Pergamon

PII: S0031-9422(97)00235-5

Phytochemistry, Vol. 46, No. 4, pp. 729–734, 1997

Printed in Great Britain
0031-9422/97 $17.00+0.00

DITERPENES OF *BAHIA GLANDULOSA**

ANA-L. PÉREZ-CASTORENA, MARIANO MARTÍNEZ-VÁZQUEZ and ALFONSO ROMO de VIVAR†

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México D. F.

(*Received* 10 *December* 1996)

Key Word Index—*Bahia glandulosa*; Compositae; flavonoids; *ent*-kauranes; manoyloxides; *ent*-rosanes.

Abstract—*Bahia glandulosa* afforded ten new diterpenes in addition to some known compounds. The structures of the new compounds were established by spectroscopic studies and chemical transformations. © 1997 Elsevier Science Ltd

INTRODUCTION

Previous studies [1–5] show that the genus *Bahia* contains sesquiterpene lactones, diterpenes, acylglucopyranoses and flavonoids. In a continuation of our investigations on the genus *Bahia* [1–3], we isolated from *B. glandulosa* Greenman 10 new diterpenes along with some known compounds.

RESULTS AND DISCUSSION

Aerial parts of *B. glandulosa* afforded 10 new diterpenes and the known compounds β-sitosterol, stigmasterol, the flavonoids ayanin (**1a**) [6] and velutin (**1b**) [7], the diterpenes *ent*-16α,17,19-kauranetriol (**2d**) [8], 3-deoxy-4-*epi*-julslimtetrol (**4c**) [9] and its acetonide **4e**. The last compound was isolated from fractions previously decolourized with benthonic earth in Me_2CO, during which step it was probably formed from **4c**. The free compound (**4c**) was obtained by hydrolysis of **4e**.

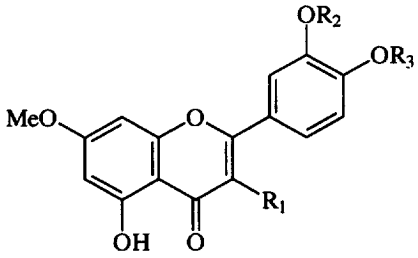
The first four new diterpenes were obtained as a mixture of compounds with general formula **2a**. The ^1H NMR spectrum of **2a** (Table 1) showed two methyl singlet at δ 0.91 and 1.04, thus suggesting a kaurane skeleton with two oxidized methyl groups. An AB system at δ 3.75 and 3.62 was assigned to the C-17 methylene. A second AB system (δ 4.19 and 3.83) was attributed to the C-19 methylene which was joined to an acyloxy function. The ^{13}C NMR spectrum (Table 2) showed two triplets (δ 66.3 and 66.9) that corresponded to C-17 and C-19, respectively. A singlet at δ 81.8 was attributed to C-16 which supports a hydroxyl group. Acetylation of the mixture gave the monoacetates **2b** whose IR spectrum still show an alcohol band, thus indicating its tertiary nature. The presence of two neighbouring alcohols in **2a** was proved when the acetonides **2c** were obtained. Thus the ester had to be attached to C-18 or C-19. Saponification of **2a** gave a triol whose mp, $[\alpha]_D$, acetylated derivative and spectral data were identical to those described for *ent*-16α,17,19-kauranetriol (**2d**) [8], therefore the acyloxy group was attached to C-19. The saponification products of **2a** were the triol **2d** and a mixture of acids, which were treated with CH_2N_2 and identified by GC and GC-MS as the methyl esters of capric, lauric, myristic and palmitic acids.

The new diterpene **3a**, $C_{25}H_{44}O_6$, presented in its ^1H NMR spectrum (Table 1) two AB systems (δ 3.49, 3.34 and 4.14, 3.86). The first was assigned to the C-16 methylene and the second was attributed to the C-19 methylene which bears an ester group. Comparison of the ^1H and ^{13}C NMR spectral data of **3a** with those described for 14, 15, 16, 19-tetrahydroxy-*ent*-manoyloxide 19-*O*-acetate [10] established that they only differed in the ester group attached to C-19. The presence of three free alcohols, two of them in an α, β relative position, was corroborated by the formation of the derivatives **3b** and **3c**. The constitution of the side chain was proved by mass spectrometry and its position by the saponification product **3d**. The configuration *R* proposed for C-14 is based on the differences in the C-12 chemical shifts observed for **3a** *vs* **3b** ($\Delta\delta$ −3.05) and **3a** *vs* **3c** ($\Delta\delta$ −1.75). These are in agreement with those observed for borjatriol and their triacetyl and acetonide derivatives [11].

The next four new compounds were found as a mixture of general formula **3e** and differ from **3a** in the acyl group to C-19. This was inferred from the ^1H

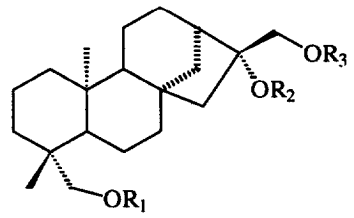
*Contribution no. 1552 of the Instituto de Química, UNAM.

