SESQUITERPENE LACTONES FROM *EREMANTHUS* SPECIES*

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Abstract—The investigation of three *Eremanthus* species afforded, in addition to known compounds, several new sesquiterpene lactones, a cumambrin B isobutyrate, four lactones related to the eremantholides, two to zexbrevin and one to goyazensolide. Furthermore, a new coniferyl alcohol derivative was isolated. The overall picture of the genus is very uniform. The occurrence of eremanthine and germacranolides with a furanone ring seems to be especially typical.

INTRODUCTION

So far only two species of the genus *Eremanthus* (tribe Vernonieae) have been investigated chemically. Both contain eremanthine [1, 2]. While one afforded, in addition to flavones and triterpenes, three unusual heliangolides, eremantholide A, B and C [1], the second one contains guaianolides and a heliangolide of a more common type [2]. Heliangolides with a furanone ring may be characteristic of the genus, though such lactones have been reported from a few other genera belonging to this tribe: *Centratherum* [3], *Stokesia* [4], *Vanillosmopsis* [5], *Lychnophora* [6], *Mattfeldanthus* [7] and *Vernonia* [8]. We have now investigated three further species. Again two contain eremanthine and also simple sesquiterpene lactones. In addition, a new cumambrine B ester and seven new germacranolides with a furanone ring were isolated, four of them closely related to the eremantholides, two to zexbrevin and one to goyazensolide. The third species, however, only contains very common constituents and no lactones.

RESULTS AND DISCUSSION

The aerial parts of *E. incanus* Less. contain bisabolol (3) [9], costunolide (8) [10], eremanthine (9) [1, 2], lupeol and its acetate as well as a mixture of two sesquiterpene lactones which could be separated only with difficulty. The main compound was identical with eremantholide A (17) [1]. As the structure of this unusual lactone has been elucidated by X-ray analysis only, the ¹H NMR data are given in Table 2. All signals were assigned by double resonance. The second lactone was obviously a guaianolide. ¹H NMR studies led to structure 14, a cumambrin B isobutyrate (Table 1). A double doublet at δ 3.24 (in C_6D_6) can only be assigned to 6β-H, as on

irradiation of this signal the four-fold doublet at 3.67 collapsed to a three-fold one and the broadened double doublet at 2.50 collapsed to a doublet. Irradiation of the signal at 3.67 further collapsed the signals of 13-H (6.22 *d* and 5.38 *d*) to singlets and the three-fold doublet at 4.96 to a double doublet, clearly indicating that the signals mentioned must be assigned to 7- and 8-H. Irradiation at 2.50 (5-H) collapsed the three-fold broadened doublet at 2.20 to a double doublet. The latter was coupled further with the signals at 1.85 and 1.69 as shown by double resonance, indicating that these were the signals of 1- and 2-H. The allylic character of the signals at 1.85 and 1.69 was

Table 1. ¹H NMR spectral data of compound 14 (270 MHz)

	CDCl₃	C₆D₆
1α-H	2.60 *ddd(br)*	2.20 *ddd(br)*
2α-H	2.26 *dd(br)*	2.85 *dd(br)*
2β-H	2.08 *dd(br)*	1.69 *dd(br)*
3-H	5.52 *s(br)*	5.33 *s(br)*
5α-H	2.79 *dd(br)*	2.50 *dd(br)*
6β-H	4.02 *dd*	3.24 *dd*
7α-H	3.88 *dddd*	3.67 *dddd*
8β-H	5.21 *dd(br)*	4.96 *ddd*
9α-H	2.33 *dd*	1.74 *dd*
9β-H	1.79 *d(br)*	1.57 *d(br)*
13-H	6.18 *d*	6.22 *d*
13'-H	5.50 *d*	5.38 *d*
14-H	1.24 *s*	0.87 *s*
15-H	1.92 *s(br)*	2.01 *s(br)*
OCOR	2.64 *qq*	2.33 *qq*
	1.26 *d*	1.07 *d*
	1.25 *d*	1.06 *d*

J (Hz): 1α, 2α = 9; 1α, 2β = 10; 1α, 5α = 8; 2α, 2β = 16; 5α, 6β = 10; 6β, 7α = 9; 7α, 8β = 10; 7α, 13 = 3.5; 7α, 13' = 3; 8β, 9α = 5; 8β, 9β = 1.5; 9α, 9β = 16; OCOR: 2', 3' = 2', 4' = 7.

