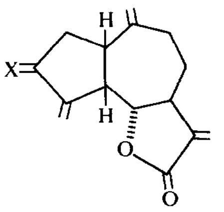
5



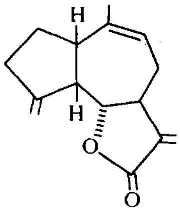
6



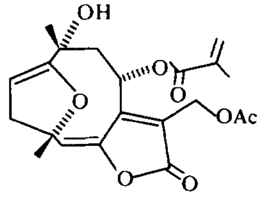
7



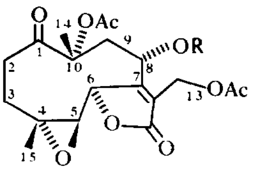
8 X = H_2
9 X = O
10 X = *β*OH, H
11 X = *β*OSen, H



12



13

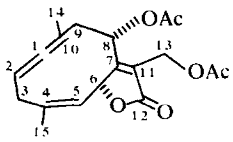


14a R = COEt
14b R = Ac

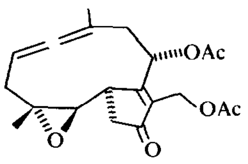
couplings would agree with a normal germacranolide conformation for **16** with both methyl groups (C-4 and C-10) above the plane. It may be noted that the magnitude of the allenic couplings $J_{2,9\alpha}$ and $J_{2,14}$ are remarkably high.

The structure of the third lactone, isomeric with **16**, also clearly follows from the spectroscopic data. The IR spectrum indicates that a hydroxyl group is present, while the ^{1}H NMR spectrum (see Table 1) displays a sharp singlet at 6.39, typical for an enol-lactone [4]. Though most of the other signals are shifted, when compared with those of **16**, the pattern is very similar. Again double resonance experiments establish the assignments of the signals. Also the ^{13}C NMR data (see Table 1) support the structure **17**, though several signals could not be assigned with certainty due to the small amount of material available. Furthermore a triacetate was isolated. From the ^{1}H NMR spectrum the structure **19** was deduced, a lactone closely related to glaucolide E, only the ester residue at C-8 being replaced by an acetoxy group. Spin decoupling allowed the assignment of all signals (see Table 3). The roots of *V. lilacina* only afforded lupeyl acetate and stigmasterol.

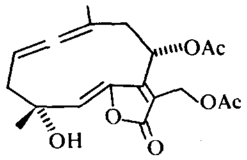
The aerial parts of *V. arkansana* DC., grown from seeds, also afforded lupeyl acetate together with the isomers **2** and **3**. The polar fractions, however, afforded two lactones, which only could be separated by (reversed phase) HPLC. The spectral data lead to the structures **18a** and **b** (see Table 2), both being lactones related to bourbonene. The ^{1}H NMR data show that both compounds obviously only differ in their ester residues, **18a** having a tiglate and **18b** a methylacrylate group. The ^{1}H NMR spectra further show that the lactones have two tertiary methyls and methylene



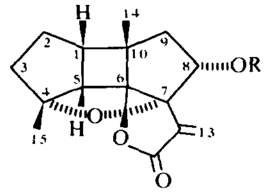
15



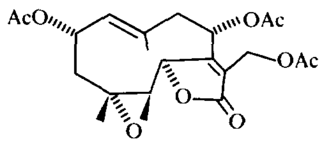
16



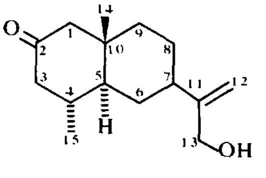
17



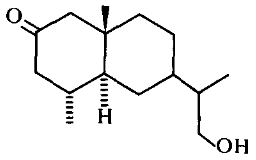
18a R = Tigl
18b R = Meacr



19



20



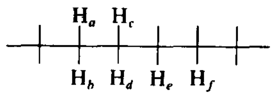
21

Table 3. ^{1}H NMR data of **14a**, **14b** and **19** (270 MHz, TMS as internal standard)