†Author to whom correspondence should be addressed.

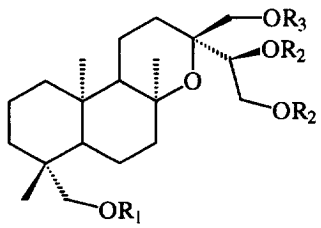


1a R_1=OMe R_2=H R_3=Me
1b R_1=H R_2=Me R_3=H

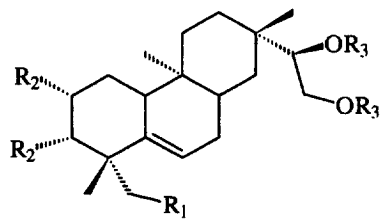
n = 8, 10, 12, 14



2a R_1=$CO(CH_2)_nCH_3$ R_2=H R_3=H
2b R_1=$CO(CH_2)_nCH_3$ R_2=H R_3=Ac
2c R_1=$CO(CH_2)_nCH_3$ R_2 and R_3=CMe_2
2d R_1=H R_2=H R_3=H



3a R_1= *i*-Val R_2=H R_3=H
3b R_1= *i*-Val R_2=Ac R_3=Ac
3c R_1= *i*-Val R_2=CMe_2 R_3=H
3d R_1=H R_2=H R_3=H
3e R_1=$CO(CH_2)_nCH_3$ R_2=H R_3=H
3f R_1=$CO(CH_2)_nCH_3$ R_2=Ac R_3=Ac
3g R_1=$CO(CH_2)_nCH_3$ R_2=CMe_2 R_3=H



4a R_1=H R_2=OH R_3=H
4b R_1=H R_2=OAc R_3=Ac
4c R_1=OH R_2=H R_3=H
4d R_1=OAc R_2=H R_3=Ac
4e R_1=OH R_2=H R_3=CMe_2

and ^{13}C NMR spectra (Tables 1 and 2) which show the signals of fatty acids instead of those of an isovaleroyloxy group. Saponification of the mixture afforded **3d**, the same saponification product obtained from **3a**. As was described for **2a**, the acyl groups attached to the C-19 hydroxyl in **3e** were identified as the methyl esters of capric, lauric, myristic and palmitic acids. The triacetates **3f** and the acetonides **3g** were obtained as mixtures.

The last new diterpene is the *ent*-rosane tetrol **4a** whose molecular formula $C_{20}H_{34}O_4$ was established by high resolution mass spectrometry. The IR spectrum showed the presence of hydroxyl groups (bands at 3389 and 3399 cm^{-1}) and the ^1H NMR spectrum (Table 1) showed an ABX system (δ 3.19, 3.42 and 3.71) assigned to a 1,2-dihydroxyethyl side chain attached to C-13. The C-2 and C-3 methynes joined to hydroxyl groups were observed as a *ddd* signal at δ 3.97 and a *d* at δ 3.37, respectively. The H-6 signal was localized at δ 5.54 as a broad *dd*. The existence of four hydroxyl groups was evidenced by the derivative **4b** and the relative configuration of **4a** was established by X-ray analysis (Fig. 1).

The absolute configuration of **2d** is known and belongs to the *ent*-series. The optical rotation of **2d** is negative as well as those of the new substances **2a**, **3a**, **3e** and **4a**. Therefore the new diterpenes isolated of *B. glandulosa* probably belong to the *ent* series.

EXPERIMENTAL

General. FID-GC: 25 m × 0.32 mm, methyl-5% phenylsilicone gum fused-silica capillary column with a 0.33 μm film thickness, column temp 170° for 15 min and then programmed to 280° at 10° min^{-1}, split ratio of 50:1, H_2 1.0 ml min^{-1}. GC-MS: 25 m × 0.32 mm HP-PAS 1701 column with 0.25 μm film thickness, column temp 80° for 1.0 min and then programmed to 290° at 8° min^{-1}. EI 70 eV.

Plant material. Bahia glandulosa Greenman was col-

Table 1. ^{1}H NMR spectral data of compounds **2–4** (300 MHz, $CDCl_3$)