Table 2. ^{1}H NMR spectral data of compounds 16, 17 and 22 (270 MHz, CDCl$_3$)

	16	17	22
2-H	5.65 s	5.61 s	5.71 s
5-H	6.04 dq	6.03 dq	6.00 dq
6-H	5.02 ddq	4.95 ddq	5.28 ddq
7-H	2.79 dd	2.80 dd	3.73 dddd
8-H	4.06 ddd	4.04 ddd	4.54 ddd
9α-H	2.00 dd	2.00 dd	2.47 dd
9β-H	2.48 dd	2.32 dd	2.30 dd
13-H } 13'-H }	} 1.12 s	} 1.33 s	6.20 d 5.44 d
14-H	1.43 s	1.48 s	1.53 s
15-H	2.07 dd	2.07 dd	2.08 dd
R	5.91 q* 1.65 d(br)* 1.77 s(br)	2.05 m 1.08 d* 0.99 d*	— —
OCOR		—	6.77 qq† 1.77 dq 1.73 dq
OH	4.22 s	2.80 s	—

*J = 7 Hz.

†J = 7 and 1.5 Hz.

J (Hz): 16/17: 5, 6 = 2; 5, 15 = 1.5; 6, 7 = 7; 6, 15 = 2; 7, 8 = 8; 8, 9α = 12; 8, 9β = 2.5; 9α, 9β = 14; 22: 5, 6 = 3; 5, 15 = 1.7; 6, 7 = 5; 6, 15 = 2.5; 7, 8 = 2.5; 7, 13 = 3.2; 7, 13' = 2.8; 8, 9α = 12; 8, 9β = 2; 9α, 9β = 14.

shown by irradiation at 5.39 and 2.01. The latter can only be assigned to the 4-methyl group. The 8-H is further coupled with the double doublet at 1.74 and the broadened doublet at 1.57, which therefore must be assigned to 9-H. Inspection of models showed that the unusual downfield shift of the 7-H signal only can be explained by a 10α-hydroxy group, which established the stereochemistry at C-10. The nature of the ester residue easily followed from the corresponding ^{1}H NMR signals (2.33 qq, 1.07 d, 1.06 d), while the stereochemistry at C-1 and C-5 followed from the observed coupling $J_{1,5}$ = 8 Hz. The optical rotation was also very similar to that given for cumambrin B [11]. Though cumambrin B (1) [11, 12] or its derivatives so far have not been isolated from species of the tribe Vernonieae, 14 obviously is closely related to other guaianolides, which are widespread in the tribe.

Furthermore, the coniferyl alcohol derivative 7 was present. Its structure clearly followed from the ^{1}H NMR data, especially if we compare them with those of similar compounds (see Experimental).

The aerial parts of E. bicolor (Sch. Bip.) Baker afforded trideca-3,5,7,9,11-pentayn-1-ene (1) [13], trideca-3,5,7,9-tetrayne-1,11-diene (2) [13], lupeol, lupeyl acetate and its isomer 26. A complex mixture of sesquiterpene lactones was also present. Only three of these, eremantholide A and C (15 and 17) [1] as well as 15-desoxygoyazensolide (21) [2] have been isolated previously. The structure of another lactone was established by comparing its ^{1}H NMR spectrum with that of 15 (Table 2). Signals at δ6.91, 1.65 and 1.77 indicated that only the residue at C-16 was

changed from a iso-propenyl to a but-2-enyl group. The structure therefore must be 16, though the configuration of the side-chain double bond was assigned only on biogenetic considerations (see below). A second lactone (22) showed ^{1}H NMR signals very similar to 21 (Table 2) with the ester residue being replaced by a tiglate as could be seen from the typical ^{1}H NMR signals (6.77 qq, 1.77 dq and 1.73 dq). The chemical shifts of the other signals are only slightly different from those of 21 and the corresponding angelate, which is present in a Lychnophora species [14]. If we compare the 9-H signals in the spectra of 16 and 22, it is obvious that due to the different ring closures the conformations are not the same (Table 2).

Five further lactones were separated with difficulty and then not completely. The major compound must be a dihydro derivative of 16, as deduced from the ^{1}H NMR data (Table 3) and the molecular formula (C$_{20}$H$_{26}$O$_6$). Inspection of models and decoupling experiments showed that the 4,5-double bond must be saturated. Therefore most probably we were dealing with the lactone 20, a 4β,5-dihydro derivative of 16. The α-orientation of the 4-methyl group followed from the observed couplings (see below). Two further lactones displayed very similar ^{1}H NMR signals; only the ester residues at C-16 must be different. The corresponding ^{1}H NMR signals indicated in one case an iso-propyl and in the other an iso-propenyl group (Table 3) leading to structures 18 and 19.