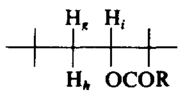
	14a		**14b**	**19**
	$CDCl_3$	C_6D_6 80°	C_6D_6 80°	
1-H	—	—	—	5.58 *dqd*
2-H	2.75 *m*	2.42 *ddd*	2.51 *ddd*	5.69 *ddd*
2'-H		2.21 *ddd* (*br.*)	2.22 *ddd* (*br.*)	—
3-H	1.6 *m*	1.38 *m*	1.38 *m*	2.27 *dd*
3'-H	—	—	—	1.84 *dd* (*br.*)
5-H	2.75 *m*	2.28 *d*	2.36 *d*	2.32 *d*
6-H	4.9 *m*	4.74 *d* (*br.*)	4.74 *d* (*br.*)	4.89 *d* (*br.*)
8-H		4.90 *dd*	4.85 *dd*	5.14 *dd*
9-H	2.75 *m*	2.51 *dd*	2.52 *dd*	2.98 *dd* (*br.*)
9'-H	2.35 *m*	2.00 *d* (*br.*)	2.04 *d* (*br.*)	2.48 *dd*
13-H	4.93 *d*	4.98 *dd*	4.95 *dd*	5.07 *d*
13'-H	4.82 *d*	4.85 *dd*	4.83 *dd*	4.89 *d*
14-H	1.65 *s*	1.53 *s*	1.52 *s*	1.69 *s* (*br.*)
15-H				1.59 *s*
OAc	2.13 *s*	1.80 *s*	1.80 *s*	2.12 *s*
	2.06 *s* (*br.*)	1.68 *s*	1.68 *s*	2.08 *s*
			1.72 *s*	2.07 *s*
OCOEt	2.36 *q*	2.02 *q*		
	2.35 *q*	2.03 *q*		
	1.14 *t*	0.92 *t*		

J (Hz): **14a**: 2,2' = 16; 2,3 = 10; 2,3' = 4.5; 2',3 = 4; 2',3' = 10; 5,6 = 10; 6,13 = 1; 8,9 = 8; 7,9' = 2; 9,9' = 16; 13,13' = 13; 2',3' = 7; **19**: 1, 2 = 8; 1, 9 = 1, 14 ~ 1; 2, 3 = 2; 2, 3' = 8; 3, 3' = 15; 5, 6 = 9; 8, 9 = 5; 8, 9' = 12; 9, 9' = 13; 13, 13' = 12.5.

protons, which display singlets in $CDCl_3$, while in C_6D_6 a geminal coupling can be observed. Careful double resonance experiments led to the further partial structures **C** and **D**.



C



D

Together with the other parts and the assumption, that the carbon skeleton is that of a normal sesquiterpene lactone only a few possibilities remain. As the signals of H_e and H_f occur at relatively low field, a four membered ring is very likely. The IR band at 1788 cm^{-1} indicates a γ-lactone, while in the ^1H NMR spectrum no downfield signal is visible, except those for H_i and the methylene protons. This requires that all other carbon oxygen bonds must be tertiary. Furthermore obviously there is no proton at the carbon next to the methylene group. The ^{13}C NMR spectrum of **18a** (see Table 2) displays several downfield singlets, which only can be assigned to oxygen-bearing carbons (95.7, 100.1, 100.9 ppm) and not to olefinic ones. Together with the other signals reported **18a** appears to be a pentacyclic compound. The only explanation for the chemical shifts of these signals therefore are strong α- and β-effects on the oxygen bearing carbons. The proposed structure **18a** therefore seems to be the only plausible one, though no ^{13}C values are available of similar compounds. The mass spectra are also in agreement with the structure proposed. Most pronounced is the fragment *m/e* 81 ($C_6H_9^+$), which probably is formed by splitting of the 1—10, 5—6 and 4—*O* bonds (formation of a methylcyclopentenyl cation) and elimination of ethylene probably from the carbons 2 and 3.

The roots of this plant contain the widespread tridecapenta-3.5.7.9.11-yn-1-ene, germacrene A, caryophyllene, sitosterol, costunolide (**7**), dehydrocostus-lactone (**8**) [5] dehydro-zaluzanin C (**9**) [6], zaluzanin C (**10**) [6] and the corresponding senecioate (**11**) [4].

The aerial parts of *V. lanuginosa* Gardn. afforded germacrene D, α-humulene, caryophyllene, lupeol, and small amounts of a new glaucolide, the propionate **14a**, as can be easily seen from the ^1H NMR in C_6D_6 at higher temperatures if compared with that of glaucolide B (**14b**) [7]. Only the splitting of the propionate methylene protons is somewhat unusual, but is obviously due to the asymmetric center at C-8. The roots gave, in addition to lupeyl acetate, minor quantities of the two eudesmane derivatives **20** and **21**. Their structures follow from the ^1H NMR data, especially if compared with those of costol [9] and similar compounds (see Table 4). The position of the keto group and the α-orientation of the 4-methyl group clearly can be assigned from the observed couplings of the protons next to them.