H	2a*	2b*	2c	3a	3b	3c	3d†	3e	3f	3g	4a*†	4b*
2											3.97 *ddd* (2.6, 4.9, 11.5)	5.23 *ddd* (2.5, 5.3, 11.7)
3											3.37 *d* (2.6)	5.0 *d* (2.4)
6											5.54 *br dd* (3.8, 5.4)	5.52 *br*
10											2.04 *ddd* (2.2, 4.7, 13)	
13	2.01 *m*	2.02 *m*	2.12 *m*									
14				3.76 *dd* (3.4, 3.9)	5.19 *dd* (3, 9)	4.21 *dd* (7.2, 7.5)	3.81 *dd* (3.7, 6)	3.74 *dd* (3.9, 4.5)	5.18 *dd* (3, 9)	4.25 *m*		
15a				3.72 *dd* (3.4, 10.2)	4.44 *dd* (3, 12)	3.91 *dd* (7.5, 15)	3.78 *dd* (3.7, 10.6)	3.71 *dd* (3.9, 10.8)	4.45 *dd* (3, 12)	3.85 *m*	3.19 *dd* (2.6, 8.8)	4.93 *dd* (2.3, 9.2)
15b				3.61 *dd* (3.9, 10.2)	4.13 *dd* (9, 12)	3.81 *dd* (7.2, 15)	3.63 *dd* (6, 10.6)	3.59 *dd* (4.5, 10.8)	4.12 *dd* (9, 12)			
16a				3.49 *d* (11.2)	4.05 *d* (11.7)	3.49 *d* (10.5)	3.53 *d* (11.2)	3.41 *d* (11)	4.05 *d* (11.6)	3.45 *m*	3.71 *dd* (2.6, 11)	4.44 *dd* (2.3, 11.7)
16b				3.34 *d* (11.2)	3.97 *d* (11.7)	3.39 *d* (10.5)	3.45 *d* (11.2)	3.32 *d* (11)	3.98 *d* (11.6)		3.42 *dd* (8.8, 11)	4.02 *dd* (9.2, 11.7)
17a	3.75 *d* (11)	4.19	4.05 *d* (8.6)	1.31	1.24	1.39	1.41	1.31	1.25	1.38	0.90	1.0
17b	3.62 *d* (11)		3.90 *d* (8.6)									
18	1.04	1.0	1.03	0.95	0.96	0.95	1.02	0.93	0.95	0.93	1.15	1.15
19a	4.19 *d* (11)	4.19 *d* (11)	4.22 *d* (11.1)	4.14 *d* (11)	4.17 *d* (11)	4.15 *d* (11)	3.73 *d* (11.2)	4.14 *d* (11)	4.17 *d* (11)	4.25 *m*	1.02	1.05
19b	3.83 *d* (11)	3.84 *d* (11)	3.86 *d* (11.1)	3.86 *d* (11)	3.87 *d* (11)	3.86 *d* (11)	3.44 *d* (11.2)	3.86 *d* (11)	3.87 *d* (11)	3.85 *m*	0.74	0.73
20	0.91	0.91	0.93	0.79	0.81	0.80	0.90	0.78	0.82	0.78		
R, H-ω	0.85 *t* (6.6)	0.86 *t* (6.5)	0.88 *t* (6.5)	0.94 *d* (6.3)	0.95 *d* (6.6)			0.85 *t* (7)	0.88 *t* (7)	0.85 *t* (7)		
	1.23 *br*	1.23 *br*	1.26 *br*	2.8 *oct* (6.3)	2.1 *m*	2.1 *oct* (6.3)		1.23 *br*	1.26 *br*	1.23 *br*		
H-α	2.27 *t* (7.5)	2.27 *t* (7.5)	2.29 *t* (7.5)	2.16 2.19 *d* (6.3)	2.19 *d* (6.6)	2.16 *d* (6.3)		2.27 *t* (7.5)	2.29 *t* (7.4)	2.26 *t* (7.4)		
Ac		2.08			2.02 2.10				2.1 2.0			
CMe_2			1.38 1.35			1.32 1.29				1.32 1.30		

Unmarked signals are singlets. Values in parentheses are coupling constants in Hz.
* 200 MHz.
† MeOH-d_4

Table 2. ^{13}C NMR spectral data of compounds **2–4** (75 MHz, $CDCl_3$)

