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FURANOHELIANGOLIDES FROM TWO *EREMANTHUS* SPECIES AND FROM *CHRESTA SPHAEROCEPHALA**

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Key Word Index—*Eremanthus crotonoides*; *E. glomerulatus*; *Chresta sphaerocephala*; Compositae; sesquiterpene lactones; furanoheliangolides; guaianolide.

Abstract—The investigation of *Eremanthus crotonoides* afforded in addition to known compounds three new furanoheliangolides, while from *E. glomerulatus* six new furanoheliangolides and eremantholides were isolated. From the aerial parts of *Chresta sphaerocephala* a new guaianolide was obtained, while the roots contained known furanoheliangolides. The chemotaxonomy of the subtribe Lychnophorinae is discussed briefly.

INTRODUCTION

So far the chemical investigations of the genus *Eremanthus* have shown that furanoheliangolides and related eremantholides may be characteristic for this genus [1–4], though other types of sesquiterpene lactones were also isolated [2, 4–6]. We have now studied the constituents of *Eremanthus crotonoides* (DC.) Sch. Bip. and reinvestigated *E. glomerulatus* and *Chresta sphaerocephala* DC. Again, mainly furanoheliangolides were isolated.

RESULTS AND DISCUSSION

The aerial parts of *E. crotonoides* afforded germacrene D, bicyclogermacrene, α-humulene, caryophyllene, lupeol and its acetate, taraxasterol and its acetate, stigmasterol and a complex mixture of sesquiterpene lactones. After troublesome separation the known eremantholides **1** [1], **2** [7] and **3** [8] as well as the furanoheliangolides **9** [2], **20** [9] and **22** [2] were finally identified. Furthermore, three additional lactones were obtained, the isobutyrate **12**, which, however, was not free from **9**, and the hydroxy lactones **16** and **17**. The structure of **12** was deduced from the ^{1}H NMR spectral data (Table 1), which were similar to those of **9–11**, only the signals of the ester group being replaced by those of isobutyrate. The other signals were slightly shifted when compared with those of the unsaturated esters. The ^{1}H NMR spectral data of **16** and **17** (Table 2), which could not be separated, indicated that these lactones again differed only in the nature of the ester groups. The molecular formula of **16** was $C_{19}H_{24}O_7$. All oxygen functions were deduced from the ^{1}H NMR spectrum. In addition to signals of a methylene lactone, of a furanone moiety and a methacrylate, a downfield double doublet was present, which was separated from a second signal only in deuteriobenzene. Spin decoupling showed that a hydroxyl group was at C-5, since on irradiation of the corresponding signal the double doublet at δ4.40 collapsed to a doublet and a double doublet quartet (separated from a second signal only in deuteriobenzene) to a broadened quartet. The latter further showed allylic coupling with H-2, typical in cases when a 4β-proton is present [9]. The observed couplings of H-5 therefore required a β-position of the hydroxyl group. Further decoupling led to the assignment of H-7 through H-9. The H-7 signal was easily assigned, since its irradiation collapsed the H-13 signals to singlets and those of H-6 to a doublet. The stereochemistry at C-6 through C-8 followed from the couplings observed, while the presence of an 8,12-lactone was deduced by comparing the corresponding signals with those of similar lactones. Accordingly, **16** was the 4(15)-dihydro derivative of a goyazensanolide isolated from a *Vanillosmopsis* species [10].

A reinvestigation of aerial parts of *E. glomeratus* Less., where a small sample had been studied previously [4], afforded, in addition to lupeol and lupenone, several furanoheliangolides. The main constituent was the epoxy angelate **13** [11] together with seven further lactones the eremantholides **4**, **7** and **8** [9], as well as the furanoheliangolides **14**, **15**, **18** and **19**. The ^{1}H NMR spectrum of **4** (Table 1) indicated the presence of an eremantholide with a 15-hydroxy group. Consequently, the H-5 signal was shifted downfield. Acetylation gave the monoacetate **5**. Most signals were close to those of **3**; therefore, identical stereochemistry at all asymmetric centres could be assumed. The molecular formula of **7**, being $C_{20}H_{24}O_7$ showed that this lactone was most probably an isomer of **6**. All ^{1}H NMR signals therefore were

*Part 413 in the series "Naturally Occurring Terpene Derivatives". For Part 412 see Bohlmann, F., Adler, A., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 1349.

