Phytochemistry, Vol. 26, No. 3, pp. 761–764, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

AMBROSANOLIDES FROM *PARTHENIUM LOZANIANUM*

J. JAKUPOVIC, V. P. PATHAK, F. BOHLMANN and X. A. DOMINGUEZ*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.; *Instituto Tecnologico y de Estudios Superiores de Monterrey, Mexico

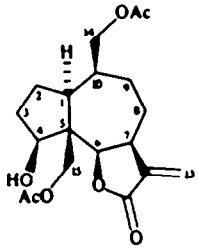
(*Received* 21 *April* 1986)

Key Word Index—*Parthenium lozanianum*; Compositae; sesquiterpene lactones; ambrosanolides; triterpenes; cycloartenone derivatives; germacra-5*E*,10(14)-dien-1β,4α-diol.

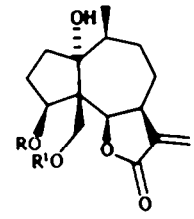
Abstract—The reinvestigation of *Parthenium lozanianum* afforded, in addition to tetraneurins C and D reported previously from this species, 13 further ambrosanolides, ten of them being new, a sesquiterpene diol and several triterpenes including two new cycloartenone derivatives. The structures were elucidated by high-field ^{1}H NMR spectroscopy.

INTRODUCTION

The genus *Parthenium* (Compositae, tribe Heliantheae, subtribe Ambrosiinae) has been studied chemically by several groups [1, 2] but in most cases the investigations were done long ago. Nearly all species contain ambrosanolides, especially those with oxygen functions at C-14 and/or C-15, the so-called parthenolides [1]. *P. lozanianum* Bartlett gave tetraneurins B, C and D [3]. A reinvestigation of this species gave five known and ten new ambrosanolides as well as six triterpenes, two not being reported previously. The results are discussed in this paper.



1



	2	**3**	**4**	**5**
R	Ac	H	Ac	*i*Bu
R^1	H	*i*Bu	*i*Bu	H

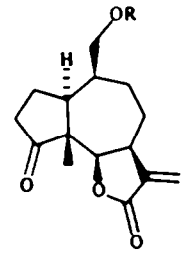
RESULTS AND DISCUSSION

The extract of the aerial parts afforded the ambrosanolides ligulatin C [4], tetraneurins C [5] and D [3], coronopilin [6], chiapin A [2] and compounds **1**–**10**, the triterpenes incanilin, fruticin A, fruticin B and argentatin A [7], the epoxide **14** and the related ether **15** as well as germacra-5*E*-10(14)-dien-1β,4α-diol (**11a**).

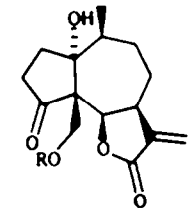
The structure of the latter followed from the spectral data, which were identical with those of a diol obtained by triphenyl phosphine reduction of the corresponding hydroperoxide **11b** [8].

The structures of the known lactones ligulatin C and tetraneurins C and D were determined by their ^{1}H NMR spectra, which agreed with those reported in the literature. Furthermore, the stereochemistry of tetraneurin C was investigated by NOE difference spectroscopy. Clear effects were observed between H-14, H-15, H-2β and H-3β, between H-3α, H-4 and H-2α, between H-4, H-6 and H-3α, between H-6, H-4 and H-7, between H-15, H-8β and H-14, between H-7, H-6 and H-9, and between H-2β, H-3β and H-14. Also the ^{13}C NMR data supported the structure and configuration.