C	**2a***	**2b***	**2c**	**3a**	**3b**	**3c**	**3d†**	**3e**	**3f**	**3g**	**4a*†**	**4b***
1	40.3 *t*	40.3 *t*	40.3 *t*	43.7 *t*	43.6 *t*	43.9 *t*	44.9 *t*	43.7 *t*	43.5 *t*	43.9 *t*	28.6 *t*	24.9 *t*
2	18.3 *t*	18.2 *t*	18.2 *t*	18.0 *t*	17.9 *t*	18.1 *t*	19.2 *t*	18.1 *t*	18.0 *t*	18.1 *t*	69.5 *d*	69.9 *d*
3	36.4 *t*	36.5 *t*	36.4 *t*	38.9 *t*	38.5 *t*	38.9 *t*	40.4 *t*	38.9 *t*	38.7 *t*	38.9 *t*	80.2 *d*	77.0 *d*
4	39.2	39.2	39.1	37.0	37.1	37.2	39.7	37.0	36.9	37.2	42.3	40.5
5	56.7 *d*	56.7 *d*	56.4 *d*	56.9 *d*	56.9 *d*	57.0 *d*	58.6 *d*	56.9 *d*	57.1 *d*	57.0 *d*	142.7	140.1
6	20.7 *t*	20.7 *t*	20.6 *t*	20.2 *t*	20.2 *t*	20.4 *t*	21.3 *t*	20.2 *t*	20.3 *t*	20.3 *t*	120.9 *d*	119.9 *d*
7	42.3 *t*	42.2 *t*	41.8 *t*	36.5 *t*	36.4 *t*	36.6 *t*	36.9 *t*	36.5 *t*	37.2 *t*	36.6 *t*	30.1 *t*	29.1 *t*
8	44.6	44.8	44.4	76.3	75.1	75.5	76.7	76.1	75.2	75.5	37.3 *d*	35.6 *d*
9	56.8 *d*	56.7 *d*	56.7 *d*	55.5 *d*	52.6 *d*	54.6 *d*	56.4 *d*	55.6 *d*	52.7 *d*	54.5 *d*	35.9	34.9
10	39.2	37.1	37.1	36.9	36.8	36.9	38.3	37.0	36.5	37.0	46.7 *d*	44.9 *d*
11	18.3 *t*	18.2 *t*	18.8 *t*	14.5 *t*	14.1 *t*	14.5 *t*	15.7 *t*	14.6 *t*	14.2 *t*	14.5 *t*	31.7 *t*	33.5 *t*
12	26.2 *t*	26.2 *t*	27.0 *t*	25.9 *t*	22.9 *t*	24.2 *t*	25.9 *t*	26.0 *t*	23.1 *t*	24.2 *t*	35.1 *t*	30.1 *t*
13	45.4 *d*	46.1 *d*	45.7 *d*	77.2	73.8	74.4	77.6	76.4	73.9	74.4	37.9	36.5
14	37.1 *t*	36.9 *t*	38.3 *t*	74.8 *d*	73.9 *d*	79.1 *d*	76.9 *d*	74.8 *d*	74.3 *d*	79.0 *d*	37.6 *t*	36.3 *t*
15	53.1 *t*	53.0 *t*	59.5 *t*	66.8 *t*	66.8 *t*	66.8 *t*	66.5 *t*	66.8 *t*	66.4 *t*	66.8 *t*	82.7 *d*	79.2 *d*
16	81.8	79.9	89.0	64.9 *t*	66.2 *t*	65.8 *t*	65.2 *t*	64.9 *t*	66.9 *t*	65.8 *t*	63.6 *t*	63.1 *t*
17	66.3 *t*	68.5 *t*	69.9 *t*	24.3 *q*	25.4 *q*	25.1 *q*	25.2 *q*	24.3 *q*	25.4 *q*	25.0 *q*	18.8 *q*	18.3 *q*
18	27.2 *q*	27.6 *q*	27.6 *q*	27.4 *q*	27.4 *q*	27.5 *q*	27.7 *q*	27.4 *q*	27.4 *q*	27.4 *q*	28.9 *q*	28.1 *q*
19	66.9 *t*	66.9 *t*	66.9 *t*	62.1 *t*	62.9 *t*	65.1 *t*	63.8 *t*	62.2 *t*	62.9 *t*	65.1 *t*	26.2 *q*	24.8 *q*
20	18.2 *q*	18.2 *q*	18.2 *q*	15.7 *q*	15.0 *q*	15.5 *q*	16.1 *q*	15.7 *q*	15.1 *q*	15.4 *q*	12.8 *q*	12.2 *q*
RCO_2	174.2	174.2	174.2	173.4	173.4	173.3		174.0	173.9	173.9		
	34.2 *t*	34.6 *t*	34.5 *t*	43.6 *t*	43.4 *t*	43.7 *t*		34.5 *t*	34.5 *t*	34.5 *t*		
	31.9 *t*	31.9 *t*	31.9 *t*	25.7 *d*	25.7 *d*	25.7 *d*		31.9 *t*	31.9 *t*	31.9 *t*		
	29.6 *t*	29.6 *t*	29.6 *t*	22.4 *q*	22.4 *q*	22.4 q		29.6 *t*	29.6 *t*	29.6 *t*		
	29.5 *t*	29.5 *t*	29.5 *t*	22.4 *q*	22.4 *q*	22.4 *q*		29.5 *t*	29.5 *t*	29.5 *t*		
	29.3 *t*	29.3 *t*	29.3 *t*					29.3 *t*	29.3 *t*	29.4 *t*		
	29.2 *t*	29.2 *t*	29.2 *t*					29.2 *t*	29.2 *t*	29.3 *t*		
	25.1 *t*	25.1 *t*	25.1 *t*					25.1 *t*	25.1 *t*	29.2 *t*		
	22.7 *t*	22.7 *t*	22.7 *t*					22.7 *t*	22.7 *t*	25.0 *t*		
	14.1 *q*	14.1 *q*	14.1 *q*					14.1 *q*	14.1 *q*	22.6 *t*		
										14.0 *q*		
Ac		171.2			170.8				170.7			170.9
		20.9 *q*			170.7				170.6			170.8
					170.4				170.2			170.6
					20.9 *q*				20.9 *q*			170.5
					20.8 *q*				20.8 *q*			21.1 *q*
												20.9 *q*
CMe_2			108.3			108.9				108.9		
			26.9 *q*			26.3 *q*				26.3 *q*		
			26.8 *q*			25.1 *q*				25.0 *q*		

Unmarked signals are singlets.
* Run at 50 MHz.
† MeOH-d_4.