Table 1. ^{1}H NMR spectral data of compounds **4**, **5**, **7**, **12**, **14** and **15** (400 MHz, $CDCl_3$, TMS as internal standard)

	4	**5**	**7**	**7**(C_6D_6,65°)	**12**	**14**	**15**
H-2	5.81 *s*	5.72 *s*	5.61 *s*	5.18 *s*	5.70 *s*	5.73 *s*	5.72 *s*
H-5	6.31 *dq*	6.34 *dq*	6.00 *dq*	5.70 *dq*	5.90 *dq*	6.01 *dq*	6.01 *dq*
H-6	5.03 *ddq*	5.06 *ddq*	4.96 *ddq*	4.87 *ddq*	5.23 *ddq*	5.25 *ddq*	5.22 *ddq*
H-7	2.97 *dd*	2.85 *dd*	2.84 *dd*	2.70 *dd*	3.72 *dddd*	3.74 *dddd*	3.72 *dddd*
H-8	4.04 *ddd*	4.10 *ddd*	4.10 *ddd*	4.11 *ddd*	4.42 *ddd*	4.54 *ddd*	4.57 *ddd*
H-9α	2.44 *dd*	2.45 *dd*	2.38 *dd*	2.34 *dd*	2.40 *dd*	2.33 *dd*	2.33 *dd*
H-9β	2.03 *dd*	2.02 *dd*	2.05 *dd*	1.78 *dd*	2.25 *dd*	2.49 *dd*	2.50 *dd*
H-13 } H-13′ }	1.13 *s*	1.13 *s*	1.43 *s*	1.23 *s*	6.26 *d* 5.47 *d*	6.21 *d* 5.46 *d*	6.23 *d* 5.45 *d*
H-14	1.45 *s*	1.45 *s*	1.50 *s*	1.27 *s*	1.52 *s*	1.54 *s*	1.56 *s*
H-15	4.39 *br d* 4.34 *br d*	4.77 *br s*	2.05 *dd*	1.58 *dd*	2.08 *dd*	2.08 *dd*	2.08 *dd*
H-18	5.92 *qq*	5.92 *qq*	2.84 *m*	2.71 *m*	—	—	—
H-19	1.65 *dq*	1.64 *dq*	1.43 *d*	1.49 *d*	—	—	—
H-20	1.76 *dq*	1.76 *dq*	1.42 *br s*	1.40 *br s*	—	—	—
OCOR	—	—	—	—	2.39 *qq*	4.48 *br dq*	6.40 *q*
					1.40 *d*	1.30 *d*	1.99 *d*
					1.08 *d*	6.10 *s*	4.18 *br dd*
						5.84 *br s*	4.09 *br dd*
OAc	—	2.11 *s*	—	—	—	—	—
OH	3.49 *s*	3.29 *s*	—	—	—	2.37 *br d*	1.88 *dd*
	3.82 *br*	—	—	—	—	—	—

J(Hz): Compounds **4**, **5**, and **7**: 5, 6 = 2.5; 5, 15 = 6, 15 = 1.5; 6, 7 = 7; 7, 8 = 4; 8, 9α = 12; 8, 9β = 2.5; 9α, 9β = 13.5; compounds **12**, **14** and **15**: 5, 6 = 3; 5, 15 = 6, 15 = 1.5; 6, 7 = 5; 7,8 = 2.5; 7, 13 = 3; 7, 13′ = 2.5; 8.9α = 2; 8, 9β = 11.5; 9α, 9β = 14; (**4**: 15, 15′ = 14; **4**/**5**: 18, 19 = 7; 18, 20 = 19, 20 = 1.5; **7**: 18, 19 = 6; **12**: *i*Bu: 2′, 3′ = 2′, 4′ = 7; **14**: OCOR: 3′, 4′ = 3′, OH = 6.5; **15**: OCOR: 3′, 4′ = 7; 5′, 5′ = 13; 5′, OH = 6).