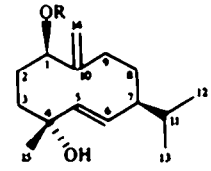
The ^{1}H NMR spectrum of compound **1** was close to that of tetraneurin D [3]. The presence of an acetoxyl group at C-14 caused the expected shift differences. The spectrum of **2** (Table 1) was similar to that of tetraneurin



6 R = *i*Val
7 R = Ac



8 R = *i*Bu
9 R = *i*Val
10 R = MeBu



11a R = H
11b R = OH

Table 1. ^{1}H NMR spectral data of compounds 2–5 (400 MHz, $CDCl_3$, TMS as internal standard)

	2	3	4	5
H-2	2.71 *ddd*	2.61 *ddd*	2.71 *ddd*	2.74 *ddd*
H-2′	1.31 *ddd*	1.30 *ddd*	1.33 *ddd*	1.30 *ddd*
H-3	2.57 *dddd*	2.42 *dddd*	2.55 *dddd*	2.61 *dddd*
H-3′	1.60 *m*	1.75 *m*	1.62 *m*	1.55 *m*
H-4	5.77 *dd*	4.83 *ddd*	5.74 *dd*	5.73 *dd*
H-6	5.27 *d*	5.37 *d*	5.28 *d*	5.26 *d*
H-7	3.36 *m*	3.40 *m*	3.36 *m*	3.35 *m*
H-8	2.05 *m*	2.10 *br ddd*	2.05 *m*	2.10 *br ddd*
H-8′	1.86 *br ddd*	1.87 *br ddd*	1.85 *br ddd*	1.85 *br ddd*
H-9	2.21 *br ddd*	2.22 *br ddd*	2.24 *br ddd*	2.21 *br ddd*
H-9′	1.63 *m*	1.62 *ddd*	1.65 *m*	1.64 *ddd*
H-10	1.98 *m*	1.93 *ddq*	2.00 *m*	1.96 *m*
H-13	6.15 *d*	6.22 *d*	6.20 *d*	6.14 *d*
H-13′	5.46 *d*	5.53 *d*	5.50 *d*	5.44 *d*
H-14	1.20 *d*	1.09 *d*	1.08 *d*	1.20 *d*
H-15	3.89 *br s*	4.22 *d* 4.18 *d*	4.26 *d* 4.10 *d*	3.90 *br s*
OR	2.12 *s*	2.50 *qq*	2.51 *qq*	2.58 *qq*
		1.15 *d*	1.16 *d*	1.24 *d*
		1.14 *d*	2.04 *s*	1.22 *d*
		2.17 *d*(OH)		

J (Hz): 6,7 = 10; 7,13 = 3.7; 7,13′ = 3.5; compound 1: 3,4 = 3′,4 = 9; 10,14 = 3; 10,14′ = 10; 14,14′ = 11; 15,15′ = 12; compounds 2–5: 2,2′ = 3,3′ = 14; 2,3 = 3′,4 = 7; 2,3′ = 12; 2′,3 = 9.5; 2′,3′ = 3.5; 3,4 = 10; 7,8 = 7; 7,8′ = 12; 8,8′ = 15; 8,9′ = 8; 8′,9 = 13; 9,9′ = 14; 9,10 = 9′,10 = 4; 10,14 = 8; compound 3: 4, OH = 3; compounds 3 and 4: 15,15′ = 12; OiBu: 2,3 = 2,4 = 7.

C. The presence of a free 15-hydroxyl group followed from the upfield shift of the H-15 signal. In the case of tetraneurin C, a pair of doublets were observed while **2** showed a broadened singlet at δ3.89.

The ^{1}H NMR spectrum of compound **5** (Table 1) was very close to that of **2**. However, the acetate singlet was replaced by the typical signals of an isobutyrate (δ2.58, *qq*; 1.24, *d*; 1.22, *d*). The spectrum of compound **4** (Table 1) was similar to that of tetraneurin C. Again one of the acetate singlets was replaced by the signals of an isobutyrate. The relative positions of the ester groups were deduced from the mass spectrum. After loss of acetic acid elimination of $CH_2OCOCHMe_2$ is visible.

The ^{1}H NMR spectrum of **3** (Table 1) was close to that of tetraneurin D. Again the acetate singlet was replaced by signals of an isobutyrate.

