Phytochemistry, Vol. 20, No. 4, pp. 751–756, 1981.
Printed in Great Britain.

0031–9422/81/040751–06 $02.00/0

EUDESMANOLIDES AND DITERPENES FROM *WEDELIA TRILOBATA* AND AN *ENT*-KAURENIC ACID DERIVATIVE FROM *ASPILIA PARVIFOLIA**

FERDINAND BOHLMANN,† JÜRGEN ZIESCHE,† ROBERT M. KING‡ and HAROLD ROBINSON‡

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

(*Revised received* 13 *July* 1980)

Key Word Index—*Wedelia trilobata*; *Aspilia parvifolia*; *Gnaphalium undulatum*; Compositae; sesquiterpene lactones; eudesmanolides; *ent*-kaurenic acid derivatives; degradated kaurene derivatives.

Abstract—The reinvestigation of the aerial parts of *Wedelia trilobata* afforded, in addition to known compounds, six new eudesmanolides, two *ent*-kaurenic acid derivatives as well as a degraded one. A corresponding hydroxy compound was present in *Gnaphalium undulatum*. From *Aspilia parvifolia* new *ent*-kaurenic acid epoxides were isolated. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The large genus *Wedelia* (Compositae, Heliantheae) is placed in the subtribe Ecliptinae [1]. A few species only have been investigated chemically. Some contain thiophenacetylenes [2], also present in Eclipta [2], and *ent*-kaurenic derivatives [3, 4]. From one species pseudoguaianolides [5] and from another the eudesmanolide ivalin [6] were isolated. Two species of a second large genus, *Aspilia*, also placed in the same subtribe, so far gave thiophenacetylenes [2] only. We have reinvestigated *W. trilobata* (L.) Hitchc. In addition to kaurene derivatives six new eudesmanolides and a new diterpene type were isolated. The corresponding 15-hydroxy derivative is present in *Gnaphalium undulatum*. *Aspilia parvifolia* Mattf. afforded several kaurene derivatives.

RESULTS AND DISCUSSION

The aerial parts of *W. trilobata* afforded several known compounds (see Experimental) and two further *ent*-kaurenic acid derivatives, which could be separated only after esterification. The ^{1}H NMR data showed (Table 1) that the angelate **4b** and the cinnamate **5b** were present. All data were very similar to those of the known 9-desoxy compounds [3]. The position of the tertiary hydroxyl was indicated by the typical downfield shift of the 15β-H signal.

The polar fractions contain a complex mixture of small amounts of sesquiterpene lactones, which could be separated with difficulty only. The less polar fractions contained three lactones, which could not be separated. However, after acetylation two lactones were separated by HPLC. The third lactone, an isobutyrate, was still present as a mixture with the main compound. The other two lactones were the corresponding angelate and methacrylate, respectively. The ^{1}H NMR spectral data (Table 2) of the isobutyrate and the corresponding acetate were in agreement with the structures **11a** and **11b**, respectively. The observed Eu(fod)$_3$ induced shifts and the ^{13}C NMR spectral data (Table 2) indicated a β-orientated oxido bridge and spin decoupling allowed the assignment of all signals. The observed couplings were in good agreement with the stereochemistry proposed for C-5 through C-9.

Table 1. ^{1}H NMR spectral data of compounds **4b**, **5b** and **10b** (270 MHz, TMS as internal standard)

	4b	**5b**	**10b**
2α-H	2.43 *dddd*	2.48 *dddd*	
3β-H	4.65 *dd*	4.72 *dd*	
13-H	2.65 *s* (*br.*)	2.66 *s* (*br.*)	
15α-H	1.80 *m*	1.80 *m*	4.75 *d*
15β-H	2.71 *d* (*br.*)	2.71 *d* (*br.*)	—
17-H	4.80 *s* (*br.*)	4.82 *s* (*br.*)	3.08 *d*
17′-H	4.77 *s* (*br.*)	4.78 *s* (*br.*)	2.76 *d*
18-H	1.26 *s*	1.27 *s*	1.18 *s*
20-H	1.07 *s*	1.08 *s*	0.87 *s*
OMe	3.67 *s*	3.74 *s*	3.65 *s*
OCOR	6.06 *qq*	6.47 *d*	6.86 *qq*
	1.98 *dq*	7.68 *d*	1.80 *dq*
	1.87 *dq*	7.53 *m*	1.86 *dq*
		7.37 *m*	

