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EUDESMANE DERIVATIVES FROM *VERBESINA* SPECIES*

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Key Word Index—*Verbesina luetzelburgii*; *V. glabrata*; *V. macrophylla*; *V. cinerea*; *V. boliviana*; *V. pentantha*; *V. semidecurrens*; new eudesmane and germacrane derivatives; new acetophenone derivatives; new bisabolene derivative.

Abstract—The investigation of seven *Verbesina* species afforded, in addition to known compounds, several new eudesmane and germacrane derivatives, all bearing a cinnamate or derivatives as residue. Furthermore, a new bisabolene aldehyde and two acetophenone derivatives were isolated. The structures were elucidated mainly by spectroscopic methods and some chemical transformations. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The large genus *Verbesina* belongs to the subtribe Verbesininae in the tribe Heliantheae (family Compositae) [1]. So far only a few species have been investigated chemically. However, the results already indicate that most probably the genus is not very uniform. While some species contain typical eudesmane derivatives with a cinnamate or an oxygenated one as a residue at C-6 [2, 3], two species afforded elemanolides [4, 5], some a large variety of cadinane derivatives [2] and some mainly kaurene derivatives [6]. Besides the widespread pentaynene **1** and related polyynes [7], most species contain compounds with a cinnamate or a related residue. We now have investigated seven further South American species. Again most species afforded eudesmane and germacrane derivatives but most of them have not been isolated before. Furthermore, a new bisabolene, two hydroxy-acetophenone derivatives and a geranyl ether of an oxygenated cinnamic alcohol were isolated.

RESULTS AND DISCUSSION

The aerial parts of *V. glabrata* Hook. et Arn. afforded germacrene D (**12**) and 6β-cinnamoyleudesman-15-al (**16**) [2]. The main compounds were two isomeric alcohols, both being 6β-cinnamates of eudesmane derivatives as deduced from the ^{1}H NMR data, which further indicated that the two esters differed only in the position of the double bond, one with an exocyclic one at C-4, the other with a 3,4-double bond. The position of the hydroxyl group followed from double resonance experiments and the coupling constants, which indicated a 1β-position. Therefore structures **19** and **22** were assigned for these compounds. This assumption was further supported by the ^{1}H NMR data of the corresponding acetates **20** and **23** as well as those of the ketone **24**, obtained by oxidation of **22** with pyridine chlorochromate and of the epoxide **32** obtained by peracid oxidation (Table 1).

Somewhat more polar was an aromatic compound, which was identified as **8a**. In the MS no molecular ion was detected. The ^{1}H NMR spectrum, however, clearly indicated that we were dealing with a geranyl ether. Acetylation afforded the acetate **8b**, which has been isolated before from *Senecio longifolius* [8]. The ^{1}H NMR data of the acetate were identical with those of the natural compound (Table 2).

A further cinnamate was the diol **26a**. The 1,4-position of the hydroxy groups followed from the ^{1}H NMR data and those of the corresponding mono- and diacetate, as well as from those of the ketone formed by oxidation with pyridine chlorochromate (Table 1). Therefore we were dealing with a diol isomeric with a cinnamate isolated previously from a *Verbesina* species [2]. To establish the stereochemistry at C-4 we measured the ^{13}C NMR spectra of the two diols as well as that of the monohydroxy derivative where we had assigned a 4β-methyl structure [2] (Table 3). Inspection of the observed chemical shifts showed that the structure of the monol has to be revised, as only the stereochemistry given in **25**, **26a** and **26b** is in agreement with the ^{13}C NMR data. The chemical shift of the 4-methyl signal is especially useful for the assignment of the stereochemistry, the equatorial methyl signal always being shifted downfield in comparison with that of an axial methyl at C-4 (Table 3). The stereochemistry at C-1, already shown by the ^{1}H NMR data, also followed from the ^{13}C NMR data, an equatorial hydroxyl causing a shielding effect of the 10-methyl group.

Another major constituent was the eudesmane **33** with a 1,4-ether ring. The orientation of the oxygen bridge was assigned from the ^{13}C NMR data (Table 3). If we compare the chemical shifts of **33** with those of **26a** and **26b**, the only explanation of the upfield shift of the C-9 signal is a γ-effect of the oxygen at C-1, which requires an α-position. Consequently an α-position must also be assumed at C-4. A further indication of this stereochemistry was the observed

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*Part 285 in the series "Naturally Occurring Terpene Derivatives". For Part 284 see Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2473.