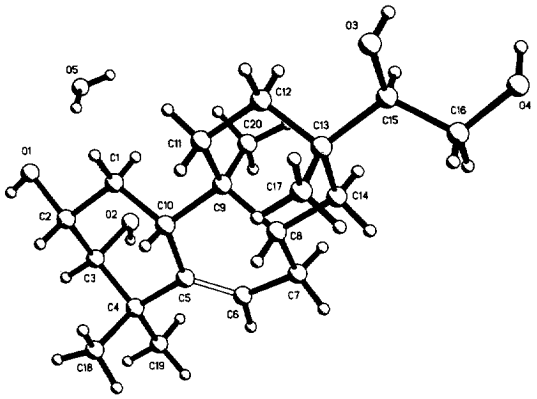


Fig. 1. Structure of **4a**, as determined by X-ray analysis.

lected in the State of Zacatecas, September 1990. Voucher MMTZ 078 is deposited in the Herbarium of the Instituto de Biología, UNAM.

Extraction and separation. Air-dried and ground aerial parts (1.7 kg) of *B. glandulosa* were extracted with hexane, EtOAc and MeOH. The EtOAc extract (35 g) after successive CCs over Kieselgel G eluting with mixts of hexane–EtOAc, $CHCl_3$–Me_2CO, $CHCl_3$–EtOAc and hexane–Me_2CO afforded a mixt. of β-sitosterol–stigmasterol (98.6 mg), ayanin (**1a**, 61.4 mg), velutin (**1b**, 49.4 mg), **2a** (1.098 g), **2d** (23.3 mg), **3a** (74.2 mg) and **3e** (304.3 mg). The MeOH extract (240 g) was purified by CC on Kieselgel G using as eluent a gradient of hexane–EtOAc. Frs eluted with hexane–EtOAc (4:1) were dissolved in Me_2CO and filtered over benthonic earth (Tonsil), the solvent was eliminated under red. pres. and the residue purified by consecutive CCs eluting with mixts of hexane–Me_2CO and C_6H_6–EtOAc to give **4e** (mp 110–112°, 610.8 mg). Frs eluted with hexane–EtOAc (7:3) after successive CCs eluting with mixts of hexane–Me_2CO, hexane–EtOAc and $CHCl_3$–Me_2CO afforded **4c** (52.2 mg). Frs eluted with hexane–EtOAc (3:2) were submitted to successive CCs eluting with mixts of hexane–Me_2CO and $CHCl_3$–Me_2CO gave **4a** (206.3 mg).

19-O-*Acyl*-ent-16, 17, 19-*kauranetriol* (**2a**). White solid from hexane, mp 55–59°, $[\alpha]_D$ −26.42° (*c* 0.318, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 3406, 2929, 1736; FAB-MS (nitro benzyl alcohol), *m/z*: 560 [M, $C_{36}H_{64}O_4$]$^+$, 556 [$C_{34}H_{60}O_4$+1+Na]$^+$, 555 [$C_{34}H_{60}O_4$+Na]$^+$, 532 [M, $C_{34}H_{60}O_4$]$^+$, 528 [$C_{32}H_{56}O_4$+1+Na]$^+$, 527 [$C_{32}H_{56}O_4$+Na]$^+$, 504 [M, $C_{32}H_{56}O_4$]$^+$, 500 [$C_{30}H_{52}O_4$+1+Na]$^+$, 499 [$C_{30}H_{52}O_4$+Na]$^+$; EIMS 70 eV, *m/z* (rel. int.): 304 [M-RCO_2H]$^+$ (3.3), 286 [304-H_2O]$^+$ (14), 273 [304-CH_2OH]$^+$ (100), 255 [273-H_2O]$^+$ (36.7), 135 [$C_{10}H_{15}$]$^+$ (27), 123 [C_9H_{15}]$^+$ (36.7), 111 [C_8H_{15}]$^+$ (30.8), 109 [C_8H_{13}]$^+$ (33.5), 97 [C_7H_{13}]$^+$ (39.4), 95 [C_7H_{11}]$^+$ (39.4), 85 [C_6H_{13}]$^+$ (22.7), 83 [C_6H_{11}]$^+$ (34.2), 81 [C_6H_9]$^+$ (46.2), 71 [C_5H_{11}]$^+$ (35.4), 69 [C_5H_9]$^+$ (58.7), 57 [C_4H_9]$^+$ (46.2), 55 [C_4H_7]$^+$ (49.2), 43 [C_3H_7]$^+$ (50.8), 41 [C_3H_5]$^+$ (29.8).