similar to those of **6** (Table 1), though some typical differences were visible. In particular, the chemical shifts of H-13, H-18 and H-19 differed from those of **6** and the coupling $J_{18,19}$ was slightly larger. Since the mass spectra of **6** and **7** were also similar, they appeared to have related structures. The ^{1}H NMR spectral data of **14** (Table 1) indicated the presence of a furanoheliangolide with an 8, 12-lactone ring as the corresponding signals were similar to those of **9**–**13**. The nature of the ester group at C-6 followed from the additional ^{1}H NMR signals, a broadened double quartet at δ 4.48, a methyl doublet at 1.30, a broadened doublet at 2.37 and two singlets at 6.10 and 5.84. Irradiation at δ 4.48 collapsed the doublets at δ 1.30 and 2.37 to singlets and sharpened the olefinic signals. The presence of such an ester group was further supported by the mass spectrum, which showed elimination of the corresponding ketene, acyl radical, acyloxy radical and acid. This type of ester group seems to be new.

15 was obviously an isomer of **14**; this followed from both the mass spectrum and ^{1}H NMR spectrum (Table 1). Also, the changed nature of the ester group was deduced from the typical ^{1}H NMR signals of a 5-hydroxytiglate. All other signals were very similar to those of **14**. **18** was also an epoxy angelate. Its ^{1}H NMR spectral data (Table 2) were similar to those of **16** and **17**; all couplings were the same as in the latter. Thus the stereochemistry was the same in all three lactones. The structure of **19** followed from the molecular formula and the ^{1}H NMR spectrum (Table 2). The presence of a 6, 12-lactone was deduced from the typical signals of H-5 through H-8, which were similar to those of **20**. The 8β-hydroxyl group followed from the couplings observed and from the chemical shifts of H-13, which were as usual at lower fields due to the free hydroxyl at C-8. The roots afforded lupeyl acetate and its Δ-12, 13-isomer, stigmasterol, costunolide and eremantholide.

So far the roots of *Chresta sphaerocephala* DC. belonging to the same subtribe, have not been chemically investigated. In addition to tridecapentaynene, tetradeca-4, 6-dien-8, 10, 12-triyn-1-ol, lupeyl acetate and its Δ-12, 13-isomer, the furanoheliangolide **20** [12] was isolated, while a reinvestigation of the aerial parts gave, in addition to those compounds previously isolated, minute amounts of **20** and a further lactone, which was most probably **21**. After purification as its acetate **22**, the ^{1}H NMR spectrum (Table 2) was in part very similar to that of eremanthin. However, the 11, 13-methylene group was obviously oxygenated. Accordingly, the H-13 signals were a pair of doublets, which were at higher fields in the crude diol **21**. The position of the second hydroxyl group followed indirectly from the absence of an 11, 13-coupling and from the hydrogen bridge, which was deduced from the the IR spectrum. As the signal of H-6 was at lower fields as in the spectrum of eremanthin, an

Table 2. ^{1}H NMR spectral data of compounds **16–19** and **22** (400 MHz, $CDCl_3$, TMS as internal standard)

	16		**17**	**18**	**19**	**22**
H-1	—		—	—	—	2.55 *m*
H-2	5.79 *d*		5.78 *d*	5.80 *d*	5.60 *s*	1.58 *m*; 2.15 *m*
H-3	—		—	—	—	2.30–2.45 *m*
H-4		3.40 *m*†		3.41 *ddq*	—	—
H-5		4.35 *br dd*		4.32 *br dd*	5.90 *dq*	2.55 *m*
H-6	4.49 *dd*		4.45 *dd*	4.42 *dd*	4.86 *ddq*	4.10 *dd*
H-7		3.39 *m**		3.44 *dddd*	3.68 *dddd*	2.4 *m*
H-8		4.34 *ddd*		4.32 *ddd*	3.82 *m*	2.00 *br dd*; 2.40 *m*
H-9α	2.45 *dd*		2.40 *dd*	2.46 *dd*	2.31 *dd*	5.54 *ddq*
H-9β	2.35 *dd*		2.30 *dd*	2.31 *dd*	2.17 *dd*	
H-13	6.25 *d*		6.30 *d*	6.38 *d*	6.45 *dd*	4.38 *d*
H-13′	5.51 *d*		5.50 *d*	5.60 *d*	5.86 *dd*	4.08 *d*
H-14		1.50 *s*		1.49 *s*	1.44 *s*	1.82 *br s*
H-15		1.38 *d*		1.37 *d*	2.07 *dd*	5.20 *br s*; 5.03 *br s*
OCOR	6.00 *br s*		2.35 *qq*	2.98 *q*	—	—
	5.55 *dq*		1.04 *d*	1.37 *d*		
	1.83 *dd*		1.07 *d*	1.24 *s*		
OAc	—		—	—	—	2.09 *s*