Table 1. ^{1}H NMR spectra data of compounds **19**, **20**, **22**–**24**, **26a**, **28**, **29** and **32** (270 MHz, $CDCl_3$)

	19	**20**	**22**	**23**	**24**	**26a**	**28**	Δ	**29**	Δ	**32**
1-H	3.39 *dd*	4.66 *dd*	5.53 *dd*	4.77 *dd*		3.30 *dd*(*br*)	4.57 *dd*	0.55			3.34 *dd*
2-H	1.60 *m*		2.27 *d*(*br*) 1.98 *dd*(*br*)		3.09 *d*(*br*) 2.71 *d*(*br*)				2.67 *ddd* 2.40 *ddd*	0.19	2.38 *dd*
3-H	2.33 *d*(*br*) 2.18 *m*	2.35 *d*(*br*) 2.2 *m*	5.33 *s*(*br*)	5.33 *s*(*br*)	5.51 *s*(*br*)		2.62 *ddd*	0.44	2.0 *m*		2.99 *d*(*br*)*
5-H	1.93 *s*(*br*)	2.03 *s*(*br*)	2.09 *s*(*br*)	2.21 *s*(*br*)	2.44 *s*(*br*)	1.42 *d*	1.84 *d*	0.26	1.86 *d*	0.41	1.78 *d*
6-H	5.77 *s*(*br*)	5.78 *s*(*br*)	5.74 *dd*(*br*)	5.75 *dd*(*br*)	5.81 *s*(*br*)	5.89 *dd*(*br*)	6.03 *s*(*br*)	0.29	6.91 *dd*(*br*)	0.56	5.83 *s*(*br*)
7-H 8-H	1.60 *m*		1.65 *m*								
9-H	2.06 *ddd*		2.00 *dd* 1.19 *m*								1.90 *ddd*
11-H	1.35 *dqq*		1.47 *dqq*	1.45 *dqq*	1.45 *dqq*						1.40 *dqq*
12-H	1.06 *d*	1.05 *d*	1.05 *d*	1.04 *d*	1.06 *d*	0.92 *d*	1.00 *d*	0.04	0.94 *d*	0.0	1.08 *d*
13-H	0.87 *d*	0.87 *d*	0.88 *d*	0.87 *d*	0.89 *d*	0.91 *d*	0.87 *d*	0.05	0.92 *d*	0.02	0.88 *d*
14-H	1.03 *s*	1.12 *s*	1.10 *s*	1.19 *s*	1.39 *s*	1.17 *s*	1.36 *s*	0.17	1.40 *s*	0.27	1.11 *s*
15-H	4.80 *s*(*br*) 4.66 *s*(*br*)	4.82 *s*(*br*) 4.72 *s*(*br*)	1.19 *s*(*br*)	1.69 *s*(*br*)	1.77 *s*(*br*)	1.21 *s*	1.51 *s*	0.32	1.43 *s*	0.14	1.28 *s*
OCOR†	7.70 *d*	7.70 *d*	7.67 *d*	7.67 *d*	7.70 *d*	7.73 *d*	7.70 *d*	0.08	7.75 *d*	0.03	7.73 *d*
	6.41 *d*	6.41 *d*	6.38 *d*	6.38 *d*	6.42 *d*	6.47 *d*	6.44 *d*	0.08	6.43 *d*	0.17	6.44 *d*
	7.54 *m*	7.54 *m*	7.57 *m*	7.52 *m*	7.54 *m*	7.56 *m*	7.55 *m*	0.02	7.57 *m*	0.0	7.55 *m*
	7.39 *m*	7.38 *m*	7.38 *m*	7.38 *m*	7.40 *m*	7.47 *m*	7.40 *m*	0.0	7.42 *m*	0.0	7.40 *m*
OAc	—	2.08 *s*	—	2.08 *s*	—	—	2.06 *s* 2.05 *s*	0.36 0.39	—		—

J (Hz): **19**: 1, 2 = 11, 1, 2′ = 4.5; 3, 3′ = 14; 7, 11 = 11, 12 = 11, 13 = 7; **22**: 1, 2 = 10; 1, 2′ = 6; 2, 2′ = 17; 2, 3 = 5; 2′ 3 = 2.5; 3′, 5 = 1.5; 5, 6 = 6, 7 = 1; 7, 11 = 11, 12 = 11, 13 = 7.

* $J_{2,3}$ = 2 Hz.