J (Hz): **4b**/**5b**: 1α, 2α = 4; 1β, 2α = 12; 2, 2′ = 12; 2α, 3β = 12; 2β, 3β = 4.5; 15, 15′ = 18; OCOR: OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5; OCinn: 2′, 3′ = 16; **10b**: 14, 16 = 1.5; 17, 17′ = 6; OTigl: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

* Part 300 in the series 'Naturally Occurring Terpene Derivatives'. For Part 299 see Bohlmann, F. and Ziesche, J. (1981) *Phytochemistry* **20**, 469.

Table 2. ^{1}H NMR spectral data of compounds **11a**, **11b**, **12b**, **13b**, **14**, **15** and **16** (270 MHz, TMS as internal standard, $CDCl_3$)

	11a*	Δ†	**11b**	**12b**	**13b**	**14**	**15**	**16**	**11b** ^{13}C ($CDCl_3$)	
1-H	3.99 *d*	0.15	3.98 *d*		4.00 *d*	4.61 *dd*	4.60 *dd*	4.62 *dd*	C-1	70.9 *d*
2-H	2.80 *ddd*	0.07	2.10 *m*		2.10 *m*				C-2	28.5 *t*
2′-H	1.60 *m*								C-3	29.2 *t*
3-H	2.13 *m*		1.8 *m*		1.8 *m*				C-4	87.6 *s*
5-H	1.52 *dd*	0.06	1.61 *dd*		1.65 *dd*	1.93 *d*	1.95 *m*	1.94 *d*	C-5	58.9 *d*
6-H	5.72 *dd*	0.10	5.55 *dd*	5.66 *ddd*	5.64 *ddd*	5.98 *dd*	6.08 *dd*	6.04 *dd*	C-6	72.7 *d*
7-H	3.20 *dddd*	0.07	3.26 *dddd*		3.29 *dddd*	3.19 *dddd*	3.27 *dddd*	3.30 *m*	C-7	34.3 *d*
8-H	4.89 *dd*	0.06	4.96 *dd*		4.98 *dd*	4.90 *dd*	4.93 *dd*	4.93 *dd*	C-8	84.3 *d*
9-H	4.08 *dd*	0.06	5.48 *d*		5.51 *d*	5.24 *d*	5.25 *d*	5.26 *dd*	C-9	75.0 *d*
13-H	6.24 *d*	0.09	6.27 *d*		6.27 *d*	6.26 *d*	6.28 *d*	6.28 *d*	C-10	47.3 *s*
13′-H	5.59 *d*	0.06	5.61 *d*	5.59 *d*	5.57 *d*	5.68 *d*	5.72 *d*	5.72 *d*	C-11	134.8 *s*
14-H	1.19 *s*	0.06	1.30 *s*	1.31 *s*		1.38 *s*	1.36 *s*	1.36 *s*	C-12	169.4 *s*
15-H	1.34 *s*	0.11	1.37 *s*	1.37 *s*		1.37 *s*	1.39 *s*	1.40 *s*	C-13	123.8 *t*
OAc				2.10 *s*		2.02 *s*	2.01 *s*	2.02 *s*	C-14	22.3 *q*
	—	—	2.07 *s*	—		1.96 *s*	1.95 *s*	1.96 *s*	C-15	29.19
OCOR	2.58 *qq*	0.03	2.61 *qq*	6.23 *qq*	6.21 *s br.*	2.61 *qq*	6.24 *qq*	6.14 *s* (*br.*)		
	1.22 *d*	0.03	1.25 *d*	2.05 *dq*	5.64 *s br.*	1.23 *d*	2.08 *dq*	5.71 *s* (*br.*)		
				1.95 *dq*	2.00 *s br.*	1.21 *d*	1.94 *dq*	2.00 *s* (*br.*)		
OH	3.01 *d*		—			—	—	—		