The ^{1}H NMR spectrum of coronopilin agreed well with spectra reported in the literature. The spectra of compounds **8**–**10** (Table 2) clearly indicated that these compounds were the corresponding 15-*O*-isobutyrate, isovalerate and 2-methyl butyrate. Accordingly, in addition to the ester signals the H-15 singlet was replaced by pairs of doublets around δ4.4.

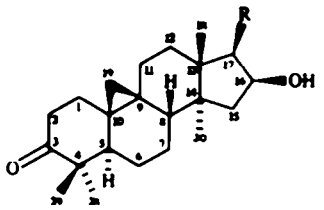
The ^{1}H NMR spectra of compounds **6** and **7** were very close to that of the corresponding isobutyrate chiapin A [2], which was also present in the extract. Again the spectra differed only in the signals of the ester group while all the others were almost identical.

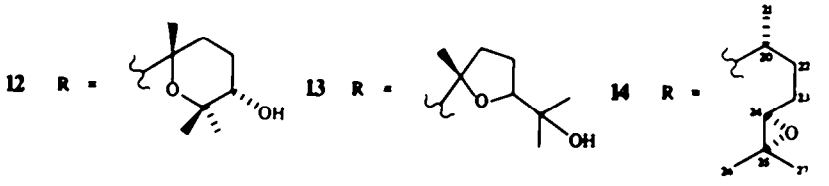
The ^{1}H NMR spectra of incanilin, fruticin A, fruticin B (**12**) and argentatin A (**13**) agreed with those reported in the literature [7] and the data of **14** were close to those of

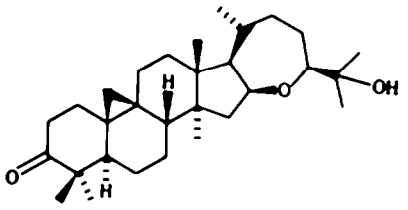
Table 2. ^{1}H NMR spectral data of compounds 8–10 (400 MHz, $CDCl_3$, TMS as internal standard)

	8	9	10
H-2	2.79 *ddd*	2.80 *ddd*	2.81 *ddd*
H-2′	1.67 *ddd*	1.63 *ddd*	1.65 *m*
H-3	2.56 *ddd*	2.56 *ddd*	2.56 *ddd*
H-3′	2.43 *ddd*	2.44 *ddd*	2.44 *ddd*
H-6	4.97 *d*	4.98 *d*	4.97 *d*
H-7	3.36 *m*	3.36 *m*	3.36 *m*
H-8	1.94 *br ddd*	1.95 *br ddd*	1.95 *br ddd*
H-8′	1.75 *m*	1.76 *m*	1.75 *m*
H-9	2.25 *br ddd*	2.23 *br ddd*	2.24 *br ddd*
H-9′	1.65 *m*	1.66 *m*	1.65 *m*
H-10	2.13 *m*	2.10 *m*	2.12 *m*
H-13	6.25 *d*	6.27 *d*	6.26 *d*
H-13′	5.59 *d*	5.59 *d*	5.59 *d*
H-14	1.16 *d*	1.16 *d*	1.17 *d*
H-15	4.40 *d* 4.32 *d*	4.32 *d* 4.32 *d*	4.41 *d* 4.34 *d*
OR	2.49 *qq*	2.14 *d*	2.32 *ddq*
	1.13 *d*	2.07 *m*	1.65 *m*
	1.12 *d*	0.92 *m*	1.43 *ddq*
			1.12 *d*
			0.95 *t*

J (Hz): 2,2′ = 14; 2,3 = 2′,3 = 9; 2,3′ = 10.5; 2′,3′ = 2; 3,3′ = 18; 6,7 = 8; 7,8 = 12; 7,13 = 3; 7,13′ = 2.6; 8,8′ = 15; 8,9 = 9,9′ = 13; 9,10 = 5; 10,14 = 7.5; 15,15′ = 12.