*In C_6D_6 2.85 *dddd*.
†In C_6D_6 2.72 *ddq*.
OH 3.20 *s*.
J(Hz): Compounds **16–18**: 2,4 = 1; 4, 5 = 4, 15 = 7; 5, 6 = 9; 6, 7 = 4, 5; 7, 8 = 8, 9β = 2.5; 7, 13 = 3.3; 7, 13′ = 2.8; 8, 9α = 11.5; 9α, 9β = 14; compound **19**: 5, 6 = 3.5; 5, 15 = 6, 15 = 1.5; 6, 7 = 4; 7, 8 ~ 2; 7, 13 = 3; 7, 13′ = 2.5; 13, 13′ = 0.7; 8, 9α = 2.5; 8, 9β = 8.3; 9α, 9β = 14.5; compound **22**; 5, 6 = 6, 7 = 10; 7, 8β = 11; 8α, 8β = 13; 8α, 9 = 8; 8β, 9 = 2.5; 9, 14 = 1; OMeacr: 3′, 3′ = 3′, 4′ = 1; O*i*Bu: 2′, 3′ = 2′, 3′ = 2′, 4′ = 7; Epang: 3′, 4′ = 5.5.

11β-hydroxy was indicated. Therefore the natural lactone was most probably 11β, 13-dihydroxy-11, 13-dihydroeremanthin, though several signals were multiplets. Spin decoupling, however, allowed the assignment of most signals.

The results on the two further *Eremanthus* species and on the *Chresta* species again showed that the chemistry of the genera placed in the subtribe Lychnophorinae [13] is very uniform, furanoheliangolides, especially goyazensanolides and eremanthanolides, being characteristic. As such components were also isolated from the roots of a *Chresta* species, this genus is unexceptional. No sesquiterpene lactones have been isolated so far from *Albertinia* but also in this case the roots have not been investigated.

EXPERIMENTAL

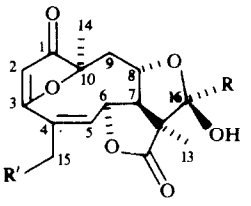
The air-dried plant material, collected in north-eastern Brazil, voucher deposited in the U.S. National Herbarium, Washington, was extracted with Et_2O–petrol (1:2), and the resulting extracts separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material.

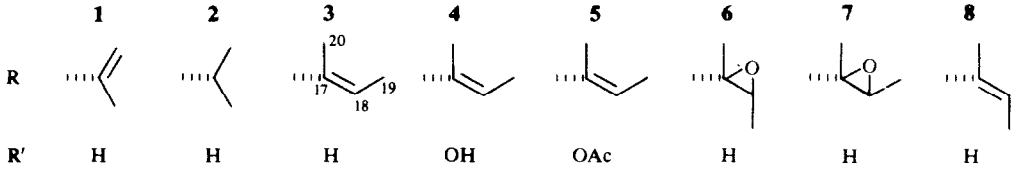
Eremanthus crotonoides (*voucher RMK* 8519). The aerial parts (300 g) afforded 7 mg germacrene D, 3 mg bicyclogermacrene, 1 mg α-humulene, 10 mg caryophyllene, 50 mg lupeol and 15 mg of its acetate, 50 mg taraxasterol and 100 mg of its acetate, 12 mg stigmasterol, 5 mg **1**, 2 mg **2**, 5 mg **3**, 20 mg **9**, 3 mg **10**, 1 mg **11**, 6 mg **12** (C_6H_6–CH_2Cl_2–Et_2O, 1:1:1), 1 mg **6** and 2 mg **17** (same solvent, no separation).

