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TRITERPENES FROM *EUPHORBIA BROTERI*

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Key Word Index—*Euphorbia broteri*; Euphorbiaceae; triterpenes.

Abstract—The triterpenes have been investigated in the aerial part and the latex of *Euphorbia broteri*. The aerial part contains two new triterpenes, 25,26,27-trisnor-3β-hydroxy-24-dimethoxycycloartane and 3,4-*seco*-4(23),14-taraxeradien-3-oic acid, and eleven other triterpenes identified as cycloartenol, butyrospermol, 24-methylenecycloartanol, cycloart-25-ene-3β,24-diol, euphan-8,25-diene-3β,24-diol, 3β-hydroxycycloart-25-ene-24-one, obtusifoliol, 3,4-*seco*-4(23),20(30)-lupadien-3-oic acid (canaric acid), betulin, cycloart-23-ene-3β,25-diol and the C-24 diastereomers of cycloartane-3β,24,25-triol. The latex contains a new triterpene, 24,25-epoxycycloartanol (C-24 diastereomers), and nine other compounds identified as euphol acetate, cycloartenyl acetate, butyrospermyl acetate, 24-methylenecycloartanyl acetate, euphol, cycloartenol, butyrospermol, 24-methylenecycloartanol and obtusifoliol.

INTRODUCTION

Euphorbia broteri is an endemic Hispano-Lusitanian plant growing on acidic and sandy dry soils. The plant contains much latex, which has an irritant effect on the skin and mucous membranes. We have studied the components of the *n*-hexane extract of the aerial part of the plant, which contains a high proportion of linear compounds and a mixture of triterpenes which are difficult to separate. We have also studied the latex, whose study is relatively easier as it lacks the wax components present in the aerial part. The differences between the two studies were the isolation of some triterpenes from the latex as natural acetates (**1**, **2**, **10**, **12**), while from the aerial part they were isolated as alcohols or esterified with fatty acids. On the other hand, the total extract contains diols (**5**, **6**, **11**, **14**), a triol (**7**) and two acids with secolupane (**16**) and secotaraxerane (**15**) skeletons, which are absent in the latex.

The major compounds of the latex as well as of the total plant extract are cycloartenol and 24-methylenecycloartanol, which is in agreement with the classification made by Ourisson and Ponsinet [1, 2] because *Euphorbia broteri* is a herbaceous shrub.

RESULTS AND DISCUSSION

Column chromatography of the crude hexane extract gave seven fractions, which have been designated A to G. By saponification of fraction A and subsequent acetylation of the less polar material, three acetates were isolated and identified by their spectroscopic properties (Tables 1 and 2) as cycloartenyl acetate (**1**) [3], butyrospermyl acetate (**12**) [4, 5] and 24-methylenecycloartanyl acetate (**2**) [3].

Fraction B was a mixture of two substances which were separated by saponification and preparative TLC on the acetylated material. The less polar compound showed signals corresponding to a cyclopropane ring, characteristic of a cycloartane skeleton, and it was identified by its spectroscopic properties as cycloart-24-ene-3β,24-diol diacetate (**6**) [6, 7]. The more polar compound showed a methyl scheme in the ^{1}H NMR spectrum typical of a euphane or tirucallane skeleton and its properties were identical to those of euphan-8,25-diene-3β,24-diacetate (**11**).

Fraction C was dewaxed with methanol and acetylated. Column chromatography of the acetates gave **4** and **8** besides **2** and **12** (previously isolated from fraction A as the fatty acyl esters). The properties of **4** were identical with those described for 3β-acetoxycycloart-25-en-24-one [6]. Compound **8**, $[M]^+$ at *m/z* 488 ($C_{31}H_{52}O_4$), possessed a ^{1}H NMR spectrum with the following signals: two cyclopropane protons (0.34 *d* and 0.57 *d*), an acetyl group (1H, *dd*, 4.56; 3H, *s*, 2.05), five methyl groups (four of them on quaternary carbons and one of them on a methine group), and finally the signal corresponding to a $-CH(OCH_3)_2$ grouping (1H, *t*, 4.33, J = 5.32 Hz and 6H, *s*, 3.21). The latter was clearly observed in the ^{13}C NMR spectrum with a methine group at δ 107.17 and peaks at 52.64 and 52.44 corresponding to the two methoxyl groups. These signals agree with the assignment of the structure as 25,26,27-trisnor-3β-acetoxy-24-dimethoxycycloartane, which was confirmed by hydrolysis to the aldehyde (**9**) obtained from ozonolysis of cycloartenol (**1**).