15

12 and 13. However, in the spectrum of compound 14 (Table 3) the broadened, narrowly split triplet at δ3.40 in the spectrum of 12 was replaced by a triplet at 2.82 and one of the methyl singlets was now a doublet at 0.97. In agreement with the mass spectrum, therefore the presence of an epoxide was proposed. Also the fragmentation pattern supported the structure. After elimination of water (*m/z* 438), loss of the whole side chain produced *m/z* 311. Biogenetically the epoxide 14 may be transformed after introduction of a tertiary hydroxyl group at C-20 to 12 and 13. In the spectrum of compound 15 (Table 3), the second lowfield signal was now a double doublet at δ3.59. The molecular formula indicated that compound 15 was isomeric with 14. However, a pronounced mass spectral fragment at *m/z* 397 (73%) was obviously due to elimination of a hydroxyisopropyl group. Thus the proposed structure was very likely correct because compound 14 would be the direct precursor of 15. These triterpenes may be, in addition to the parthenolides, typical for *Parthenium*. However, similar cycloartenone derivatives are not only present in *Parthenium* [7] but also in *Balsamorhiza* [9], *Lindheimera* [10] and *Viguiera* species [8].

Table 3. ^{1}H NMR spectral data of compounds 14 and 15 (400 MHz, $CDCl_3$, TMS as internal standard)

	14	15
H-1α	1.85 *br ddd*	1.84 *br ddd*
H-1β	1.55 *m*	1.55 *m*
H-2α	2.30 *ddd*	2.30 *ddd*
H-2β	2.71 *ddd*	2.71 *ddd*
H-15	2.04 *m*	2.07 *m*
H-16	4.44 *ddd*	4.60 *ddd*
H-18	1.19 *s*	1.17 *s*
H-19α	0.58 *d*	0.57 *d*
H-19β	0.81 *br d**	0.81 *br d*
H-21	0.97 *d*	0.94 *d*
H-24	2.82 *t*	3.59 *dd*
H-26	1.31 *s*	1.09 *s* (6H)
H-27	1.26 *s*	
H-28	1.04 *s*	1.04 *s*
H-29	1.10 *s*	1.10
H-30	0.89 *s*	0.88 *s*

* *W*-coupling with H-1α.

J (Hz): 1α,1β = 1α,2β = 13; 1α,2α = 4.5; 1β,2α = 2; 1β,2β = 3.5; 2α,2β = 14; 15,16 = 16,17 = 7; 15',16 = 23,24 = 6 (compound 15: 23α,24 = 2; 23β,24 = 12).

EXPERIMENTAL

The air-dried plant material (500 g) (voucher Dominguez 8002, deposited in the Herbarium of the Instituto Tecnologico, Monterrey) was extracted with MeOH Et_2O petrol (1:1:1) and worked up as reported previously [11]. The defatted extract (7.3 g) was separated first by CC (silica gel) into three fractions (fraction 1: Et_2O petrol, 1:1; fraction 2: Et_2O–petrol, 3:1; fraction 3: Et_2O MeOH, 9:1). Prep. TLC (silica gel, PF 254, Et_2O petrol, 2:1) of fraction 1 gave four bands (1/1–1/4). Repeated TLC of 1/1 gave 7 mg 15 (R_f 0.66), of 1/2 7 mg 14 (R_f 0.53), of 1/3 6 mg fruticin A, and of 1/4 6 mg incanilin, 10 mg fruticin A, 5 mg fruticin B and 5 mg argentatin A. Fraction 2 was separated further by flash chromatography (silica gel ϕ