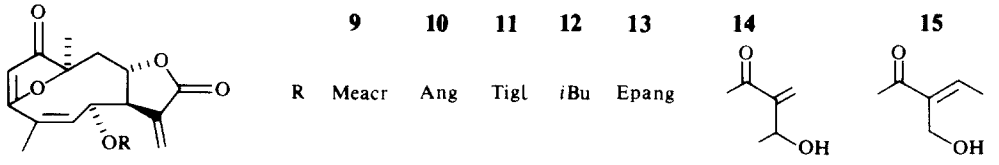
Chresta sphaerocephala (*voucher RMK* 8919). The roots (55 g) afforded traces of tridecapentaynene, 1 mg tetradeca-4, 6-diene-8, 10, 12-triyn-1-ol, 20 mg lupeol acetate and its Δ-12, 13-isomer (2:1), 5 mg **20** 1 mg **21** (Et_2O–CH_2Cl_2–C_6H_6, 1:1:1), while the aerial parts (320 g) gave, in addition to compounds isolated before, 2 mg **20**.

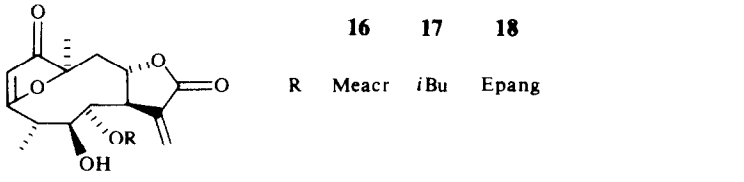
Eremanthus glomerulatus (*voucher RMK* 8924). The aerial parts (780 g) afforded to 20 mg lupeol, 10 mg lupenone, 25 mg **4** (Et_2O–petrol, CH_2Cl_2–C_6H_6–MeOH, 10:10:1), 30 mg **6**, 10 mg **7** (Et_2O–petrol, 3:1, several developments), 600 mg **13**, 40 mg **14** (CH_2Cl_2–C_6H_6–MeOH, 10:10:1), 5 mg **15** (same solvent), 5 mg **18** (same solvent) and 2 mg **19** (Et_2O–petrol, 3:1, several times), while the roots (190 g) gave 10 mg lupeol acetate and 5 mg of its Δ-12, 13-isomer, 5 mg stigmasterol, 2 mg constunolide and 2 mg eremantholide.

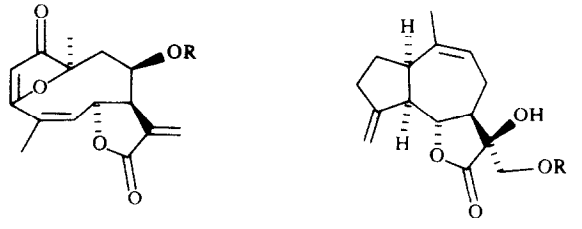
15-*Hydroxy*-16α (1′-*methylprop*-1Z-*enyl*)-*eremanthanolide* (**4**). Colourless gum, which was purified as its acetate **5** (Ac_2O, 1 hr, 70°), colourless crystals, mp 210° (Et_2O–petrol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1720 (C=CCO$_2$R,











19 R = H
20 R = Tigl

21 R = H
22 R = Ac

C=O), 1600 (C=C–OR); MS *m/z* (rel. int.): 418.173 $[M]^+$(0.5) ($C_{22}H_{26}O_8$), 400 $[M-H_2O]^+$ (1), 358 $(M-HOAc]^+$ (3), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (30).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{-20 \quad -19 \quad -14 \quad +95 \quad +1039} (CHCl_3;\ c0.2).$$

16α-(1′-*Methyl*-1,2-*epoxypropyl*)-*eremanthanolide* (**7**). Colourless crystals, mp 198° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 1780 (γ-lactone), 1710, 1590 (O=C–C=C–OR); MS *m/z* (rel. int.): 376. 152 $[M]^+$ (14) ($C_{20}H_{24}O_7$), 358$[M-H_2O]^+$ (1), 332 $[M-CO_2]^+$ (15), 95 (100), 83 (82), 69 (77), 55 (75).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-33 \quad -33 \quad -23 \quad +113} (CHCl_3;\ c0.2).$$