The aerial parts of *V. polyanthes* Less. afforded tridecapentaynene, germacrene D, bicyclogermacrene, α-humulene, lupeyl acetate and its isomer **2**, stigmasterol and the hirsutinolide **13** [4], while the roots contain in addition to germacrene D, α-humulene, lupeyl acetate and **2**, the two sesquiterpenes **5** and **6**. Their structures again follow from the ^1H NMR data (see Table 5). The presence of a 2,4-disubstituted furanoketone can easily be deduced from the chemical shifts of the broadened singlets at 7.04 and 7.35 ppm and the other end groups can be assigned by the typical vinylic proton signals. The chemical shifts are characteristic for a compound with a neighbouring tertiary hydroxyl. The position of the secondary methyl group is clearly indicated by the lowfield triplet of quartets at 3.20 ppm. Also the mass spectrum supports the structure **6**, the absolute and relative configuration at C-3 and C-7 not being estimated. The ^1H NMR data of **5** first led to some problems as the signals around 4.5 ppm did not directly indicate a clear assignment. However, as the signal separates on heating, the participation of hydroxyl became obvious. Furthermore the vinyl proton signals, very similar to those of **5**, are all split, indicating an epimeric mixture. Although the relative configuration at

Table 4. ^1H NMR data of **20** and **21** (270 MHz, TMS as internal standard, $CDCl_3$)

	20	**21**
1α-H	2.17 *d*	2.19 *d*
1β-H	2.10 *dd*	2.12 *dd*
	2.00 *dd*	2.01 *dd*
3β-H	2.37 *ddd*	2.39 *ddd*
12-H	0.96 *d*	5.06 *dt*
12′-H		4.92 *s* (*br.*)
13-H	3.66 *dd*	4.16 *s* (*br.*)
13′-H	3.54 *dd*	
14-H	0.79 *s*	0.84 *s*
15-H	1.00 *d*	1.00 *d*

J (Hz): **20/21**: 1α, 1β = 14; 1β, 3β = 2; 3α, 3β = 14; 3α, 4β = 13; 3β, 4β = 4; 4β, 15 = 7; **20**: 11, 12 = 7; 11, 13 = 5.5; 13, 13′ = 10; **21**: 7, 12 = 12, 13 ~ 1.5; (6α-H 1.88 *d* (*br.*) (*J* = 13), 6β-H 1.11 *dd* (*J* = 13, 13), 7-H 2.10 *m*).

Table 5. ^1H NMR data of **5** and **6** (270 MHz, TMS as internal standard)

	5a (C_6D_6)	**5b**	**6** ($CDCl_3$)
1t-H	5.20 *dd*	5.19 *dd*	5.16 *dd*
1c-H	4.98 *dd*	4.97 *dd*	5.03 *dd*
2-H	5.74 *dd*	5.73 *dd*	5.88 *dd*
4-H	1.38 *m*		1.4–1.8 *m*
5-H	2.09 *m*		
6-H	5.53 *t*(*br*)		3.20 *tq*
7-H			
8-H	4.53 *d*		—
10-H	6.08 *qq*		7.35 *s* (*br.*)
12-H	1.46 *d*	1.45 *d*	9.04 *s* (*br.*)
13-H	2.12 *d*		2.09 *s* (*br.*)
14-H	1.57 *s* (*br.*)		1.18 *d*
15-H	1.11 *s*		1.26 *s*
OH	4.48 *d**		—

* At 80° 4.23.

J (Hz): **5a/5b**: 1t, 1c = 1.5; 1t, 2 = 17; 1c, 2 = 10.5; 5, 6 = 7; 8, OH = 4; 10, 12 = 10, 13 = 1.5; **6**: 1t, 1c ~ 1; 1t. 2 = 17; 1c, 2 = 10.5; 6, 7 = 7, 14 = 7.

C-3 and C-8 has not been estimated, the proposed structure seems to be true and is strongly supported by the mass spectrum (see Experimental). We have named **5** vernopolyanthone and **6** vernopolyanthofuran.