30–60 μm, Et_2O–petrol, 1:1 Et_2O, 20 ml fractions). HPLC (RP 8, MeOH–H_2O, 3:2, *ca* 100 bar) of fraction 2/1 gave 1.5 mg **9** (R_t 9.5 min) and a mixture (R_t 8.8 min) which gave by TLC (CH_2Cl_2 C_6H_6–Et_2O, 3:3:1, two developments) 3.5 mg chiapin A and 2 mg **10** (R_f 0.23). HPLC of fraction 2/2 (RP 8, MeOH–H_2O, 13:7) gave 20 mg coronopilin (R_t 5.6 min), 500 mg tetraneurin C (R_t 6.9 min) and 13 mg **8** (R_t 7.9 min). TLC of fraction 2/3 ($CHCl_3$–Me_2CO, 19:1) gave 5 mg ligulatin C, 7 mg **4** (R_f 0.64) and 3.5 mg **5** (R_f 0.21). TLC of fraction 2/4 (same solvent, four developments) gave 3 mg **6** (R_f 0.57) and 10 mg **11a** (R_f 0.15). TLC of fraction 2/5 (same solvent, four developments) gave 26 mg **2** (R_f 0.67) and 3 mg **11a**. TLC of fraction 2/6 ($CHCl_3$–Me_2CO, 9:1, two developments) gave 75 mg **3** (R_f 0.61) and 0.5 mg **7** (R_f 0.38). TLC of fraction 2/7 ($CHCl_3$–MeOH, 97:3, two developments) gave 3 mg tetraneurin D. Flash chromatography of fraction 3 (Et_2O–MeOH, 9:1) gave two polar fractions (3/1 and 3/2). TLC of 3/1 ($CHCl_3$–MeOH, 47:3) gave 0.5 mg **7** (R_f 0.61) and TLC of 3/2 (same solvent) gave 4 mg **1** (R_f 0.58). The structures of known compounds were established by comparing the 400 MHz ^1H NMR spectra with those of authentic material and with literature data as well as by rigorous ^1H NMR investigations.

Tetraneurin C. ^{13}C NMR ($CDCl_3$, C-1–C-15): δ86.1 *s*, 28.5 *t*, 36.8 *t*, 80.7 *d*, 56.3 *s*, 83.4 *d*, 42.7 *d*, 25.0 *t*, 27.7 *t*, 42.1 *d*, 140.0 *s*, 170.7 *s*, 120.3 *t*, 15.9 *q*, 60.2 *t* (OAc: 21.3 *q*, 21.1 *q*, 170.0 *s*, 169.9 *s*).

14-*Acetoxytetraneurin D* (**1**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1735, 1255 (OAc); MS *m/z* (rel. int.): 306.147 [M – HOAc]$^+$ (3) (calc. for $C_{17}H_{22}O_5$: 306.147), 246 [306 – HOAc]$^+$ (40), 228 [246 – H_2O]$^+$ (42), 57 (100); ^1H NMR ($CDCl_3$): δ4.24 (*dd*, H-4), 4.54 (*d*, H-6), 3.41 (*m*, H-7), 6.21 (*d*, H-13), 5.51 (*d*, H-13'), 4.32 and 4.05 (*dd*, H-14), 4.18 and 4.09 (*d*, H-15); (*J*: 3,4 = 3',4 = 9; 6,7 = 10; 7,13 = 3.7; 7,13' = 3.5; 10,14 = 3; 10,14' = 10; 14,14' = 11, 15,15' = 12 Hz); $[\alpha]_D^{24}$ –112° ($CHCl_3$; *c* 0.4).

15-*Desacetyltetraneurin C* (**2**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1760 (γ-lactone), 1745 (OAc); MS *m/z* (rel. int.): 306.147 [M – H_2O]$^+$ (6) (calc. for $C_{17}H_{22}O_5$: 306.147), 264 [M – HOAc]$^+$ (94), 246 [264 – H_2O]$^+$ (78), 215 [246 – CH_2OH]$^+$ (56), 123 (100); $[\alpha]_D^{24}$ –31° ($CHCl_3$; *c* 1.0).

Desacetyltetraneurin D-15-O-*isobutyrate* (**3**). Colourless crystals, mp 213°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1740 (OCOR); MS *m/z* (rel. int.): 352.189 [M]$^+$ (0.6) (calc. for $C_{19}H_{28}O_6$: 352.189), 264 [M – RCO_2H]$^+$ (2), 246 [264 – H_2O]$^+$ (1), 71 [RCO]$^+$ (50), 57 (100); $[\alpha]_D^{24}$ –42° ($CHCl_3$; *c* 1.5).