6α-[2′-(1′)-*hydroxyethyl acryloyloxyl*]-*goyazensanolide* (**14**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1785 (γ-lactone), 1720 (C=CCO_2R, C=O), 1600 (C=C–OR); MS *m/z* (rel. int.): 374.137 $[M]^+$ (74) ($C_{20}H_{22}O_7$), 359 $[M-Me]^+$ (7), 276 $[M-C_5H_6O_2]^+$ (17), 275 $[M-COR]^+$ (11), 259 $[M-O_2CR]^+$ (14), 258 $[M-HO_2CR]^+$ (15), 232 $[276-CO_2]^+$ (100), 99 $[RCO]^+$ (46), 83 (95), 81 $[99-H_2O]^+$ (86), 69 (57), 55 (95), 53 (87).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+0.6 \quad -1 \quad +5 \quad +102} (CHCl_3;\ c2.0).$$

6α-(5′-*Hydroxytigloyloxy*)-*goyazensanolide* (**15**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1715 (C=CCO$_2$R, C=O), 1590 (C=C–OR); MS *m/z* (rel. int.): 374.137 $[M]^+$ (37) ($C_{20}H_{22}O_7$), 356 $[M-H_2O]^+$ (6), 275 $[M-COR]^+$ (10), 258 $[M-HO_2CR]^+$ (8), 232 $[276-CO_2]^+$ (44), 99 $[RCO]^+$ (100), 83 (79), 69 (51), 55 (65), 53 (80).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-16 \quad -16 \quad -12 \quad +56} (CHCl_3;\ c0.1).$$

6α-(2′-*Methyl*-2′, 3′-*epoxybutyryloxy*)-5β-*hydroxy*-4(15)-*goyazensanolide* (**18**). Colourless crystals, mp 210° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1790 (γ-lactone), 1750 (CO_2R), 1720, 1600 (O=C–C=C–OR); MS *m/z* (rel. int.): 392.131 $[M]^+$ (10) ($C_{20}H_{22}O_8$), 276 $[M-HO_2CR]^+$ (12), 248 $[276-CO]^+$ (8), 126 (100), 125 (71), 99 $[RCO]^+$ (10), 81 $[99-CO]^+$ (14).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+40 \quad +40 \quad +48 \quad +135} (CHCl_3;\ c0.3).$$

2′,3′-*Dihydro*-15-*desoxygoyazensolide* (**12**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (γ-lactone), 1730 (CO_2R), 1720, 1590 (RO–C=C–C=O); MS *m/z* (rel. int.): 346.142 $[M]^+$ (8) ($C_{19}H_{22}O_6$), 258 $[M-HO_2CR]^+$ (4), 232 (100), 71 $[C_3H_7CO]^+$ (25) $[\alpha]_D = -158^\circ$ ($CHCl_3$; *c*0.54).

5β-*Hydroxy*-4, 5-*dihydro*-15-*desoxygoyazensolide* (**16**) *and* 5β-*hydroxy*-4, 5, 2′, 3′-*tetrahydro*-15-*desoxygoyazensolide* (**17**). Colourless gum, not separated, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580 (OH), 1775 (γ-lactone), 1735 (CO_2R), 1720 (C=CCO$_2$R), 1720, 1590 (RO–C=C–C=O); MS *m/z* (rel. int.): 364.153 (2) and 362.137 (8) $[M]^+$ ($C_{19}H_{24}O_7$ and $C_{19}H_{22}O_7$), 276.100 $[M-HO_2CR]^+$ (10) ($C_{15}H_{16}O_5$), 248 $[276-CO]^+$ (6), 71 $[C_3H_7CO]^+$ (4) 69 $[C_3H_5CO]^+$ (100). $[\alpha]_D = +72^\circ$ ($CHCl_3$; *c*0.1).

11β, 13-*Dihydroxy*-11, 13-*dihydroeremanthin* (21). Colourless gum, which was purified as its acetate **22**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3550 (OH), 1787 (γ-lactone), 1745, 1240 (OAc); MS *m/z* (rel. int.): 306.147 $[M]^+$ (2) ($C_{17}H_{22}O_5$), 228 $[M-HOAc, H_2O]^+$ (9) 213 $[228-Me]^+$ (10), 159 $[C_{12}H_{15}]^+$ (100).

8β-*Hydroxyzexbrevanolide* (19). Colourless gum, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1710, 1590 (O=C–C=COR); MS *m/z* (rel. int.): 276.100 $[M]^+$ (6) ($C_{15}H_{16}O_5$), 83 (52), 69 (67), 57 (100), 55 (85).

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