We also have isolated **6** from the aerial parts of *V. fagifolia* Gardn. together with lupeol, its acetate and stigmasterol, while the roots gave γ- and δ-cadienene, germacrene D, caryophyllene, lupeol, its acetate and the isomer **1**.

The roots of *V. chinensis* Less. afforded dehydro zaluzanin C (**19**) and the senecioate **11**, while the aerial parts only gave sitosterol, lupeol, its acetate, the isomer **1** and its acetate as well as the isomer **3** The roots of *V. alvimii* H. Robins, afforded lupeol and its acetate, while the aerial parts gave germacrene D, caryophyllene, lupeol and its acetate as well as friedelin (**4**).

If we examine the structures of the new lactone types described above and those known before from *Vernonia* we may speculate on the biogenetic pathways in this genus. Unfortunately, the usual configurations reported for glaucolide A and B are opposite to those of glaucolide D, E, G and marginatin [1]. Identical configurations at C-4 through C-8, however, are very likely and most probably the absolute configurations of all these lactones is the same as those for glaucolide D, E and G, since nearly all lactones from Vernonieae have the 6*β*-H configuration as established by X-ray [8]. We have therefore shown the lactones **13**, **14a**, **14b** and **15**–**19** in this configuration. Although not all the species investigated contain typical highly oxygenated germacranolides these compounds are obviously important markers perhaps for the whole tribe. Further investigations may show whether there are indications of different subgroups but so far the taxonomy of the tribe is complicated [10].

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as internal standard; MS: 70 eV, direct inlet, optical rotation: $CHCl_3$. The plant material from the Brazilian species was extracted after air drying while those grown from seed were extracted fresh, both with Et_2O–petrol, 1 : 2. The resulting extracts were first separated by column chromatography (SiO_2, act. grade II). The extracts of the aerial parts were first treated with MeOH to remove long chain saturated hydrocarbons. The resulting fractions of different polarity were further separated by TLC (SiO_2, GF 254). Known compounds were identified by comparison of their IR- and ^{1}H NMR spectra with those of authentic specimens.

Vernonia lilacina (*voucher RMK* 8113). The roots (15 g) afforded 50 mg lupeyl acetate and 20 mg stigmasterol, while the aerial parts (120 g) gave 50 mg germacrene D, 50 mg α-humulene, 20 mg caryophyllene, 100 mg lupeyl acetate, 10 mg **15**, 55 mg **16** (Et_2O–petrol, 1:1), 8 mg **17** (Et_2O–petrol, 1:1) and 5 mg **19** (Et_2O–petrol, 3:1).

Vernonia arkansana (*voucher* 79/1395, *from seeds Botanical Garden Zagreb*). The roots (100 g) afforded 0.1 mg tridecapentaynene, 5 mg germacrene A, 5 mg caryophyllene, 5 mg **7**, 5 mg **8**, 10 mg **9**, 20 mg **10**, 10 mg **11** and 20 mg sitosterol, while the aerial parts (600 g) gave 20 mg lupeyl acetate, 20 mg **2**, 10 mg **3** and 10 mg of a mixture of **18a** and **b** (Et_2O–petrol, 1:1) (*ca* 3:1), which were separated by HPLC (reversed phase, MeOH–H_2O (7:3).

Vernonia lanuginosa (*voucher RMK* 8025). The roots (50 g) afforded 50 mg lupeyl acetate, 4 mg **20** (Et_2O–petrol, 1:1) and 3 mg **21** (Et_2O–petrol, 1:1), while the aerial parts (100 g) gave 50 mg germacrene D, 50 mg α-humulene, 100 mg caryophyllene, 50 mg lupeol and 4 mg **14a** (Et_2O–petrol, 3:1).

Vernonia polyanthes (*voucher RMK* 8072). The roots (1.8 kg) afforded 10 mg germacrene D, 50 mg α-humulene, 200 mg lupeyl acetate, 100 mg **2**, 6 mg **5** (Et_2O–petrol, 3:1) and 30 mg **6** (Et_2O–petrol, 3:1), while the aerial parts gave 5 mg tridecapentaynene, 50 mg germacrene D, 50 mg bicyclogermacrene, 15 mg α-humulene, 50 mg lupeyl acetate, 50 mg **2**, 10 mg stigmasterol and 10 mg **13**.