† $J_{2',3'}$ = 16 Hz.

strong shielding effect of C-2 by the 10-methyl group. The ^{1}H NMR data (Table 5) were also in good agreement with **33**, though the question of the stereochemistry at C-1 and C-4 cannot be given with certainty from the observed data. The fact that 1-H showed one coupling would be in agreement with both possible structures, as can be seen from models; one angle between 2-H and 3-H could be nearly 90° in both cases.

The roots of *V. luetzelburgii* Mattf. contained the pentaynene **1** [7], borneol cinnamate (**5**) [9], germacrene D (**12**), bicyclogermacrene (**13**), 6β-cinnamoyloxy-germacra-1(10),4-diene (**15a**) [2], 6β-cinnamoyloxy-1β-hydroxy-eudesm-4(15)-ene (**19**), 6β-cinnamoyloxy-1β-hydroxy-eudesm-3-ene (**22**), 6β-cinnamoyloxy-4β-hydroxyeudesmane (**25**), 6β-cinnamoyloxy-1β,4β-dihydroxyeudesmane (**26a**) and the three acetophenone derivatives **9**–**11**, as shown by the spectral data.

Table 2. ^{1}H NMR spectral data of compounds **8a** and **8b** (270 MHz, $CDCl_3$)

	8a	**8b**		**8a**/**8b**
2,6-H	6.61 *s*	6.61 *s*	4′,5′-H	2.05 *m*
7-H	6.55 *d*(*br*)	6.58 *d*(*br*)	6′-H	5.09 *t*(*br*)
8-H	6.29 *dt*	6.20 *dt*	8′-H	1.60 *s*(*br*)
9-H	4.33 *d*(*br*)	4.72 *d*(*br*)	9′-H	1.66 *s*(*br*)
1′-H	4.54 *d*(*br*)	4.54 *d*(*br*)	10′-H	1.68 *s*(*br*)
2′-H	5.57 *t*(*br*)	5.56 *t*(*br*)	OMe	3.86 *s*

J (Hz): 7, 8 = 16; 8, 9 = 6; 1′, 2′ = 5′, 6′ = 7.

Compound **9** has been isolated before from an *Espeletia* species [10]. The structure of the closely related ketone **11** followed from the ^{1}H NMR data, especially if we compare them with those of the corresponding methoxy compound [11] (see Experimental). Furthermore, the bisabolene derivative **17** was present whose structure was elucidated by the spectral data. The position of the aldehyde group followed from the MS (*m/e* 109) and from the ^{1}H NMR data (see Experimental). The downfield shift of 4-H and comparison of the ^{1}H NMR data with those of other bisabolenes established the structure. However, the stereochemistry at C-6 and C-7 cannot be assigned.

Together with the germacrane **15a** [2] a second derivative was present, which was isolated in larger quantities, together with a second one from *V. macrophylla* (see below). The structures **15b** and **15c** followed from the ^{1}H NMR data, especially if we compare them with those of **15a** [2]. Compound **15c** was also transformed to the phenolacetate. The ^{1}H NMR spectra of these germacranes were much broadened at room temperature. However, in C_6D_6 at 75° the signals were sharpened (Table 4). The

Table 3. ^{13}C NMR spectral signals of compounds **25**, **26a**, **26b** and **33** ($CDCl_3$, TMS as internal standard*)

	25	**26a**	**26b**	**33**
C-1	44.2† *t*	80.4 *d*	78.9 *d*	84.5 *d*
C-2	20.0 *t*	28.7 *t*	26.7 *t*	23.4 *t*
C-3	45.4† *t*	41.6† *t*	45.2 *t*	42.7 *t*
C-4	71.7 *s*	71.2 *s*	75.4 *s*	82.4 *s*
C-5	57.2 *d*	55.3 *d*	55.3 *d*	57.2 *d*
C-6	69.4 *d*	69.8 *d*	69.7 *d*	69.5 *d*
C-7	50.2 *d*	49.9 *d*	49.9 *d*	49.9 *d*
C-8	21.3 *t*	20.8 *t*	21.2 *t*	23.2 *t*
C-9	43.5† *t*	41.4† *t*	41.0 *t*	33.0 *t*
C-10	34.5 *s*	39.1 *s*	34.8 *s*	48.3 *s*
C-11	28.8 *d*	28.8 *d*	28.9 *d*	29.3 *d*
C-12	21.3 *q*	21.3 *q*	21.2 *q*	21.6 *q*
C-13	20.7 *q*	20.7 *q*	20.8 *q*	20.6 *q*
C-14	21.3 *q*	14.9 *q*	15.3 *q*	17.3 *q*
C-15	24.6 *q*	24.7 *q*	21.6 *q*	22.5 *q*
C-1′	167.9 *s*	168.2 *s*	168.4 *s*	166.0 *s*
C-2′	118.5 *d*	118.3 *d*	118.3 *d*	118.6 *d*
C-3′	145.4 *d*	145.3 *d*	146.0 *d*	144.6 *d*
C-4′	134.4 *s*	134.3 *s*	134.3 *s*	134.5 *s*
C-5′, 9′	128.2 *d*	128.3 *d*	128.3 *d*	128.0 *d*
C-6′, 8′	128.9 *d*	128.9 *d*	128.9 *d*	128.7 *d*
C-7′	130.4 *d*	130.6 *d*	130.0	130.1 *d*