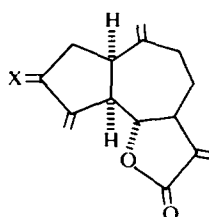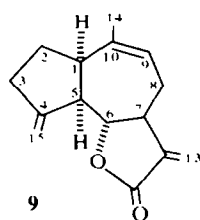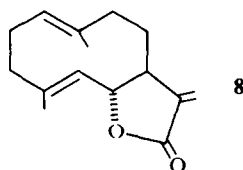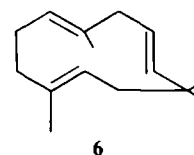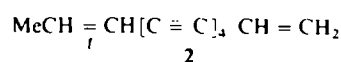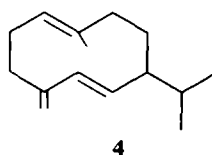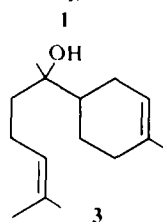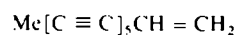The remaining two most polar lactones, which could not be separated, again showed very similar ^{1}H NMR data. However, the presence of typical signals of methylene protons indicated that these two compounds must be methylene lactones. The ^{1}H NMR data further showed that one was a methacrylate and the other a tiglate. The ^{1}H NMR spectrum of the former was very similar to that of zexbrevin [15]; however, the coupling constants of 8-H were not identical, indicating a different configuration at this centre. By comparing a large number of heliangolides it has been shown [16] that most probably the configuration assigned earlier to zexbrevin at C-8 [15] has to be changed. As a consequence the lactones isolated here should be 8α-substituted heliangolides. Inspection of models showed that the observed coupling ($J_{8,9}$ = 10 Hz) was in agreement with this assumption. Therefore the structures of these two lactones must be 23 and 24. Double resonance experiments with all five lactones (18–20, 23 and 24) further established the stereochemistry of C-4, C-6, C-7 and C-8. In the spectra of 18–20, irradiation at 2.53 and 2.57 respectively, allowed the assignments of 6-, 7- and 8-H, while the signals of 5-H could be assigned by irradiation of 3.00 and 4.22 (4.24), respectively. It was also shown that the signal at 3.00 must be assigned to 4β-H as it was coupled with the methyl doublet. As can be seen from models, only the configuration of the 4-methyl group is in agreement with the observed couplings $J_{4,5}$; 4-H is coupled with 2-H. The assignments in the spectra of 23 and 24 were established by double resonance. Again by irradiation at 3.66 the signals of 6-, 7-, 8-, 13- and 15'-H were assigned and by irradiation at 2.49 those of 5- and 4-H were assigned. As mentioned before, the configuration at C-8 clearly followed from the observed coupling $J_{8,9}$ which was established by double resonance (irradiation of the signal of 9α-H). Compounds 18–20 therefore are 4β,5-dihydroeremantholides, while 23 and 24 obviously are the precursors. As already proposed before [1], in the biogenesis of the eremantholides a reductive cyclization, for example of 24, would lead to 20 (see 24a). This also

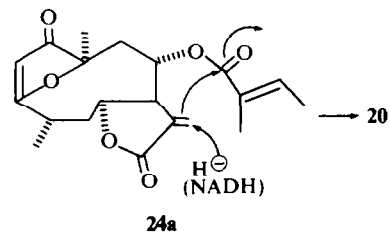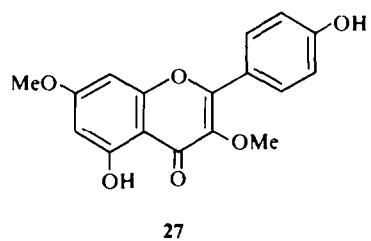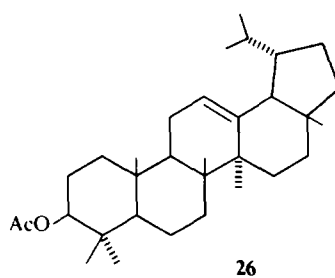Table 3. ¹H NMR spectral data of compounds 18–20, 23 and 24 (270 MHz, CDCl₃)