After acetylation of fraction D, obtusifoliol acetate (**13a**) was isolated [8, 9] together with a mixture of two acids which were separated as methyl esters **15** and **16**. Compound **15** had a parent molecular ion at *m/z* 454 ($C_{31}H_{50}O_2$), and its ^{1}H NMR spectrum showed peaks corresponding to an olefinic annular proton (5.50 *dd*, J = 8.06 and 3.42 Hz), a $C{=}CH_2$ (2H, *br s*, 4.66 and 4.85), a $CH_3{-}C{=}$ (3H, *s*, 1.75) and six methyl groups between 0.82 and 1.12. These data, in addition to the observed loss in the mass spectrum of a 367 fragment $[M - C_4H_7O_2]^+$ led to the conclusion that it possesses a *seco*-oleane or *seco*-taraxerane skeleton. According to the differences established [10] for both skeletons regarding the annular olefinic proton signal, the spectrum agrees with a *seco*-

Table 1. ^{1}H NMR chemical

Compound	H-3	H-18*	H-19	H-21*	H-23	H-24
1	4.56 *m*		a 0.34 *d*			
	X (ABX)	0.95 *s*	b 0.57 *d*	0.88 *d*		5.09 *t*
	$J_{AX}+J_{BX}$ = 15.1		(4.4)	(5.4)		(7.0)
1a	3.28 *m*		a 0.33 *d*			
	X (ABX)	0.96 *s*	b 0.55 *d*	0.88 *d*		5.10 *t*
	$J_{AX}+J_{BX}$ = 14.1		(3.9)	(6.2)		(7.3)
2‡	4.57 *m*		a 0.34 *d*			
	X (ABX)	0.97 *s*	b 0.58 *d*	0.90 *d*		
	$J_{AX}+J_{BX}$ = 15.8		(4.0)	(6.3)		
2a‡	3.28 *m*		a 0.33 *d*			
	X (ABX)	0.97 *s*	b 0.56 *d*	0.90 *d*		
	$J_{AX}+J_{BX}$ = 15.5		(4.2)	(6.2)		
3	3.28 *m*		a 0.34 *d*			
	X (ABX)	0.97 s	b 0.56 *d*	0.88 *d*		2.70 *dd*
	$J_{AX}+J_{BX}$ = 14.6		(4.1)	(6.1)		(6.6; 5.6)
3a	4.56 m		a 0.34 *d*			
	X (ABX)	0.96 *s*	b 0.57 *d*	0.88 *d*		2.68 *dd*
	$J_{AX}+J_{BX}$ = 15.7		(4.2)	(5.1)		(5.8; 5.8)
4	4.57 *m*		a 0.34 *d*			
	X (ABX)	0.96 *s*	b 0.58 *d*	0.89 *d*	2.64 *m*	
	$J_{AX}+J_{BX}$ = 16.0		(4.1)	(5.6)		
5	4.57 *m*		a 0.35 *d*			
	X (ABX)	0.96 *s*	b 0.58 *d*	0.86 *d*	5.60 *br s*	5.68 *br s*
	$J_{AX}+J_{BX}$ = 15.3		(3.9)	(5.4)		
6	4.57 *m*		a 0.34 *d*			
	X (ABX)	0.95 *s*	b 0.58 *d*	0.88 *d*		5.13 *t*
	$J_{AX}+J_{BX}$ = 14.7		(4.4)	(7.0)		(6.8)
7	4.56 *m*		a 0.34 *d*			
	X (ABX)	0.95 *s*	b 0.57 *d*	0.88 *d*		4.76 *dd*
	$J_{AX}+J_{BX}$ = 15.5		(4.4)	(5.3)		(12.6; 7.7)
7a			a 0.32			
	3.28 *m*	0.96 *s*	b 0.55 *d*	0.88 *d*		3.28 *m*
			(4.2)	(6.3)		
7b	4.56 *m*		a 0.33 *d*			3.28 *m*
	X (ABX)	0.96 *s*	b 0.57 *d*	0.88 *d*		X (ABX)
	$J_{AX}+J_{BX}$ = 15.7		(4.2)	(5.3)	$J_{AX}+J_{BX}$ = 12.8	
8	4.56 *m*		a 0.34 *d*			
	X (ABX)	0.96 *s*	b 0.57 *d*	0.88 *d*		4.33 *t*
	$J_{AX}+J_{BX}$ = 15.6		(4.2)	(5.3)		(5.6)
9	4.56 *m*		a 0.34 *d*			
	X (ABX)	0.95 *s*	b 0.57 *d*	0.87 *d*		8.82 *t*
	$J_{AX}+J_{BX}$ = 15.5		(4.2)	(5.4)		(1.9)
10	4.50 *m*					
	X (ABX)	0.69 *s*	1.01* *s*	0.90 *d*		5.10 *t*
	$J_{AX}+J_{BX}$ = 16			(6.1)		(7.0)
10a	3.20 *m*					
	X (ABX)	0.69 *s*	1.00* *s*	0.91 *d*		5.11 *t*
	$J_{AX}+J_{BX}$ = 15.7			(6.1)		(6.3)
11	4.45 *m*					
	X (ABX)	0.68 s	1.02* *s*	0.90 *d*		5.10 *m*
	$J_{AX}+J_{BX}$ = 15.6			(6.1)		
12‡	4.32 *m*					
	X (ABX)	0.80 *s*	0.76* *s*	0.85 *d*		5.10 *dd*
	$J_{AX}+J_{BX}$ = 15.4			(6.0)		(7.0; 7.0)
12a‡	3.26 *m*					
	X (ABX)	0.81 *s*	0.75* *s*	0.84 *d*		5.10 *dddd*
	$J_{AX}+J_{BX}$ = 15.4			(5.1)		(7; 7; 1.4; 1.4)
13‡	3.12 *m*					
	X (ABX)	0.73 *s*	0.99* *s*	1.01 *d*		
	$J_{AX}+J_{BX}$ = 14.7			(6.8)		