* Compound **12a**: 6-H 5.84 *dd*; OCOR: 6.18 *qq*, 2.03 *dq*, 1.94 *dq*; compound **13a**: 6-H, 5.82 *dd*; 2.00 *s* (*br.*), 6.21 *s* (*br.*), 5.71 *s* (*br.*).

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

J (Hz): Compounds **11a** and **11b**–**13b**: 1, 2β = 5; 2α, 2β = 12; 2α, 3β = 10; 2α, 3α = 3; 5, 6 = 11; 6, 7 = 10; 7, 8 = 9; 7, 13 = 3; 7, 13′ = 2.5; 8, 9 = 3.5; 9, OH = 3; 2′, 3′ = 7; compounds **14**/**16**: 1, 2 = 11; 1, 2′ = 4.5; 5, 6 = 3; 6, 7 = 2; 7, 8 = 8; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 = 4.5; OiBu: 2′, 3′ = 7; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5.

Table 3. ^{1}H NMR spectral data of compounds **17**, **18** and **19** (270 MHz)

	17 ($CDCl_3$)	Δ*	**18** ($CDCl_3$)	**19** ($CDCl_3$)	C_6D_6	Δ*
11-H	2.35 *m*	0.7	2.33 *ddd*	2.48 *ddd*	2.54 *ddd*	0.32
11′-H			2.12 *m*	2.35 *dd*	2.26 *dd*	0.26
13-H	2.87 *s* (*br.*)	0.25	2.87 *s* (*br.*)	2.90 *s* (*br.*)	2.45 *s* (*br.*)	0.11
15-H	2.47	0.55	4.17 *s* (*br.*)	4.37 *s* (*br.*)	4.13 *s* (*br.*)	0.35
15′-H	2.31 d	0.46				
17-H	5.06 *s* (*br.*)	0.14	5.41 *s* (*br.*)	5.26 *s* (*br.*)	5.26 *s* (*br.*)	0.10
17′-H	4.97 *s* (*br.*)	0.15	5.31 *s* (*br.*)	5.24 *d* (*br.*)	5.05 *d* (*br.*)	0.10
18-H	1.21 *s*	0.80	1.23 *s*	1.24 *s*	1.31 *s*	0.31
20-H	1.48 *s*	0.37	1.52 *s*	1.47 *s*	1.32 *s*	0.13

* Δ-values after addition of $Eu(fod)_3$.
J (Hz): **17**: 11, 11′ = 17; 15, 15′ = 17; **18**/**19**: 11, 11′ = 16; 11, 12 = 12; 11, 12′ = 8; 11′, 12 = 6; 15, 17′ = 1.5.

As the ^{1}H NMR spectra of the acetates of the two other lactones were nearly identical with those of **11b**, except for the shifts of 6-H, their structures therefore were **12b** and **13b** and those of the original compounds were **12a** and **13a**. We have named the 6-*O*-desacyl compound oxido-isotrilobolide. The more polar lactones were separated by HPLC. Again they differed in the ester residues. The ^{1}H NMR spectra (Table 2) led to the assignment of structures **14**–**16**. The relative position of the ester groups were assigned again by comparing the chemical shifts of 6-H. While those of 1- and 9-H were nearly identical in all three lactones, the 6-H shift was different depending on the nature of the ester residues. As usual the unsaturated ester groups caused a small, but typical downfield shift. Careful spin decoupling established the proposed stereochemistry and allowed the assignment of all signals except those of 2- and 3-H, which were overlapped multiplets. The observed couplings required a different stereochemistry at C-6 and C-9, if compared with those of **11a**. The 9β-position of the acetoxy group caused a pronounced downfield shift of the C-10 methyl signal. The 4α-position of the hydroxyl group was supported by the downfield shift of 6α-H, if compared with the shift in **11a**. All six lactones showed a prominent fragment at *m/e* 162 ($C_{10}H_{10}O_2$), which was probably **14a**. We have named the 6-*O*-desacyl compound of **14**–**16** trilobolide.