19-O-*Isovaleroyl*-14, 15, 16, 19-*tetrahydroxy*-ent-*manoyloxide* (**3a**). Oil, $[\alpha]_D$ −8.94° (*c* 0.235, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3566, 2960, 2933, 2874, 1723; FAB-MS (nba), *m/z*: 463 [M+Na, $C_{25}H_{44}O_6$+Na]$^+$, 441 [M+1]$^+$. EIMS 70 eV, *m/z* (rel. int.): 409 [M-CH_2OH]$^+$ (40.8), 379 [409-CH_2O]$^+$ (94), 339 [M-RCO_2]$^+$ (0.4), 307 [M-RCO_2H-CH_2OH]$^+$ (38.7), 289 [307-H_2O]$^+$ (33.2), 277 [307-CH_2O]$^+$ (62.3), 259 [277-H_2O]$^+$ (100), 241 (259-H_2O]$^+$ (34), 135 (85.6), 123 (50.8), 109 (61.9), 95 (63), 85 (62.4), 81 (57.8), 57 (70.9), 55 (34.4), 43 (28.7), 41 (23.6).

19-O-*Acyl*-14, 15, 16, 19-*tetrahydroxy*-ent-*manoyloxide* (**3e**). Oil, $[\alpha]_D$ −10.53° (*c* 0.285, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3566, 2929, 1723; EIMS 70 eV, *m/z* (rel. int.): 594 [M, $C_{36}H_{66}O_6$]$^+$ (0.1), 566 [M, $C_{34}H_{62}O_6$]$^+$ (0.1), 563 [594-CH_2OH]$^+$ (0.4), 538 [M, $C_{32}H_{58}O_6$]$^+$ (0.3), 535 [566-CH_2OH]$^+$ (4.6), 533 [563-CH_2O]$^+$ (0.4), 510 [M, $C_{30}H_{54}O_6$]$^+$ (0.05), 507 [538-CH_2OH]$^+$ (27.5), 505 [535-CH_2O]$^+$ (10), 477 [507-CH_2O]$^+$ (63.3), 339 [M-RCO_2]$^+$ (14.4), 307 [M-RCO_2H-CH_2OH]$^+$ (39), 289 [307-H_2O]$^+$ (33.3), 277 [307-CH_2O]$^+$ (66.7), 259 [277-H_2O]$^+$ (100), 135 (65.2), 109 (51.6), 95 (54.9), 81 (42.5), 69 (25.4), 57 (34.9), 55 (30.8), 43 (33.3), 41 (15).

2α-*Hydroxy*-19-*deoxy jesromotetrol* (**4a**). White crystals from Me_2CO, mp 225–231°, $[\alpha]_D$ −29.39° (*c* 0.296, MeOH). IR ν_{max}^{nujol} cm^{-1}: 3389, 3399; FAB-MS (nba), *m/z*: 361 [M+Na, $C_{20}H_{34}O_4$+Na]$^+$, 339 [M+1]$^+$, 321 [M-OH]$^+$, 303 [321-H_2O]$^+$, 289 [303-H_2O]$^+$, X-ray analysis, crystal data: monoclinic, space group $P2_1$, $a = 12.322$ (5) Å, $b = 6.097$ (2) Å, $c = 12.935$ (5) Å, $z = 2$, $d = 1.218$ mg/m^3, F(000) = 392 and μ(CuKα) = 0.688 mm^{-1}. Atom coordinates have been submitted to the Cambridge Crystallographic Data Centre.

Acetylation of **2a**. Compounds **2a** (100 mg) were acetylated by the usual manner. The residue was purified by CC using as eluent hexane–EtOAc (4:1) yielding **2b** (107.6 mg) as a gum. IR ν_{max}^{film} cm^{-1}: 3439, 1731, 1717; EIMS 70 eV, *m/z* (rel. int.): 556 [$C_{36}H_{62}O_5$-H_2O]$^+$ (0.4), 542 [$C_{38}H_{66}O_5$-AcOH]$^+$ (0.05), 528 [$C_{34}H_{58}O_5$-H_2O]$^+$ (1.8), 514 [$C_{36}H_{62}O_5$-AcOH]$^+$ (1.4), 500 [$C_{32}H_{54}O_5$-H_2O]$^+$ (0.6), 496 [514-H_2O]$^+$ (1.7), 486 [$C_{34}H_{58}O_5$-AcOH]$^+$ (5.1), 468 [486-H_2O]$^+$ (6.7), 458 [$C_{32}H_{54}O_5$-AcOH]$^+$ (1.7), 440 [500-AcOH]$^+$ (1.2), 346 [M-RCO_2H]$^+$ (0.5), 328 [346-H_2O]$^+$ (3.5), 286 [346-AcOH]$^+$ (68.8), 273 [346-CH_2OAc]$^+$ (100), 255 [273-H_2O]$^+$ (30.2).