shifts for compounds 1–16

H-25	H-26*	H-27	H-28	H-29	H-30*	OAc
	1.60 *d* (1.1)	1.68* *d* (1.3)	0.88† *s*	0.89† *s**	0.84 *s*	2.04 *s*
	1.60 *br s*	1.68* *s*	0.89* *s*	0.96* *s*	0.81 *s*	
	1.03 *d* (6.8)	1.03* *d* (6.8)	0.89† *s**	0.90*,† *s*	0.85 *s*	2.06 *s*
	1.03 *d* (6.8)	1.03* *d* (6.8)	0.90* *s*	0.97* *s*	0.81 *s*	
	1.27 *d*	1.31* *s*	0.89* *s*	0.97* *s*	0.81 *s*	
	1.26 *s*	1.30* *s*	0.88† *s**	0.89*,† *s*	0.84 *s*	2.04 *s*
	1.87 *s*	5.76 *sbr* 5.96 *sbr*	0.89† *s**	0.90† *s**	0.85 *s*	2.05 *s*
	1.32 *s*	1.32* *s*	0.89* *s*	0.89* *s*	0.85 *s*	2.06 *s*
	1.71 *t* (1.4)	4.90 *br s* 4.94 br s	0.89* *s*	0.89* *s*	0.84 *s*	2.05 *s*
	1.20 *s*	1.20* *s*	0.89* *s*	0.89* *s*	0.85 *s*	2.05 *s* 2.10 *s*
	1.15 *s*	1.21* *s*	0.89* *s*	0.96* *s*	0.81 *s*	
	1.15 *s*	1.21* *s*	0.89* *s*†	0.88† *s**	0.84 *s*	2.04 *s*
—	—	—	0.89* *s*	0.89* *s*	0.84 *s*	2.05 *s*
—	—	—	0.89* *s*	0.89* *s*	0.84 *s*	2.04 *s*
	1.61 *s*	1.69* *d* (1.1)	0.87† *s**	0.88† *s**	0.88 *s*	2.05 *s*
	1.60 *s*	1.68* *s*	0.88* *s*	0.98* *s*	0.81 *s*	
	1.68 *br s*	4.85 *br s*	0.88† *s**	0.89† *s**	0.88 *s*	2.01 *s*
	1.60 *d* (0.4)	1.68* *d* (1.3)	0.97* *s*	0.93* *s*	0.85 *s*	2.05 *s*
	1.60 *s*	1.68* *d* (1.0)	0.97* *s*	0.97* *s*	0.86 *s*	
	1.05 *d* (6.8)	1.05* *d* (6.8)	0.91* *s*	—	0.95 *d* (6.1)	

Table 1. (*Continued*)

Compound	H-3	H-18*	H-19	H-21*	H-23	H-24
14	4.46 *m*					
	X (ABX)				0.83* *s*	0.84* *s*
	$J_{AX}+J_{BX}=16$					
15‡	–COOMe				4.66 *br s*	
	3.66 *br s*				4.85 *br s*	1.75* *s*
15a‡	–COOMe				4.68 *br s*	1.76 * *s*
	3.66 *br s*				4.87 *br s*	
16	–COOMe				4.65 *br s*	
	3.66 *br s*				4.85 *br s*	1.74* *br s*

*Intensity three protons.