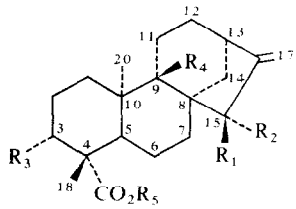
Finally a further diterpene was isolated, molecular formula $C_{20}H_{28}O_3$. The IR spectrum indicated the presence of a γ-lactone and a non-conjugated keto group, while the ^{1}H NMR spectrum (Table 3) displayed two signals for methyl groups. Furthermore the spectrum was in part similar to that of methyl-*ent*-kaurenoate. $Eu(fod)_3$ induced shifts indicated that only two hydrogens were adjacent to the carbonyl and the shifts of the methyl signals together with the ^{13}C NMR spectral data (Table 4) required a lactone ring with both methyls near the lactone carbonyl. The ^{13}C NMR chemical shifts were different from those of methyl-*ent*-kaurenoate, but the differences were likely if structure **17** was proposed. In particular the downfield shifted signals could best be assigned with a carbonyl group at C-9. We have named **17** wedeliasec-cokaurenolide.

We have previously isolated a very similar compound together with other diterpenes from *Gnaphalium undulatum* [7], the structure, however, could not be elucidated. Inspection of the ^{1}H NMR spectral data of this compound clearly indicated an additional hydroxyl group (Tables 3 and 4). Its location at C-15 clearly followed from the observed shifts of 17-H. On standing in chloroform for about 20 hr the compound was completely transformed to an isomeric compound. This was probably due to traces of hydrogen chloride which is always present in this solvent. Inspection of models indicated that the natural compound could be **18** with a 15β-hydroxyl. As shown in the scheme, **18** may be transformed through **21** in a retro-aldol-aldol reaction to **19** with a less hindered

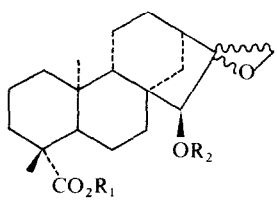
Table 4. ^{1}H NMR spectral data of compounds **17**, **19** and methyl-*ent*-kaurenoate ($CDCl_3$, TMS as internal standard)

	17	**19**	methyl-*ent*-kaurenoate
C-1	37.0 *t*†	37.0 *t*†	40.9 *t*
C-2	19.8 *t*	19.8 *t*	19.2 *t*
C-3	33.7 *t**	33.6 *t*	38.1 *t*
C-4	48.5 *s*	48.7 *s*	43.9 *s*
C-5	56.1 *d*	56.2 *d*	57.2 *d*
C-6	22.1 *t*	21.7 *t*	21.9 *t*
C-7	36.8 *t*†	31.7 *t*	41.4 *t*
C-8	57.1 *s*	61.3 *s*	44.3 *s*
C-9	212.8 *s*	210.6 *s*	55.2 *d*
C-10	84.9 *s*	85.1 *s*	39.5 *s*
C-11	43.6 *t*	37.7 *t*†	18.4 *t*
C-12	33.1 *t**	33.7 *t*	33.2 *t*
C-13	42.3 *d*	39.5 *d*	43.9 *d*
C-14	36.0 *t*†	36.8 *t*†	39.7 *t*
C-15	42.0 *t*	81.3 *d*	49.0 *t*
C-16	152.2 *s*	155.1 *s*	155.8 *s*
C-17	106.9 *t*	109.2 *t*	103.1 *t*
C-18	22.1 *q*	22.1 *q*	28.8 *q*
C-19	180.2 *s*	180.6 *s*	178.0 *s*
C-20	18.1 *q*	18.2 *q*	15.4 *q*

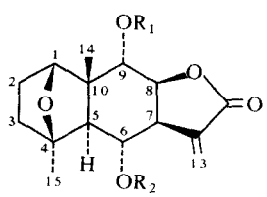
*† May be interchangeable.