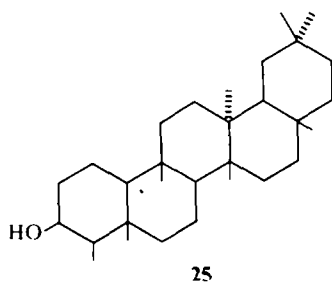|	18	19	20	23	24
2-H	5.60 d	5.61 s(br)		5.70 d	5.69 d
4β-H	3.01 dq(br)	3.00 dq(br)		3.06 dq(br)	
5α-H	2.44 ddd	2.44 ddd		2.49 ddd	
5β-H	2.15 d(br)	2.15 d(br)		2.11 d(br)	
6β-H	4.22 dd	4.24 dd		4.34 ddd	4.33 ddd
7α-H	2.53 dd	2.57 dd		3.36 ddd	
8β-H	3.91 ddd	3.98 ddd	3.99 ddd	4.50 dd(br)	4.51 dd(br)
9α-H	2.01 dd	2.01 dd	2.02 dd	2.35 dd	2.34 dd
9β-H	2.34 dd	2.46 dd	2.44 dd	2.48 dd	
13-H	} 1.35 s	} 1.22 s	} 1.17 s	6.19 d	6.16 d
13'-H				5.46 d	5.43 d
14-H	1.45 s		1.45 s	1.49 s	1.48 s
15-H	1.37 d		1.38 d		1.42 d
R	2.05 qq	5.23 s(br)	5.94 q(br)	6.00 dq	6.75 qq
	1.08 d*	5.07 s(br)	1.65 dqt	5.54 dq	1.75 dqt
	0.96 d*	1.90 s(br)	1.77 dqt	1.83 ddt	1.71 dqt
OH	2.22 s	1.71 s	2.53 s		

* J = 7 Hz.
† J = 7, 1.5; J ~ 1.5 Hz.
J (Hz): 18–20: 2, 4 ~ 1.5; 4, 5α = 7; 4, 5β ~ 1.5; 4, 15 = 7; 5α, 5β = 14; 5α, 6 = 11; 6, 7 = 6.5; 7, 8 = 5; 8, 9α = 12; 8, 9β = 2; 9α, 9β = 13.5; 23/24: 2, 4 = 1.5; 4, 5α = 7; 4, 15 = 7; 5α, 5β = 14; 5α, 6 = 11; 5β, 6 = 1.5; 6, 7 = 5; 7, 8 = 4; 7, 13 = 3.5; 7, 13' = 3; 8, 9α = 10; 8, 9β = 2; 9α, 9β = 13.5.

12

13 R = H
14 R = COCHMe₂

15 R = -C(Me) = CH₂ (A)
16 R = -CH=CH (B)
         | |
        Me   Me

17 R = -CHMe₂ (C)

18 R = C
19 R = A
20 R = B

21 R = Meacr
22 R = Tigl

23 R = Meacr
24 R = Tigl

25

26

27

24a
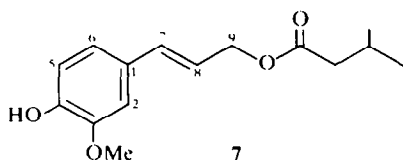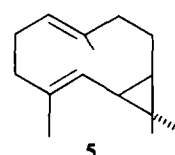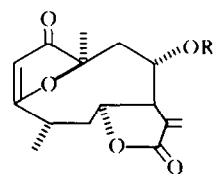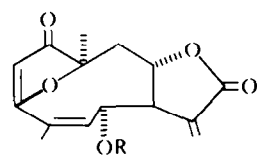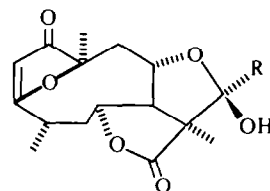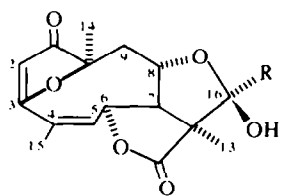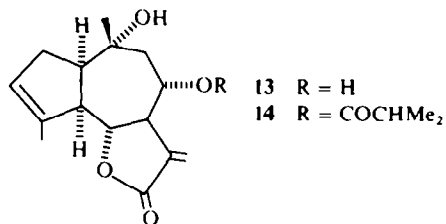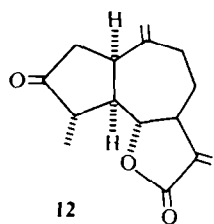
supports the 8α-position of the ester groups in **23** and **24** and established indirectly the correction of the configuration at C-8 of zexbrevin [16].