Acetonide of **2a**. Compound **2a** (37.4 mg), Tonsil (220 mg, benthonic earth, previously washed with EtOAc and Me_2CO) and Me_2CO (3 ml) were stirred at room temp. for 1 hr. The reaction mixt. was filtered, the solvent eliminated and the residue purified by CC eluting with hexane–EtOAc (47:3) to give **2c** (33.6 mg) as a gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1721; FAB-MS (nba), *m/z*: 600 [M, $C_{39}H_{68}O_4$]$^+$, 572 [M, $C_{37}H_{64}O_4$]$^+$, 544 [M, $C_{35}H_{60}O_4$]$^+$, 542 [600-Me_2CO]$^+$, 516 [M, $C_{33}H_{56}O_4$]$^+$, 501 [516-CH_3]$^+$, 487 [544-C_3H_5O]$^+$, 459 [516-C_3H_5O]$^+$, 343 [M-RCO_2H_2]$^+$, 329 [344-CH_3]$^+$, 287 [344-C_3H_5O]$^+$, 269 [287-H_2O]$^+$.

Saponification of **2a**. A suspension of **2a** (104 mg) and K_2CO_3 (216 mg) in MeOH (3 ml HPLC) was refluxed for 2.5 hr. The solvent was eliminated by a

N_2 stream. The residue was dissolved in H_2O (HPLC), extracted with EtOAc (HPLC), dried over Na_2SO_4 and concd to give **2d** (52.8 mg, mp 223–227°), $[\alpha]_D$ −35.48° (*c* 0.31, MeOH). The mother liquors were treated with CH_2N_2, and purified by CC eluting with hexane–EtOAc (9:1) to yield **2d** (8 mg) and a residue (16 mg) which contained the methyl esters of capric acid (4.85%), lauric acid (78.65%), myristic acid (15.72%) and palmitic acid (0.78%) (found by FID-GC and GC-MS analysis).

Acetylation of **3a**. 48 mg of **3a** were acetylated in the usual manner. Purification of the reaction mixt. by CC using as eluent hexane–EtOAc (4:1) yielded **3b** (52.7 mg) as a gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735; EIMS 70 eV, *m/z* (rel. int.): 507 $[M\text{-}OAc]^+$ (1.6), 493 $[507\text{-}CH_2]^+$ (34.4), 465 $[M\text{-}RCO_2]^+$ (7.36), 421 $[493\text{-}CHOAc]^+$ (88), 391 $[464\text{-}CH_2Ac]^+$ (41.6), 319 $[391\text{-}CHOAc]^+$ (85.6), 241 $[C_{17}H_{21}O]^+$ (100), 135 (70.4), 109 (52.8), 85 (53.6), 81 (40.8), 57 (57.7), 43 (62.2).

Acetonide of **3a**. The compound **3a** (21.0 mg) was treated as described for **2a** to afford **3c** (11.4 mg) as a gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3533, 1724; EIMS 70 eV, *m/z* (rel. int.): 481 $[M+1, C_{28}H_{48}O_6+1]^+$ (0.4), 449 $[M\text{-}CH_2OH]^+$ (32.7), 379 $[M\text{-}C_5H_9O_2]^+$ (91.6), 347 $[M\text{-}RCO_2H\text{-}CH_2OH]^+$ (12.2), 277 $[379\text{-}C_5H_{10}O_2]^+$ (61), 259 $[277\text{-}H_2O]^+$ (100), 241 $[C_{17}H_{21}O]^+$ (31.2), 135 (77.5), 109 (44.6), 81 (37.8), 57 (43.8), 43 (23.6).

Saponification of **3a**. Compound **3a** (40.2 mg) was saponified as already described for **2a**. The reaction mixt. was purified by CC eluting with hexane Me_2CO to yield **3d** (18.5 mg) as white crystals from EtOAc, mp 171–173°, $[\alpha]_D$ −10.89° (*c* 0.202, MeOH). IR ν_{max}^{nujol} cm^{-1}: 3332; EIMS 70 eV, *m/z* (rel. int.): 325 $[M\text{-}CH_2OH]^+$ (35.6), 307 $[325\text{-}H_2O]^+$ (35.4), 295 $[325\text{-}CH_2O]^+$ (86.4), 277 $[295\text{-}H_2O]^+$ (86.4), 259 $[277\text{-}H_2O]^+$ (43.9), 135 (61.4), 123 (83.9), 109 (71.2), 95 (100), 83 (65.7), 81 (94), 57 (86.6), 55 (100), 43 (89.8), 41 (62.4).