15-*Desacetyltetraneurin C-isobutyrate* (**4**). Colourless crystals, mp 174°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1760 (γ-lactone), 1730 (CO_2R); MS *m/z* (rel. int.): 334.178 [M – HOAc]$^+$ (6) (calc. for $C_{19}H_{26}O_5$: 334.178), 264 [334 – O=C=CMe_2]$^+$ (47), 246 [264 – H_2O]$^+$ (64), 233 [334 – CH_2OiBu]$^+$ (24), 123 (78), 71 [RCO]$^+$ (100); $[\alpha]_D^{24}$ –46° ($CHCl_3$; *c* 0.7).

Desacetyltetraneurin D-4-O-*isobutyrate* (**5**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1760 (γ-lactone), 1735 (CO_2R); MS *m/z* (rel. int.): 334.178 [M – H_2O]$^+$ (2) (calc. for $C_{19}H_{26}O_5$: 334.178), 264 [M – RCO_2H]$^+$ (50), 246 [264 – H_2O]$^+$ (40), 215 [246 – CH_2OH]$^+$ (31), 123 (81), 71 (100); $[\alpha]_D^{24}$ –69° ($CHCl_3$; *c* 0.3).

Desacyl chiapin A-isovalerate (**6**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (γ-lactone), 1745 (C=O, CO_2R); MS *m/z* (rel. int.): 348.194 [M]$^+$ (1) (calc. for $C_{20}H_{28}O_5$: 348.194), 333 [M – Me]$^+$ (7), 246 [M – RCO_2H]$^+$ (42), 231 [246 – Me]$^+$ (82), 85 [RCO]$^+$ (72), 57 [85 – CO]$^+$ (100); ^1H NMR ($CDCl_3$): δ2.48 (*ddd*, H-3), 2.26 (*ddd*, H-3'), 4.52 (*d*, H-6), 3.28 (*m*, H-7), 2.32 (*m*, H-10), 6.29 and 5.57 (*d*, H-13), 4.37 and 4.11 (*dd*, H-14), 1.05 (*s*, H-15); OCOR: 2.20 (*d*, 2H), 2.09 (*m*, 1H), 0.96 (*d*, 6H); (*J*: 2,3 = 2; 2,3' = 2',3 = 9; 2',3' = 8; 3,3' = 18; 6,7 = 8.5; 7,13 = 3; 10,14 = 4; 10,14' = 14, 14' = 11 Hz).

Desacyl chiapin A-acetate (**7**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (γ-lactone), 1740, 1250 (OAc); MS *m/z* (rel. int.): 306.147 [M]$^+$ (4) (calc. for $C_{17}H_{22}O_5$: 306.147), 291 [M – Me]$^+$ (61), 246 [M – HOAc]$^+$ (60), 231 [246 – Me]$^+$ (88), 97 (100), 93 (94); ^1H NMR ($CDCl_3$): δ2.49 and 2.26 (*ddd*, H-3), 4.53 (*d*, H-6), 3.27 (*m*, H-7), 2.33 (*m*, H-10), 6.29 and 5.57 (*d*, H-13), 4.37 and 4.11 (*dd*, H-14), 1.05 (*s*, H-15), 2.07 (*s*, OAc) (*J*: see compound **6**).

Coronopilin-15-O-*isobutyrate* (**8**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1760 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 332.162 [M – H_2O]$^+$ (0.5) (calc. for $C_{19}H_{24}O_5$: 332.162), 280 [M – O=C=CMe_2]$^+$ (4), 262 [M – RCO_2H]$^+$ (66), 244 [262 – H_2O]$^+$ (27), 123 (60), 71 [RCO]$^+$ (100); $[\alpha]_D^{24}$ –38° ($CHCl_3$; *c* 0.9).