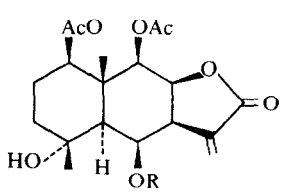
	1	2	3	4a	4b	5a	5b	6	7	8
R_1	H	H	H	H	H	H	H	OAng	OTigl	H
R_2	H	H	H	H	H	H	H	H	H	OTi
R_3	OAng	OTigl	OCinn	OAng		OCinn		H	H	H
R_4	H	H	H	OH		OH		H	H	H
R_5	H	H	H	H	Me	H	Me	H	H	H



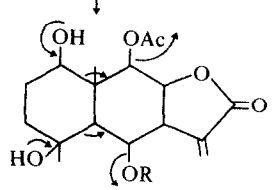
	9[8]	10a	10b
R_1	H	H	Me
R_2	Ang	Tigl	Tigl

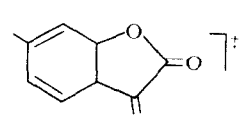


	11a	11b	12a	12b	13a	13b
R_1	H	Ac	H	Ac	H	Ac
R_2	*i*-Bu		Ang		Meacr	



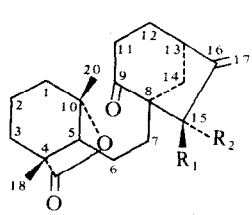
14 R = *i*-Bu
15 R = Ang
16 R = Meacr



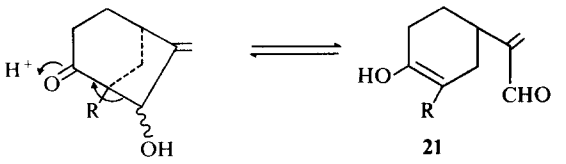


m/e 162

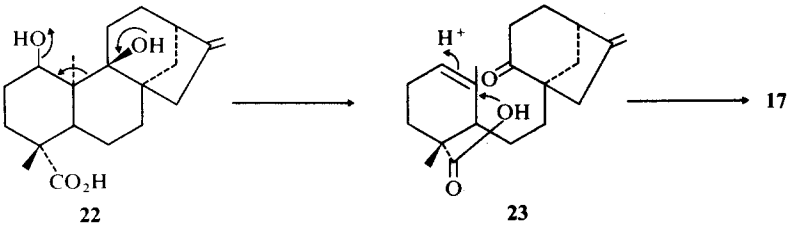
14a



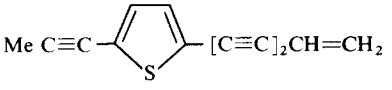
	17	18	19	20
R_1	H	OH	H	H
R_2	H	H	OH	OH
				9-OH



21



22 23



24

15α-hydroxyl. The ^{1}H NMR spectral data (Table 3) were altered very little, but the 15-H and 17-H signals were shifted slightly. Though the structures of **17**–**19** were not rigorously established the proposed structures are likely. Compound **17** could be formed from 9β-hydroxy-*ent*-kaurenic acid by further oxidation at C-1 (**22**), which would allow a fragmentation leading to the unsaturated secco-compound **23**. The latter could be transformed to the lactone.

The roots of *Aspilia parvifolia* afforded in addition to several already known *ent*-kaurene derivatives and other compounds (see Experimental) a new epoxide, the tiglate **10a**, which was isolated as its methyl ester. The ^{1}H NMR spectral data (Table 1) were nearly identical with those of the corresponding angelate **9** [8] which was also present. The aerial parts contained several *ent*-kaurene derivatives, all isolated before (see Experimental).