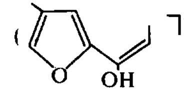
Vernonia fagifolia *Gardn*. (*voucher RMK* 8072). The roots (370 g) afforded 150 mg lupeyl acetate, 100 mg lupeol, 10 mg stigmasterol and 4 mg **6**, while the aerial parts (240 g) gave 5 mg germacrene D, 20 mg caryophyllene, 5 mg γ- and 5 mg σ-cadinine, 100 mg lupeyl acetate, 100 mg lupeol and 50 mg **2**.

Vernonia chinensis *Less*. (*voucher* 79/1414, *seeds from Botanical Garden Krakau*). The roots (100 g) afforded 50 mg **9** and 20 mg **11**, while the aerial parts (150 g) gave 20 mg sitosterol, 10 mg lupeyl acetate, 10 mg lupeol, 10 mg **1**, 10 mg **2**, and 10 mg **3**.

Vernonia alvinii (*voucher RMK* 7911). The roots (30 g) afforded 50 mg lupeol and 50 mg lupeyl acetate, while the aerial parts (400 g) gave 20 mg germacrene D, 20 mg caryophyllene, 50 mg lupeol, 50 mg lupeyl acetate and 100 mg **4**.

Vernopolyanthone (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1690, 1625 (C=CCO); MS: M$^+$ *m/e* –; 234.162 (1 %) ($C_{15}H_{22}O_2$, M – H_2O); 151 (8) (234 – COCH=ICMe$_2$); 83 (100) ($Me_2C{=}CHCO^+$); CI (isobutane): 253 (15 %) (M + 1); 235 (61) (M + 1 – H_2O); 83 (100) ($Me_2C{=}CHCO^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+27.5 \quad +29.7 \quad +34.5 \quad +79.7} (c = 0.6).$$

Vernopolyanthofuran (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1680, 1565 (furan ketone); MS: M$^+$ *m/e* 250.157 (8 %) ($C_{15}H_{22}O_3$); 232 (4) (M – H_2O); 180 (19) (M – O=C-(Me)CH=CH_2); 138 (100) , McLafferty); 109 (62) (138 – C_2H_5); 71 (36) (MeC(OH)CH=CH_2).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-1.4 \quad -1.0 \quad -1.0 \quad -2.6} (c = 3.0).$$

8-O-*Desacetyl*-8-O-*glaucolide B propionate* (**14a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1750, 1245 (OAc, CO_2R); MS: M$^+$ *m/e* –; 410.158 (0.5 %) ($C_{20}H_{26}O_8$, M – ketene); 379 (1) (M – OCOEt); 318 (1) (M – AcOH, EtCO_2H); 276 (9) (318 – ketene); 122 (51); 57 (100) ($EtCO^+$); CI (isobutane): 453 (100 %) (M + 1); 393 (38) (M + 1 – AcOH).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-104 \quad -109 \quad -124 \quad -214} (c = 0.2).$$

4*α*-5*β*-*Epoxy*-4,5-*dihydrovernonallenolide* (**16**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1965 (allene), 1780 (γ-lactone), 1750, 1235 (OAc); MS: M$^+$ *m/e* –; 319 (1) (M – $MeCO^{\cdot}$); 302.115 (22 %) ($C_{17}H_{18}O_5$, M – AcOH); 43 (100) ($MeCO^+$); CI (isobutane): M + 1 363 (72 %); 303 (33) (M – 1 – AcOH); 243 (75) (303 – AcOH); 219 (100).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-12.8 \quad -13.6 \quad -17.0 \quad -37.0} (c = 5.4).$$

4*β*-*Hydroxy*-4,5-*dihydro*-5,6-*dehydrovernonallenolide* (**17**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1965 (allene), 1770 (γ-lactone), 1759, 1235 (OAc); MS: M$^+$ *m/e* (rel. int.): 362 (0.5); 302.115 (9) ($C_{17}H_{18}O_5$, M – AcOH); 259 (43) (302 – $MeCO^{\cdot}$); 243 (58) (302 – $MeCO_2^{\cdot}$); 199 (100) (243 – CO_2).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+118 \quad +123 \quad +142 \quad +253} (c = 0.7).$$