* Multiplicity estimated by offresonance.

† May be interchangeable.

Table 4. ^{1}H NMR spectral data of compounds **15b**, **15c** and **15d** (270 MHz)

	15b	**15c**	C_6D_6 75°	**15d**
1-H	4.97 *m*	4.95 *m*	4.95 *m*	4.96 *m*
5-H				5.20 *d*(*br*)
6-H	5.72 *d*(*br*)	5.72 *d*(*br*)	5.73 *d*(*br*)	6.10 *d*(*br*)
12-H	0.98 *d*	0.96 *d*	0.98 *d*	1.14 *d*
13-H				1.05 *d*
14-H	1.57 *s*(*br*)	1.57 *s*(*br*)	1.00 *s*(*br*)	1.52 *s*(*br*)
15-H			1.60 *s*(*br*)	1.56 *s*(*br*)
2′-H	7.65 *d*	7.57 *d*	7.60 *d*	7.81 *d*
3′-H	6.44 *d*	6.28 *d*	6.38 *d*	6.50 *d*
5′-H	7.59 *m*	7.06 *m*	7.11 *m*	6.76 *d*
8′-H	7.38 *m*	6.91 *d*	7.05	6.98 *d*
9′-H		7.86 *m*	7.11 *m*	6.79 *dd*
OMe	—	3.93 *s*	3.88 *s*	3.29 *s*

J (Hz): 5, 6 = 8; 11, 12 = 11, 13 = 6.5; 2′, 3′ = 15.5; 5′, 6′ = 8.5.

Table 5. ^{1}H NMR spectral data of compounds **30**, **31** and **33** (270 MHz, $CDCl_3$)

	30	**31**	**33**
1-H			3.94 *d*
5-H	1.42 *d*	1.43 *d*	
6-H	5.89 *dd(br)*	5.92 *s(br)*	5.81 *s(br)*
12-H	0.92 *d*	0.93 *d*	0.95 *d*
13-H	0.90 *d*	0.91 *d*	0.90 *d*
14-H	1.17 *s*	1.18 *s*	1.37 *s*
15-H	1.19 *s*	1.19 *s*	1.40 *s*
OCOR	7.65 *d*	7.64 *d*	7.68 *d*
	6.31 *d*	6.29 *d*	6.41 *d*
	7.46 *d*	7.05 *d*	7.52 *m*
	6.85 *d*	6.93 *d*	7.38 *m*
		7.10 *dd*	
OMe	—	3.96 *s*	

aerial parts of *V. luetzelburgii* also contained **12**, **19** and **22**.

The aerial parts of *V. macrophylla* (Cass.) Blake contained, in addition to the germacranes mentioned before (**15b** and **15c**), germacrene D (**12**), squalene, caryophyllene epoxide and humulene (**14**), while the roots afforded the pentaynene **1**, squalene, caryophyllene epoxide, borneolferulate (**7**) [12] and the two further eudesmane esters **30** and **31** as shown by their ^{1}H NMR spectral data (Table 5). The nature of the ester groups was deduced from the NMR spectra. They also showed that the stereochemistry at C-4, C-5 and C-6 was the same as in **25**.