The investigation of these two species showed that *ent*-kaurene derivatives may be typical for these genera. However, the lactones isolated now indicate that many more species of the subtribe Ecliptinae have to be investigated to decide whether they are chemotaxonomically important. So far eudesmanolides have not been reported very often from the tribe Heliantheae [9] while they are widespread in parts of the Inuleae and Anthemideae [9]. From *Baltimora recta*, placed also in the same subtribe, several eudesmanolides have been isolated [10], while from the other genera no lactones have been reported. Thiophenacetylenes are more widespread [2]. Together with the eudesmanolides this could indicate relationships to parts of the Inuleae (*Buphthalmum*, *Telekia*, *Inula*) where both types are present.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as internal standard; MS: 70 eV, direct inlet; optical rotation: $CHCl_3$. The air dried plant material was extracted with Et_2O–petrol. The extracts obtained were separated first by CC (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254). **14**–**16** were separated by HPLC. Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

Wedelia trilobata (*voucher RMK* 7998). The aerial parts (185 g) afforded 60 mg germacrene D, 5 mg α-humulene, 10 mg caryophyllene, 20 mg squalene, 15 mg phellandrene, 10 mg *p*-cymene, 10 mg sitosterol, 500 mg *ent*-kaurenic acid, 20 mg **1** [3], 10 mg **2** [3], 25 mg **3** [3], 7 mg **4a** and 5 mg **5a** (both isolated as their methyl esters), 35 mg **11a**, 2 mg **12a** and 1 mg **13a** (Et_2O–petrol, 3:1, not separated), 7 mg **14**, 6 mg **15** and 1 mg **16** (Et_2O, separated by HPLC, reversed phase, MeOH–H_2O, 7:3).

Aspilia parvifolia (*voucher RMK* 8120). The roots (150 g) afforded 60 mg α-pinene, 40 mg β-pinene, 20 mg γ-humulene, 600 mg *ent*-kaurenic acid, 20 mg *ent*-kaurane-16-ol, 100 mg *ent*-kauren-19-al, 30 mg *ent*-kauren-19-ol, 10 mg sitosterol, 30 mg *ent*-manool, 10 mg 6-acetyl-2,2-dimethylchromene, 40 mg **6** [11], 60 mg **7** [11], 15 mg **9** [8], 20 mg **10a** (isolated as its methyl ester, Et_2O–petrol, 1:3) and 0.2 mg **24** [2]. The aerial parts (460 g) afforded 200 mg *ent*-kaurane-16-ol, 30 mg spathulenol, 100 mg phellandrene, 10 mg *p*-cymene, 20 mg β-farnesene, 300 mg germacrene D, 5 mg α-gurjunene, 30 mg α-pinene, 200 mg β-pinene, 20 mg γ-humulene, 2 g *ent*-kaurenic acid, 50 mg *ent*-kauren-19-ol, 100 mg *ent*-manool, 200 mg **6**, 600 mg **7**, 80 mg **8** [12] and 400 mg **10a**.

Isolation of **18** *from* Gnaphalium undulatum. The aerial parts (70 g) afforded in addition to the compounds reported [7] 20 mg **18** (Et_2O–petrol, 3:1).

Methyl-3α-angeloyloxy-9β-hydroxy-ent-*kaurenoate* (**4b**). Colourless crystals, mp 165–6° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1730 (CO_2R), 1710, 1655 (C=CCO_2R); MS *m/e* (rel. int.): 330.219 ($C_{21}H_{30}O_3$) (M − AngOH, 82), 312 (330 − H_2O, 55), 298 (330 − MeOH, 100), 270 (298 − CO, 43), 83 ($C_4H_7CO^+$, 38).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-51.3 \quad -52.8 \quad -59.7 \quad -102.4} (c = 0.71).$$