Acetylation of **3e**. Compound **3e** (20 mg) was acetylated in the usual manner affording **3f** (21.9 mg) as a gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1738; FAB-MS (nba), *m/z*: 687 $[M+Na, C_{38}H_{64}O_9+Na]^+$, 665 $[M+1, C_{38}H_{64}O_9+1]^+$, 647 $[C_{42}H_{72}O_9\text{-}CH_2OAc]^+$, 619 $[C_{40}H_{68}O_9\text{-}CH_2OAc]^+$, 605 $[C_{38}H_{64}O_9\text{-}OAc]^+$, 591 $[605\text{-}CH_2]^+$, 547 $[619\text{-}CHOAc]^+$, 519 $[591\text{-}CHOAc]^+$, 491 $[C_{36}H_{60}O_9\text{-}CH_2OAc\text{-}CHOAc]^+$, 465 $[M\text{-}RCO_2]^+$, 405 $[465\text{-}AcOH]^+$, 391 $[405\text{-}CH_2]^+$, 319 $[405\text{-}CHOAc]^+$.

Acetonide of **3e**. Compound **3e** (34.1 mg) was treated as described for **2a**. Purification of the reaction mixt. by CC eluting with hexane–EtOAc (4:1) gave **3g** (27.9 mg) as a gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3529, 1722; EIMS 70 eV, *m/z* (rel. int.): 619 $[C_{39}H_{70}O_6\text{-}CH_3]^+$ (0.1), 606 $[M, C_{37}H_{66}O_6]^+$ (0.15), 603 $[C_{39}H_{70}O_6\text{-}CH_2OH]^+$ (0.1), 591 $[606\text{-}CH_3]^+$ (0.65), 575 $[606\text{-}CH_2OH]^+$ (3.5), 547 $[C_{35}H_{62}O_6\text{-}CH_2OH]^+$ (18.2), 533 $[C_{39}H_{70}O_6\text{-}C_5H_9O_2]^+$ (0.1), 519 $[C_{33}H_{58}O_6\text{-}CH_2OH]^+$ (4.5), 505 $[606\text{-}C_5H_9O_2]^+$ (10.2), 477 $[C_{35}H_{62}O_6\text{-}C_5H_9O_2]^+$ (52.5), 449 $[C_{33}H_{58}O_6\text{-}C_5H_9O_2]^+$ (11.5), 379 $[M\text{-}RCO_2]^+$ (5.2), 277 $[M\text{-}RCO_2H\text{-}C_5H_9O_2]^+$ (65.5), 259 $[277\text{-}H_2O]$.

Saponification of **3e**. Compound **3e** (98.7 mg) was treated as described for **2a**. The products were purified by CC eluting with a gradient of hexane–EtOAc. Frs eluted with EtOAc gave **3d** (46.1 mg). Frs eluted with hexane–EtOAc (9:1) were esterified with CH_2N_2. The reactions mixt. (35 mg) was analysed by GC and GC-MS affording the methyl esters of capric acid (9.99%), lauric acid (72.06%), myristic acid (16.92%) and palmitic acid (1.03%).

Hydrolysis of **4e**. Compound **4e** (160 mg), pTsOH and MeOH (10 ml) were refluxed by 4.5 hr. The solvent was evapd, the mixt. dissolved in EtOAc, washed with $NaHCO_3$ and H_2O and dried. The residue was purified by CC eluting with hexane–EtOAc (2:3) to give 125.8 mg of **4c**, mp 166–168°, $[\alpha]_D$ −48.91° (*c* 0.184, MeOH). IR ν_{max}^{nujol} cm^{-1}: 3493, 3422, 3332; ^1H NMR (200 MHz, $CDCl_3$): δ 5.45 (*br s*, H-6), 3.30 (*dd*, J = 2.6, 9.4 Hz, H-15), 3.71 (*dd*, J = 2.5, 10.6 Hz, H-16a), 3.52 (*dd*, J = 9.4, 10.6 Hz, H-16b), 0.89 (*s*, H-17), 0.93 (*s*, H-18), 3.79 (*d*, J = 11.1 Hz, H-19a), 3.27 (*d*, J = 11.1 Hz, H-19b), 0.64 (*s*, H-20). ^{13}C NMR (50 MHz, $CDCl_3$, C-1–C-20): δ 25.6, 21.2, 34.6, 41.4, 142.1, 117.5, 29.0, 35.6, 34.8, 47.4, 33.6, 30.2, 36.5, 36.2, 81.2, 62.5, 18.3, 25.6, 70.0, 12.2. Acetylation of **4c** by the usual manner afforded **4d**, mp 110–112°. Its spectroscopic data were identical with those described in the literature [9].

Acknowledgements—We are indebted to Dr José Luis Villaseñor of the Instituto de Biología, UNAM, for identification of the plant. We also thank Rubén A. Toscano, Carmen Márquez, Rubén Gaviño, Isabel Chávez, Beatriz Quiroz, Hector Ríos, Rocio Patiño, Luis Velasco and Javier Pérez for their technical assistance.

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