The roots of *V. cinerea* Rusby afforded the dithioacetylene **3** [7], ethyl 3,4-dihydroxycinnamate (**4**), borneol coumarate (**6**) [8] and ferulate (**7**) [12], while the aerial parts contained germacrene D (**12**), 5β,8β-diacetoxy-12-formyloxyverboccidenten (**34**) [3] and 1α-hydroxy-furoverboccidentene (**35**) [3]. The roots of *V. semidecurrens* O. Kuntze afforded the pentaynene **1** and also borneol coumarate (**6**) [12] as well as the ferulate (**7**) [12], while the aerial parts contained in addition bicyclogermacrene (**13**) and humulene (**14**). The roots of *V. boliviana* Klatt. contained the pentaynene **1** [7], the thioacetylene **3** [7], ethyl 3,4-dihydroxycinnamate (**4**), while the aerial parts afforded only lupeol, linoleic and linolenic acid. The aerial parts of *V. pentantha* Blake afforded only germacrene D (**12**), 6β-cinnamoyloxy-germacra-1(10),4-diene (**15b**), lupeyl acetate (**36**) and its isomer **37**.

The overall picture of the chemistry of the *Verbesina* species investigated show that there is a group of species, which can be characterized by the occurrence of terpene and sesquiterpene cinnamates or related esters. However, though these compounds are the most widespread ones, there are several species which do not contain these esters. More species have to be investigated to obtain a clear picture of this large genus.

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 chopped and extracted with Et_2O–petrol (1:2). The extracts from the aerial parts were first treated with MeOH to remove long chain saturated hydrocarbons. The resulting extracts were separated by CC (Si gel, act. grade II) and further by TLC (Si gel GF 254). Known compounds were identified by comparison of the IR and ^{1}H NMR spectra with those of authentic compounds.

Verbesina glabrata (*voucher RMK* 8174, *collected in north-eastern Brazil*). The aerial parts (500 g) afforded 10 mg **8a** (Et_2O–petrol, 2:3), 380 mg **12**, 3 mg **16**, 400 mg **19** (Et_2O–petrol, 1:1), 360 mg **22** (Et_2O–petrol, 1:1), 125 mg **26a** (Et_2O–petrol, 3:1) and 280 mg **33** (Et_2O–petrol, 1:3).

Verbesina luetzelburgii (*voucher RMK* 8055, *collected in north-eastern Brazil*). The roots (220 g) afforded 0.5 mg **1**, 10 mg **5**, 15 mg **9**, 5 mg **10** (Et_2O–petrol, 1:1), 5 mg **11** (Et_2O–petrol, 1:1), 1 mg **12**, 15 mg **13**, 5 mg **15a** (Et_2O–petrol, 1:10), 5 mg **17** (Et_2O–petrol, 1:1), 50 mg **19** (Et_2O–petrol, 1:3), 100 mg **22** (Et_2O–petrol, 1:3), 67 mg **25** (Et_2O–petrol, 1:3), 10 mg **26a** (Et_2O–petrol, 3:1), while the aerial parts (410 g) gave 20 mg **12**, 10 mg **19**, 40 mg **22**.

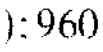
Verbesina macrophylla (*voucher RMK* 8015, *collected in north-eastern Brazil*). The roots (140 g) afforded 1 mg **1**, 10 mg squalene, 10 mg caryophyllene epoxide, 50 mg **7**, 10 mg **30** (Et_2O–petrol, 1:1) and 15 mg **31** (Et_2O–petrol, 1:1), while the aerial parts (590 g) gave 20 mg **12**, 20 mg **14**, 50 mg squalene, 10 mg caryophyllene epoxide, 18 mg **15b** (Et_2O–petrol, 1:10) and 15 mg **15c** (Et_2O–petrol, 1:10).

Verbesina cinerea (*voucher RMK* 7671, *collected in Bolivia*). The roots (140 g) afforded 1 mg **3**, 0.1 mg **4**, 5 mg **6** and 40 mg **7**, while the aerial parts (170 g) gave 20 mg **12**, 30 mg **34** and 40 mg **35**.

Verbesina semidecurrens (*voucher RMK* 7561, *collected in Bolivia*). The roots (68 g) afforded 10 mg **1**, 450 mg **6** and 350 mg **7**, while the aerial parts (94 g) gave traces of **1**, 50 mg **6**, 50 mg **7**, 5 mg **13** and 5 mg **14**.

Verbesina boliviana (*voucher RMK* 7558, *collected in Bolivia*). The roots (140 g) afforded 0.1 mg **1**, 1 mg **3** and 2 mg **4**, while the aerial parts (700 g) gave 20 mg lupeol and 30 mg linoleic and linolenic acid (1:1).

Verbesina pentantha (*voucher RMK* 7882, *collected in Ecuador*). The aerial parts (900 g) afforded 15 mg **12**, 50 mg **15b**, 200 mg **36** and 100 mg **37**.