†Assignments interchangeable. Coupling constants (*J* in Hz) are given in parentheses.

‡In **12** and **12a** (H-7) 5.25 *dd* (6.9; 3.0); olefinic proton signals (H-31) were observed at 4.72; 4.66 *dd* **15** and (H-12) at 5.20 *t* (3.5) **15a**.

Table 2(a). ^{13}C NMR signals

	1	1a	2	2a	3	3a
C-1	31.68	32.07	31.68	32.07	32.04	31.65
C-2	26.87	30.47	26.87	30.45	30.46	26.83
C-3	80.74	78.86	80.75	78.83	78.90	80.67
C-4	39.52	40.55	39.52	40.54	40.55	39.49
C-5	47.25	47.22	47.25	47.21	47.21	47.28
C-6	20.98	21.18	20.97	21.19	21.15	20.93
C-7	28.18	28.19	28.17	28.20	28.18	28.15
C-8	47.84	48.00	47.82	48.02	47.93	47.76
C-9	20.23	20.10	20.25	20.08	20.08	20.19
C-10	26.07	26.22	26.10	26.23	26.03	26.09
C-11	25.86	26.09	25.85	26.07	26.03	25.81
C-12	35.60	37.67	35.59	35.65	35.62	35.55
C-13	45.37	45.39	45.41	45.41	45.41	45.38
C-14	48.87	48.88	48.90	48.89	48.90	48.88
C-15	32.94	33.02	32.97	33.02	32.92	32.92
C-16	26.60	26.60	26.61	26.58	26.56	26.56
C-17	52.34	52.39	52.34	52.37	52.36; 52.21	52.32; 52.20
C-18	18.00	18.07	17.99	18.06	18.04	17.95
C-19	29.79	29.91	29.76	29.93	29.88	29.71
C-20	35.95	35.95	36.18	36.18	36.02; 35.88	36.00; 35.89
C-21	18.31	18.33	18.37	18.39	18.30; 18.34	18.33; 18.24
C-22	36.43	36.45	35.15	35.15	33.01	32.92
C-23	25.03	25.03	31.41	31.41	26.03	26.00; 25.71
C-24	125.34	125.36	156.94	156.79	64.96; 64.70	64.87; 64.71
C-25	130.86	130.79	33.91	33.89	58.07	58.22; 57.93
C-26	17.66	17.68	21.91	21.94	18.69	18.68; 18.78
C-27	25.73	25.76	22.03	22.06	24.95	24.93
C-28	19.33	19.38	19.35	19.40	19.36	19.31
C-29	15.17	14.05	15.17	14.06	14.02	15.15
C-30	25.48	25.52	25.47	25.52	25.48	25.44
C-31			106.03	106.10		
$\underline{CH_3}$–CO	21.31		21.28			21.22
CH_3–$\underline{CO}$	170.90		170.90			170.91

*Assignment of the signal was based on literature data.

taraxerane skeleton. Therefore, **15** is identified as 3,4-*seco*-4(23),14-taraxeradien-3-methyl ester; this structure was confirmed by isomerization in acid medium [11] which led to the methyl ester of nycktanthic acid (**15a**) [12]. The methyl ester **16** possessed a parent molecular ion at *m/z* 454 ($C_{31}H_{50}O_2$) and a fragment at *m/z* 367 $[M-87]^+$

	H-25	H-26*	H-27	H-28	H-29	H-30*	OAc
	0.85* *s*	1.05 *s*	0.97* *s*	4.25 3.85 ABq (11.6)	4.59 *br s* 4.69 *br s*	1.69 *s*	2.04 *s* 2.06 *s*
	0.92† *s** 0.95* *s*	1.12 *s* 1.03 *s*	0.96* *s* 1.16* *s*	0.83* *s* 0.84* *s*	0.94† *s** 0.88* *s*	0.90† *s* 0.88 *s*	
	0.84* *s*	1.08 *s*	0.96* *s*	0.80* *s*	4.58 *br s* 4.69 *br s*	1.69 *s*	