8α-Tiglinoyloxy-1β,5βH-4α,7α-epoxybourbon-11(13)-en-6,12-olide (**18a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1788 (γ-lactone); 1725, 1655 ($C{=}CCO_2R$); MS: M^+ *m/e* (rel. int.): 344.162 (4%) ($C_{20}H_{24}O_5$); 316 (2) ($M - C_2H_4$); 301 (1) (316 − Me); 244 ($M - RCO_2H$); 216 (2) ($244 - C_2H_4$); 83 (100) ($C_4H_7CO^+$ 83); 81 (43) ($C_6H_9^+$); 55 (69) (83 − CO).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+16.8 \quad +18.0 \quad +20.4 \quad +36.4}\,(c = 0.5).$$

8α-(2-Methylacryloyloxy)-1β,5βH-4α,7α-epoxybourbon-11(13)-en-6-12-olide (**18b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1788 (γ-lactone); 1725, 1655 ($C{=}CCO_2R$); MS: M^+ *m/e* (rel. int.): 330.147 (2%) ($C_{19}H_{22}O_5$); 302 (6) ($M - C_2H_4$); 244 (9) ($M - RCO_2H$); 81 (100) ($C_6H_9^+$); 69 (75) ($C_3H_5CO^+$).

8-O-Desacyl-glaucolide E-acetate (**19**). Colourless crystals, mp 149–50°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1745, 1260 (OAc); MS: M^+ *m/e* (rel. int.): 422 (0.3%); 362.137 (20) ($C_{19}H_{22}O_7$); 320 (8) (362 − ketene); 260 (44) (320 − AcOH); 242 (40) ($260 - H_2O$); 190 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-69.2 \quad -72.2 \quad -83.8 \quad -158.0}\,(c = 1.0).$$

13-Hydroxy-4β,15H-α-selinen-2-one (**20**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1720 (C=O); 3090, 1650, 910 ($C{=}CH_2$); MS: M^+ *m/e* (rel. int.): 236.178 (42%) ($C_{15}H_{22}O_2$); 218 (32) ($M - H_2O$); 195 (52); 177 (47); 109 (84); 95 (96); 79 (83); 69 (94); 55 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+41 \quad +42 \quad +51 \quad +107}\,(c = 0.25).$$

13-Hydroxy-4β,15,11,13H-α-selinen-2-one (**21**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH; 1720 (C=O); MS: M^+ *m/e* (rel. int.): 238.193 (38%) ($C_{15}H_{24}O_2$); 220 (17) ($M - H_2O$); 180 (29) ($M - CH(Me)CH_2CH$); 109 (60); 95 (100); 69 (83); 55 (79).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+20 \quad +22 \quad +24 \quad +52}\,(c = 0.22).$$

Acknowledgements—We thank Dr. Scott A. Mori and Dr. P. Alvim, Centro de Pesquisas at Itabuna, Bahia, Brazil for their help during plant collection, the Deutsche Forschungsgemeinschaft for financial support and R. G. thanks the Alexander von Humboldt Foundation for a fellowship. We also thank Prof. Dr. T. Mabry for an authentic sample of glaucolide B.

REFERENCES

1. Fischer, N. H., Olivier, R. J. and Fischer, H. D. (1979) *Fortschr. Chem. Org. Natur.* **38,** 47.
2. Bohlmann, F., Gupta, R. K., Jakupovic, J., King, R. M. and Robinson, H. (1980) *Justus Liebigs Ann. Chem.* (in press).
3. Stothers, J. B. (1972) *Carbon-13 NMR Spectroscopy*. Academic Press, London.
4. Bohlmann, F., Brindöpke, G. and Rastogi, R. C. (1978) *Phytochemistry* **17,** 475.
5. Mathur, S. B., Hiremath, S. V., Kulkari, G. H., Kelkar, G. R. and Bhattacharyya, S. C. (1965) *Tetrahedron* **21,** 3575.
6. Romo de Vivar, A., Cabrera, A., Ortega, A. and Romo, J. (1967) *Tetrahedron* **23,** 3903.
7. Padolina, W. G., Yoshioka, H., Nakatani, N., Mabry, T. J., Monti, S. A., Davis, R. E., Cox, P. J., Sim, A., Watson, W. H. and Beth Wu, I. (1974) *Tetrahedron* **30,** 1161.
8. Gopala Krishna, E. M., Adams, T. W., Watson, W. H., Betkourki, M. and Mabry, T. J. (1977) *Cryst. Struct. Commun.* **6,** 201.
9. Bawdekarr, A. S., Kelkow, G. R. and Bhattacharyya, S. C. (1967) *Tetrahedron* **23,** 1993.
10. Jones, S. B. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.). Academic Press, London.