Methyl-3α-cinnamoyloxy-9β-hydroxy-ent-*kaurenoate* (**5b**). Colourless crystals, mp 195–6° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730 (CO_2R), 1710, 1640 (C=CCO_2R); MS *m/e* (rel. int.): 478.272 (M^+, 4) ($C_{30}H_{38}O_5$), 330 (M − PhCH=$CHCO_2H$, 32), 312 (330 − H_2O, 27), 298 (330 − MeOH, 65), 280 (298 − H_2O, 5), 131 (PhCH=$CHCO^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-30.5 \quad -31.9 \quad -36.7 \quad -65.1} (c = 0.5).$$

Methyl-15β-tiglinoyloxy-16,17-epoxy-ent-*kaurane* (**10b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725 (CO_2R), 1710, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 430.272 (M^+, 0.5) ($C_{26}H_{38}O_5$), 412 (M − H_2O, 19), 83 ($C_4H_7CO^+$, 70), 55 (83 − CO, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-49.3 \quad -51.0 \quad -58.3 \quad -92.9} (c = 0.8).$$

Oxidoisotrilobolide-6-O-isobutyrate, angelate and methacrylate (**11a, 12a** *and* **13a**). Not separated, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1790, 1760 (lactone), 1745 (CO_2R); MS *m/e* (rel. int.): 350.173 (M^+, 13) ($C_{19}H_{26}O_6$), 362 (M^+, 1) and 348 (M^+, 0.5), 262 (M − RCO_2H, 38), 244 (262 − H_2O, 5), 162 (100), 71 ($C_3H_7CO^+$, 82).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{+33.6 \quad +35.1 \quad +40.4} (c = 3.7).$$

20 mg **11a–13a** were heated for 30 min with 0.5 Ac_2O at 70°. After evapn TLC (Et_2O–petrol, 2:1) afforded 20 mg **11b–13b**. HPLC (MeOH − H_2O, 6.5:3.5, reversed phase) afforded 10 mg **11b**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (lactone), 1740 (OAc, CO_2R); MS *m/e* (rel. int.): 392.168 (M^+, 18) ($C_{21}H_{28}O_7$), 304 (M − RCO_2H, 27), 262 (304 − ketene, 37), 244 (304 − HOAc, 28), 71 ($C_3H_7CO^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{+85.5 \quad +89.1 \quad +101.9 \quad +180.0 \quad +296.8}$$

$(c = 0.95)$.

Furthermore 2 mg **12b** were obtained, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (lactone), 1740 (OAc), 1725 (C=CCO_2R); MS *m/e* (rel. int.): 404.184 (M^+, 5) ($C_{22}H_{28}O_7$), 304 (M − AngOH, 40), 83 ($C_4H_7CO^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{+73.5 \quad +75.9 \quad +86.5 \quad +150.6 \quad +242.9}$$

$(c = 0.17)$.

Finally 1.5 mg of a mixture of **11b** and **13b** was obtained, colourless gum, MS *m/e* (rel. int.): 390 (M^+, 5), 69 ($C_3H_5CO^+$, 100).

Trilobolide-6-O-isobutyrate (**14**). Colourless crystals, mp 230–1° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1785 (lactone), 1745 (OAc, CO_2R); MS *m/e* (rel. int.): 392.184 (M^+, 5) ($C_{23}H_{32}O_9$), 364 (M − CO, 3), 304 (364 − HOAc, 51), 244 (304 − HOAc, 28), 226 (244 − H_2O, 42), 162.068 ($C_{10}H_{10}O_2$, 100), 71 ($C_3H_7CO^+$, 59).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+30.8 \quad +32.5 \quad +37.1 \quad +61.9} (c = 0.7).$$

Trilobolide-6-O-angelate (**15**). Colourless crystals, mp 180–6° (Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1785, 1765 (lactone), 1745, 1240 (OAc), 1725, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 404.184 (M^+, 3) ($C_{24}H_{32}O_9$), 304 (404 − AngOH, 23), 244 (304 − HOAc, 12), 226 (244 − H_2O, 21), 162 ($C_{10}H_{10}O_2$, 38), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 62).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+12.8 \quad +13.3 \quad +14.8 \quad +21.8} (c = 0.6).$$

Trilobolide-6-O-methacrylate (**16**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1785, 1765 (lactone), 1750, 1250 (OAc), 1735, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 390.168 (M^+, 3) ($C_{23}H_{30}O_9$), 304 (M − RCO_2H, 23), 244 (304 − HOAc, 18), 226 (244 − H_2O, 20), 162 ($C_{10}H_{10}O_2$, 61), 69 ($C_3H_5CO^+$, 100).