3,5-*Dimethoxy*-4-O-*geranyl-cinnamic alcohol* (**8a**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1575 (aromate); MS *m/e* (rel. int.): 210 (10) (M − ), 182 (210 − CO), 69 (100) ($C_5H_9^+$). 5 mg **8a** were heated for 30 min with 1 ml Ac_2O. TLC (Et_2O–petrol, 1:10) afforded 5 mg **8b**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc), 1575 (aromate); 960 (*trans* CH = CH); MS *m/e* (rel. int.): 252.100 (23) (M − ). All data identical with those of the natural product [8].

5-(1-*Hydroxy*-1-*ethyl*)-2-*isopropyliden*-2H-*benzofuran*-3-*one* (**11**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1685 (CO), 1610 (C=C); MS *m/e* (rel. int.): M^+ 218.094 (100) ($C_{13}H_{14}O_3$), 203 (80) (M − ·Me), 161 (95) (203 − C_3H_6). ^{1}H NMR ($CDCl_3$): δ 7.72 (*d*, 2-H, *J* = 2 Hz), 7.17 (*d*, 5-H, *J* = 8.5 Hz), 7.65 (*dd*, 6-H, *J* = 8.2 Hz), 2.12 (*sbr*, 10-H), 2.39 (*sbr*, 11-H), 94.95 and 1.53 (*d*, CH(OH)Me, *J* = 6.5 Hz).

6β-*Coumaroyloxy-germacra*-1(10),4-*diene* (**15b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); 1715, 1640 (C=CCO$_2$R), 1610 (aromate); MS *m/e* (rel. int.): 204.188 (44) ($C_{15}H_{24}$), 189 (15) (204 − ·Me), 147 (100) ($HOC_6H_4CH{=}CHCO^+$).

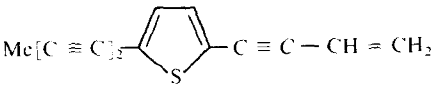
$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-64.2 \quad -67.2 \quad -79.5 \quad -175.0} \; (c = 1.4).$$

6β-*Feruloyloxy-germacra*-1(10),4-*ene* (**15c**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1700, 1650 (C=CCO$_2$R); MS *m/e* (rel. int.): 204.288 (13) ($C_{15}H_{24}$) (M − RCO_2H), 161 (35) (204 − ·C_3H_7), 177 (100) [$HO(MeO)C_6H_3CH{=}CHCO^+$].

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-81.2 \quad -83.4 \quad -102.1 \quad -230.0} \; (c = 3.0).$$

$Me[C\equiv C]_5CH=CH_2$

1



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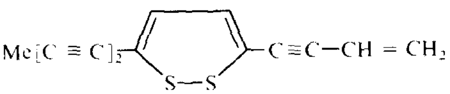
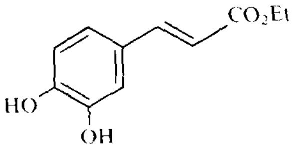


3



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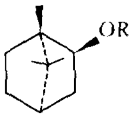
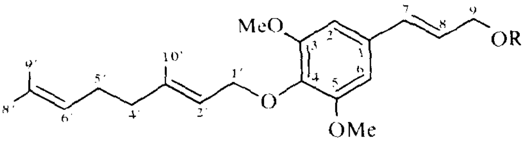
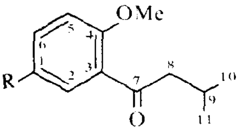


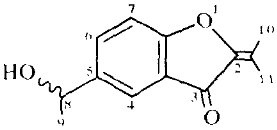
5 R = Cinn*
6 R = Coum*
7 R = Ferul*



8a R = H
8b R = Ac



9 R = COMe
10 R = CH(OH)Me



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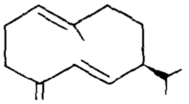

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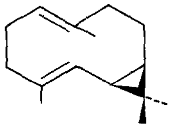

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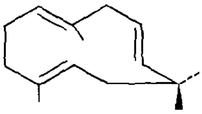

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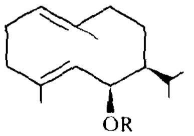
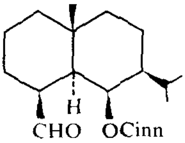
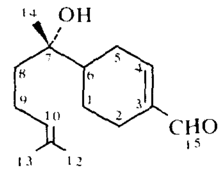