In order to simplify the nomenclature of all these lactones we propose for the parent compounds the following names: cumambranolide for 8-desoxy-**13**, eremantholanolide for 16-desalkyl (**15**), 4β,5H-eremantholanolide for **18** without an *iso*-propyl group at C-16, goyazensolanolide for the 6-desacyloxy compound of **21** and zexbrevanolide for the 8-desacyloxy derivative of **23**.

The roots of *E. bicolor* contained in addition to **1**, **2**, lupeyl acetate and its isomer **26**, polyisoprene, costunolide (**8**), eremanthine (**9**) [2], dehydrocostuslactone (**10**) [17], the 3-oxo derivatives **11** [18] as well as **12** [19] and *epi*-friedelinol (**25**).

The aerial part of *E. glomerulatus* Less. only afforded **2**, lupeol, lupeyl acetate, germacrene D (**4**), bicyclogermacrene (**5**), humulene (**6**) and 5,4'-dioxy-3,7-dimethoxyflavone **27** [20].

Though one of the species afforded no characteristic compounds the chemotaxonomic situation in the genus *Eremanthus* is relatively clear. Highly oxygenated heliangolides with a furanone ring are quite characteristic. However, the occurrence of guaianolides such as eremanthine may also be important, and this compound does not seem to be very widespread. Nevertheless, a clear separation from related genera of the tribe Vernonieae still seems to be difficult. High concentrations of lupeol and derivatives also have been shown for many species in the tribe. Clearly many more species, including species in other genera belonging to this tribe, have to be investigated chemically. So far, work has been done only on representatives of about 10 out of 70 genera.

EXPERIMENTAL

^{1}H NMR: 270 MHz; TMS as internal standard; MS: 70 eV, direct inlet; optical rotation: CHCl$_3$. The air-dried plant material, collected in north-eastern Brazil, was chopped and extracted with Et$_2$O-petrol (1:2). The resulting extracts first were treated with MeOH to remove long chain saturated hydrocarbons and then 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.

Eremanthus incanus (*voucher RMK* 8136). The aerial parts (260 g) afforded 1 g **3**, 100 mg lupeol, 500 mg lupeyl acetate, 80 mg **7** (Et$_2$O-petrol 1:3), 100 mg **8**, 500 mg **9**, 100 mg **14** and 500 mg **17** (CHCl$_3$-MeOH, 98:2).

Eremanthus bicolor (*voucher RMK* 8132). The roots (900 g) afforded 0.5 mg **1**, 0.5 mg **2**, 500 mg lupeyl acetate, 500 mg polyisoprene, 30 mg **8**, 50 mg **9**, 30 mg **10**, 3 mg **11**, 3 mg **12**, 50 mg **25** and 400 mg **26**, while the aerial parts (700 g) yielded 0.5 mg **1**, 1 mg **2**, 700 mg lupeyl acetate, 600 mg lupeol, 200 mg **15**, 100 mg **16** (Et$_2$O-petrol, 3:1), 5 mg **17**, 20 mg **18** (Et$_2$O-petrol, 3:1), 50 mg **19** (Et$_2$O-petrol, 3:1), 100 mg **20** (Et$_2$O-petrol, 3:1), 40 mg **21**, 50 mg **22** (Et$_2$O-petrol, 3:1), 50 mg **23** (Et$_2$O-petrol, 3:1), 40 mg **24** (Et$_2$O-petrol, 3:1) and 100 mg **26**.

Eremanthus glomerulatus (*voucher RMK* 8099). The aerial parts (100 g) afforded 0.2 mg **2**, 50 mg lupeol, 100 mg lupeyl acetate, 20 mg **4**, 20 mg **5**, 30 mg **6** and 10 mg **27**.

Coniferyl isovalerate (**7**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1740 (CO$_2$R), 975 (*trans* CH=CH); MS *m/e* (rel. int.): M$^-$ 264.136 (100) (C$_{15}$H$_{20}$O$_4$), 232 (33) (M − MeOH), 180 (56) (M − O=C=CHCHMe$_2$), 85 (76) (C$_4$H$_9$CO$^+$). ^{1}H NMR (CDCl$_3$):

δ 6.93 (*s br*, 2-H), 6.88 (*m*, 5, 6-H), 6.59 (*d br*, 7-H, *J* = 16 Hz), 6.15 (*dt*, 8-H, *J* = 16, 6.5 Hz), 4.72 (*d*, *J* = 6.5, 1.5 Hz), 3.92 (*s*, OMe), 2.24 (*d br*, 2-H, *J* = 7 Hz), 2.15 (*m*, 3-H), 0.98 (*d*, 4', 4'-H, *J* = 7 Hz).