Wedelia-secco-kaurenolide (**17**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (lactone), 1715 (C=O), 3080, 1660 (C=CH_2); MS *m/e* (rel. int.): 316.203 (M^+, 36) ($C_{20}H_{28}O_3$), 298.193 (M − H_2O, 68), 272 (M − CO_2, 40), 270.199 ($C_{19}H_{26}O$, 298 − CO, 100), 254 (298 − CO_2, 55).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{-44.9 \quad -47.4 \quad -54.6} (c = 3.2).$$

15β-Hydroxy-wedeliseccokaurenolide (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (lactone), 1710 (C=O); MS *m/e* (rel. int.): 332.198 (M^+, 10) ($C_{20}H_{28}O_4$), 314 (M − H_2O, 22), 288 (M − CO_2, 9), 286 (314 − CO, 32), 271 (286 − Me, 21), 43 ($C_3H_7^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-72.6 \quad -76.3 \quad -89.5 \quad -178.3} (c = 1.7).$$

15 mg **18** on standing for 20 hr in $CDCl_3$ afforded **19**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (lactone), 1710 (C=O); MS *m/e* (rel. int.): 332.198 (M^+, 6) ($C_{20}H_{28}O_4$), 314 (M − H_2O, 15), 288 (M − CO_2, 10), 286 (314 − CO, 17), 43 ($C_3H_7^+$, 100).

To 5 mg **19** in Et_2O 10 mg $LiAlH_4$ and after 5 min dil. H_2SO_4 were added. TLC (Et_2O–petrol, 3:1) afforded 3 mg of the diol **20**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1770 (lactone); MS *m/e* (rel. int.): 334 (M^+, 0.5), 316 (M − H_2O, 3), 298 (316 − H_2O, 3), 270 (288 − H_2O, 6), 149 (100); ^1H NMR ($CDCl_3$): 1.23 *s* (18-H), 1.45 *s* (20-H), 2.65 *s* (*br.*) (13-H), 3.66 *m* (9-H), 4.23 *s* (*br.*) (15-H), 5.04 *d* (*br.*) (17-H), 5.09 *s* (*br.*) (17′-H).

Acknowledgements—We thank Drs. Scott. A. Mori and P. Alvim, Centro de Pesquisas at Itabuna, Bahia, Brazil, for their help during plant collection and the Deutsche Forschungsgmeinschaft for financial support.

REFERENCES

1. Stuessy, T. F. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 621. Academic Press, London.
2. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
3. Bohlmann, F. and Le Van, N. (1977) *Phytochemistry* **16,** 579.
4. Tomassini, T. C. B. and Matos, M. E. O. (1979) *Phytochemistry* **18,** 663.
5. Bohlmann, F., Rosenberg, E., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19,** 2047.
6. Aleman, R., Rosado, A., Rodriguez, M. and Bertran, J. F. (1977) *Rev. Cubana Farm.* **11,** 47.
7. Bohlmann, F. and Ziesche, J. (1980) *Phytochemistry* **19,** 71.
8. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16,** 786.
9. Fischer, N. H., Olivier, E. J. and Fischer, H. D. (1979) *The Biogenesis and Chemistry of Sesquiterpene Lactones, Progress in the Chemistry of Organic Natural Compounds*, Vol. 38, p. 47. Springer, Wien.
10. Herz, W. and Kumar, N. (1979) *Phytochemistry* **18,** 1743.
11. Bohlmann, F., Fritz, U., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19,** 2655.
12. Bohlmann, F. and Jakupovic, J. (1978) *Phytochemistry* **17,** 1677.