15a R = Cinn
15b R = Coum
15c R = Ferul
15d R = Ferul OAc



16



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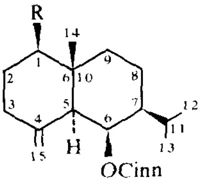
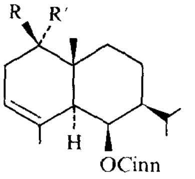
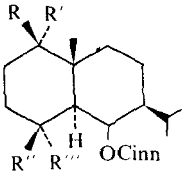


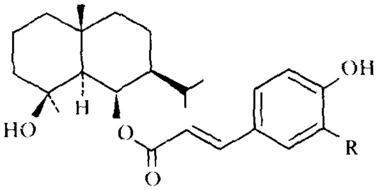
18 R = H
19 R = OH
20 R = OAc



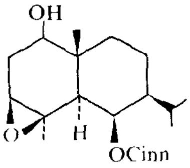
21 R = R′ = H
22 R = OH, R′ = H
23 R = OAc, R′ = H
24 R, R′ = O



	25	**26a**	**26b**	**27**	**28**	**29**
R	H	OH	OH	OAc	OAc	=O
R′	H	H	H	H	H	
R″	OH	OH	Me	OH	OAc	OH
R‴	Me	Me	OH	Me	Me	Me



30 R = H
31 R = OMe



32

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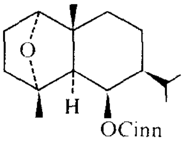
*Cinn = cinnamoyl; Coum = coumaroyl; Ferul = feruloyl.



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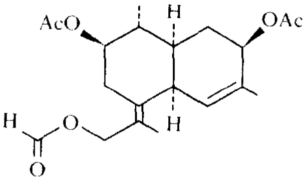
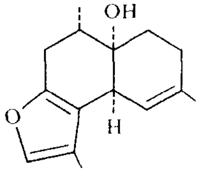
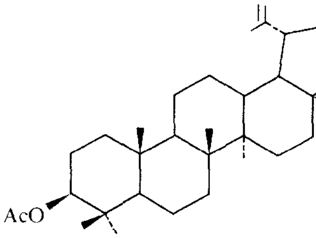


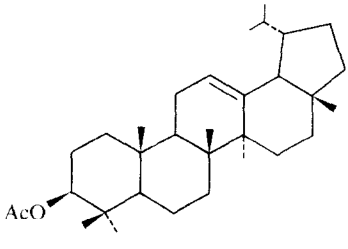
34



35



36



37

10 mg **15c** were heated 1 hr with Ac_2O. TLC afforded 8 mg **15d**, colourless gum, ^1H NMR see Table 4.

7α-Hydroxybisabola-3,10-*dien*-15-*al* (**17**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); 2730, 1690 (CHO); 1650 (C=C); MS *m/e* (rel. int.): M^+ 236.178 (5) ($C_{15}H_{24}O_2$), 218 (10) ($M - H_2O$); ^1H NMR: δ 2.06 (*m*, 2- and 9-H), 6.82 (*m*, 4-H), 5.14 (*tbr*, 10-H), $J = 7$ Hz), 1.63 (*sbr*, 12-H), 1.70 (*sbr*, 13-H), 1.17 (*s*, 14-H), 9.45 (*s*, 15-H).

6β-Cinnamoyloxy-1β-hydroxyeudesm-4(15)-*ene* (**19**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1710, 1640 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 368.235 (11) ($C_{24}H_{32}O_3$), 350 (1) ($M - H_2O$), 220 (15) ($M - PhCH{=}CHCO_2H$), 202 (11) ($220 - H_2O$), 177 (12) ($220 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO^+$), 103 (24) (131 − CO).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+70.5 \quad +74.3 \quad +85.8 \quad +160.8}\,(c = 1.5).$$

10 mg **19** were heated for 30 min in 1 ml Ac_2O at 70°. After evapn and TLC (Et_2O–petrol, 1:3), 10 mg **20** were obtained, colourless gum, MS *m/e* (rel. int.): M^+ 410.246 (8) ($C_{26}H_{34}O_4$), 350 (9) (M − HOAc), 262 (9) ($M - PhCH{=}CHCO_2H$), 202 (46) (262 − HOAc), 159 (58) ($202 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO^+$), 103 (43) (131 − CO).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+102.0 \quad +107.3 \quad +124.1 \quad +238.8}\,(c = 1.3).$$