Coronopilin-15-O-*isovalerate* (**9**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1760 (γ-lactone), 1740 (CO_2R); MS *m/z* (rel. int.): 364.189 [M]$^+$ (0.4) (calc. for $C_{20}H_{28}O_6$: 364.189), 262 [M – RCO_2H]$^+$ (48), 244 [262 – H_2O]$^+$ (20), 85 [RCO]$^+$ (65), 57 [85 – CO]$^+$ (100); $[\alpha]_D^{24}$ –31° ($CHCl_3$; *c* 0.1).

Coronopilin-15-O-[2-*methyl butyrate*] (**10**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1735 (CO_2R); MS *m/z* (rel. int.): 262.121 [M – RCO_2H]$^+$ (6) (calc. for $C_{15}H_{18}O_4$: 262.121), 244 [262 – H_2O]$^+$ (3), 85 [RCO]$^+$ (35), 57 [85 – CO]$^+$ (100); $[\alpha]_D^{24}$ –35° ($CHCl_3$; *c* 0.2).

Germacra-5E,10(14)-*diene*-1β,4α-*diol* (**11a**). Colourless oil; IR and ^1H NMR spectra identical with those of material prepared from **11b** [8]. MS *m/z* (rel. int.): 238.193 [M]$^+$ (3.5) (calc. for $C_{15}H_{26}O_2$: 238.193), 220 [M – H_2O]$^+$ (21), 177 [220 – C_3H_7]$^+$ (62), 81 (100); $[\alpha]_D^{24}$ –13° ($CHCl_3$; *c* 1.3).

Desoxyprefruticin B (**14**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 1700 (C=O); MS *m/z* (rel. int.): 456.360 [M]$^+$ (16) (calc. for $C_{30}H_{48}O_3$: 456.360), 441 [M – Me]$^+$ (15), 438 [M – H_2O]$^+$ (20), 423 [438 – Me]$^+$ (44), 311 [438 – side chain]$^+$ (19), 57 (100).

Desoxyisofruticin B (**15**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 1700 (C=O); MS *m/z* (rel. int.): 456.360 [M]$^+$ (5) (calc. for $C_{30}H_{48}O_3$: 456.360), 441 [M – Me]$^+$ (3), 423 [441 – H_2O]$^+$ (4), 398 [M – Me_2CO]$^+$ (43), 397 [M – C(OH)Me_2]$^+$ (73), 383 [398 – Me]$^+$ (12), 379 [397 – H_2O]$^+$ (20), 55 (100).

Acknowledgements V.P.P. is grateful to Alexander von Humboldt-Stiftung for a fellowship. X.A.D. thanks CONACYT of Mexico for a grant (project PCEBNA-031053.

REFERENCES

1. Seaman, F. C. (1982) *Bot. Rev.* **48**, 209.
2. Rodriguez, E., Yoshioka, H. and Mabry, T. J. (1970) *Phytochemistry* **10**, 1145.
3. Yoshioka, H., Rüesch, H., Rodriguez, E., Mears, J. A., Mabry, T. J., Calzada, J. G. A. and Dominguez, X. A. (1970) *Tetrahedron* **26**, 2167.
4. Maldonado, E., Mendoza, G. O., Cardenas, J. and Ortega, A. (1985) *Phytochemistry* **24**, 2981.
5. Rüesch, H. and Mabry, T. J. (1969) *Tetrahedron* **25**, 805.
6. Herz, W. and Högenauer (1961) *J. Org. Chem.* **26**, 5011.
7. Matsubara, C. and Romo de Vivar, A. (1985) *Phytochemistry* **24**, 613.
8. Gao, F., Mabry, T. J., Bohlmann, F. and Jakupovic, J. (1986) *Phytochemistry* **25**, 1489.
9. Bohlmann, F., Banerjee, S., Grenz, M., Misra, L. N., Schmeda-Hirschmann, G., King, R. M. and Robinson, H. (1985) *Phytochemistry* **24**, 511.
10. Herz, W., Watanabe, K., Kulanthaivel, P. and Blount, J. (1985) *Phytochemistry* **24**, 2645.
11. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.