8α-Isobutyryloxy-cumambranolide (**14**). Colourless crystals, mp 130° (Et$_2$O-petrol): IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780, 1665 (methylene lactone), 1740 (CO$_2$R); MS *m/e* (rel. int.): M$^+$ 334.178 (3) (C$_{19}$H$_{26}$O$_5$), 316 (2) (M − H$_2$O), 246 (14) (M − Me$_2$CHCO$_2$H), 228 (24) (246 − H$_2$O), 213 (12) (228 − Me), 71 (100) (Me$_2$CHCO$^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{+84.1 \quad +87.7 \quad +100.0 \quad +170.5 \quad +264.0} (c = 0.22).$$

16α-[1'-Methylprop-1E-enyl]-eremantholanolide (**16**). Colourless crystals, mp 222° (Et$_2$O-petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); 1780 (γ-lactone): 1715, 1595 (O=C−C=C−OR); MS *m/e* (rel. int.): M$^+$ 360.157 (5) (C$_{20}$H$_{24}$O$_6$): 342 (9) (M − H$_2$O): 278 (M − C$_4$H$_6$O): 260 (8) (M − RCO$_2$H): 234 (100) (278 − CO$_2$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-42.2 \quad -41.7 \quad -38.8 \quad +58.1 \quad +940.7} (c = 0.59).$$

16α-Isopropyl-4β,5H-eremantholanolide (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1710, 1590 (O=C−C=C−OR): MS *m/e* (rel. int.): M$^+$ 350.173 (3) (C$_{19}$H$_{26}$O$_6$), 332 (2) (M − H$_2$O), 279 (12) (M − RCO), 236 (17) (279 − CO, Me), 110 (100) (C$_6$H$_6$O$_2$).

16α-Isopropenyl-4β,5H-eremantholanolide (**19**). Colourless crystals, not free from **20**, mp 245° (Et$_2$O-petrol): IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1712, 1595 (O=C−C=C−OR): MS *m/e* (rel. int.): M$^+$ 348.157 (7) (C$_{19}$H$_{24}$O$_6$), −C$_3$H$_5$CO 279 (8), 236 (279 − CO, Me), 69 (100) (C$_3$H$_5$CO$^+$).

16α-[1'-Methylprop-1Z-enyl]-4β,5H-eremantholanolide (**20**). Colourless crystals, not free from **19**, mp 227° (Et$_2$O-petrol): IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1713, 1595 (O=C−C=COR): MS *m/e* (rel. int.): M$^+$ 362.173 (2) (C$_{20}$H$_{26}$O$_6$), 344 (9) (M − H$_2$O), 279 (7) (M − C$_4$H$_7$CO), 236 (91) (279 − CO, Me), 83 (100) (C$_4$H$_7$CO$^+$).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{+40.9 \quad +44.5 \quad +58.2 \quad +215.9 \quad +1011.3} (c = 0.22).$$

6α-Tiglinoyloxy-goyazensolanolide (**22**). Colourless gum, not free from **21**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1718, 1655 (C=CCO$_2$R), 1718, 1595 (O=C=C=OR): MS *m/e* (rel. int): M$^+$ 358.142 (28) (C$_{20}$H$_{22}$O$_6$), 330 (1) (M − CO), 275 (14) (M − RCO), 258 (6) (M − RCO$_2$H), 232 (27) (275 − CO, Me), C$_4$H$_7$CO$^+$ 83 (100), 55 (84) (83 − CO).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-54.3 \quad -55.0 \quad -54.0 \quad +31.5 \quad +962.5} (c = 2.0).$$

8α-[2-Methylacryloyloxy]- and tiglinoyloxy-zexbrevanolide (**23** and **24**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1715, 1593 (O=C−C=C−OR): MS *m/e* (rel. int.): M$^+$ 360.157 (7) and 346.142 (5) (C$_{20}$H$_{24}$O$_6$ and C$_{19}$H$_{22}$O$_6$), 278 (4) (M − O=C=C(Me)−CH=CH$_2$), 227 (5) (M − RCO), 260 (5) (M − RCO$_2$H), 232 (6) (260 − CO), 217 (2) (232 − Me), C$_4$H$_7$CO$^+$ 83 (100), C$_3$H$_5$CO$^+$ 69 (61).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+77.0 \quad +82.5 \quad +89.4 \quad +268.4} (c = 3.54).$$

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