6β-Cinnamoyloxy-1β-hydroxy-eudesm-3-ene (**22**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH), 1710, 1640 ($C{=}CCO_2R$); MS *m/e* (rel. int.): M^+ 368.253 (8) ($C_{24}H_{32}O_3$), 220 (17) ($M - PhCH{=}CHCO_2R$), 202 (37) ($220 - H_2O$), 131 (100) ($PhCH{=}CHCO^+$).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+56.5 \quad +59.4 \quad +69.0 \quad +135.6}\,(c = 3.3).$$

20 mg **22** were acetylated as above. TLC (Et_2O–petrol), 1:3) afforded 18 mg **23**, colourless gum, MS *m/e* (rel. int.): 410.246 (2) ($C_{26}H_{34}O_4$), 350 (17) (M − HOAc), 202 (77) ($350 - PhCH{=}CHCO_2H$), 159 (90) ($202 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO_2H$). 20 mg **22** in 2 ml CH_2Cl_2 were stirred for 2 hr with 20 mg pyridine chlorochromate and 10 mg $NaHCO_3$. TLC (Et_2O–petrol, 1:2) afforded 15 mg **24**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715 ($C{=}O$, $C{=}CCO_2R$), 1635 (C=C); MS *m/e* (rel. int.): M^+ 366.220 (4) ($C_{24}H_{30}O_3$), 348 (1) ($M - H_2O$), 218 (29) ($M - PhCH{=}CHCO_2H$), 175 (14) ($218 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO^+$). 50 mg **22** in 3 ml $CHCl_3$ were stirred for ? hr with 50 mg *m*-chloroperbenzoic acid and 30 mg $NaHCO_3$. TLC (Et_2O–petrol, 1:1) afforded 40 mg **32**, colourless gum, MS *m/e* (rel. int.): M^+ 384 (3), 236 (15) $M - PhCH{=}CHCO_2H$), 193 (15) ($236 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO_2H$).

6β-Cinnamoyloxy-1β,4β-dihydroxyeudesmane (**26a**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640, 3510 (OH), 1700, 1640 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 371.222 (0.2) ($M - {}^{\cdot}Me$), 220 (3) ($M - H_2O - PhCH{=}CHCO_2H$), 215 (3) ($220 - {}^{\cdot}Me$), 131 (52) ($PhCH{=}CHCO^+$), 101 (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+13.1 \quad +10.9 \quad +12.5 \quad +23.9}\,(c = 3.3).$$

30 mg **26a** were heated for 3 hr with Ac_2O. After evapn, TLC (Et_2O–petrol, 1:3) afforded 15 mg **27**, colourless gum, ^1H NMR see Table 1, and 10 mg **28**, colourless gum, ^1H NMR see Table 1. 20 mg **26a** were oxidized as above with pyridine chlorochromate. TLC (Et_2O–petrol, 1:1) afforded 12 mg **29**, colourless gum, ^1H NMR see Table 1.

6β-Coumaroyloxy-4β-hydroxyeudesmane (**30**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1700, 1635 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 204.188 (15) ($C_{15}H_{24}$, $M - RCO_2H$, $-H_2O$), 164 (100) ($HOC_6H_4CH{=}CHCO_2H$), 147 (34) ($HOC_6H_4CH{=}CHCO^+$).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+0.5 \quad +0.5 \quad +4.0 \quad +30.0}\,(c = 0.2).$$

6β-Feruloyloxy-4β-hydroxyeudesmane (**31**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1705, 1640 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 204.188 (5) ($C_{15}H_{24}$, $M - RCO_2H$, $-H_2O$), 195 (100) [$HO(MeO)C_6H_3CH{=}CHC(OH)_2$].

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+0.7 \quad +2.0 \quad +4.6 \quad +26.7}\,(c = 0.3).$$

6β-Cinnamoyloxy-1α,4α-oxidoeudesmane (**33**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1640 ($C{=}CCO_2R$), 1455, 1310, 1170, 990, 915; MS *m/e* (rel. int.): M^+ 368.235 (0.3) ($C_{24}H_{32}O_3$), 220 (9) ($M - PhCH{=}CHCO_2H$), 205 (6) ($220 - {}^{\cdot}Me$), 177 (10) ($220 - {}^{\cdot}C_3H_7$), 131 (100) ($PhCH{=}CHCO^+$), 103 (37) (131 − CO).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-52.0 \quad -54.5 \quad -62.7 \quad -114.6}\,(c = 4.18).$$

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