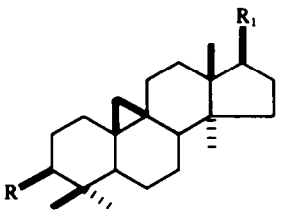
(3.0; 1.1) for **2** and **2a**; at 4.68; 4.78 *br s* for **13**; (H-15) was observed at 5.50 *dd* (8.0; 3.6)

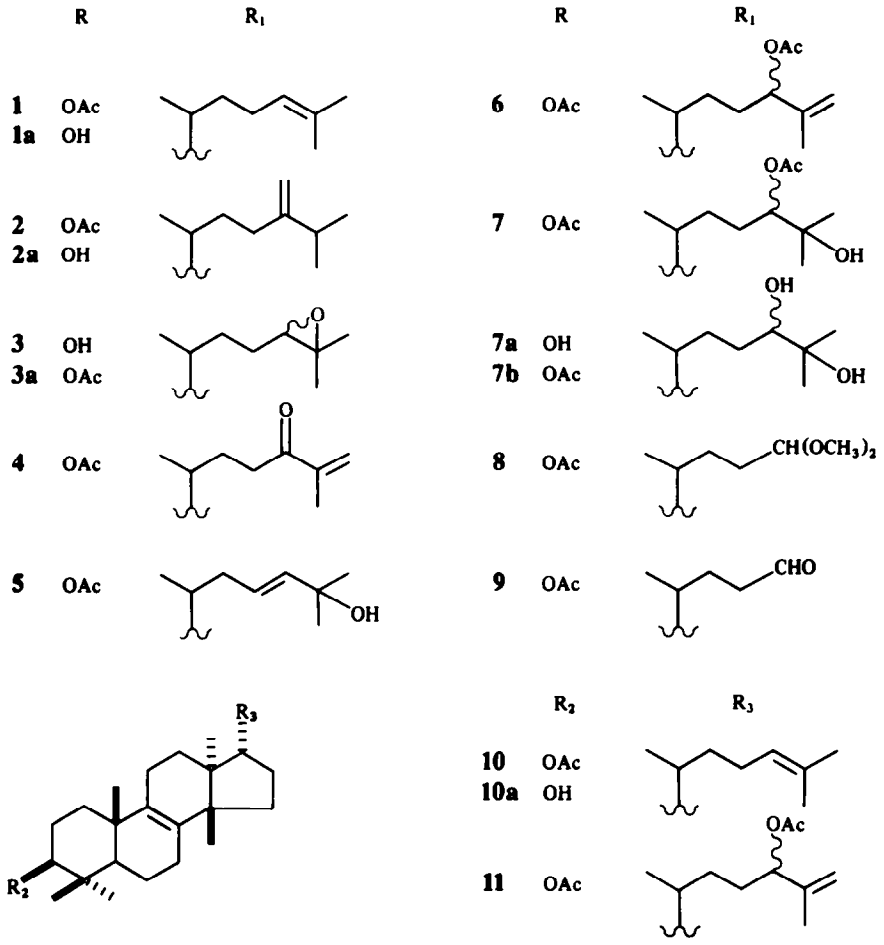
of compounds **1**–**7b** ($CDCl_3$)

4	5	6	7	7a	7b
31.68	31.68	31.67	31.67	32.01	31.66
26.86	26.85	26.86	26.86	30.44	26.84
80.75	80.75	80.74	80.74	78.88	80.78
39.51	39.52	39.52	39.51	40.53	39.49
47.24	47.25	47.25	47.24	47.20	47.22
20.95	20.94	20.95	20.96	21.15	20.95
28.11	28.11	28.08	28.07	28.16	28.18
47.81	47.79	47.82	47.85	47.95	47.83
20.21	20.23	20.22	20.21	20.05	20.20
26.10	26.12	26.10	26.09	26.07	26.09
25.83	25.83	25.85	25.84	26.03	25.84
35.56	35.59	35.56	35.55	35.81	35.56
45.43	45.41	45.39	45.38	45.42	45.39
48.90	48.92	48.90	48.88	48.88	48.88
32.95	32.86	32.93	32.82	33.03	32.96
26.56	26.57	26.57	26.56	26.23	26.84
52.30	52.08	52.18	52.19; 52.25	52.44; 52.54	52.39; 52.50
18.02	18.01	17.99	17.99	18.05	18.04
29.76	29.74	29.77	29.74	29.86	29.78
35.92	36.48	35.82	35.73; 36.34	35.91; 36.44	36.43; 35.93
18.22	18.34	18.31	18.15; 18.45	18.22; 18.51	18.22; 18.50
34.77*	39.10	31.67*	32.91; 32.48*	33.23; 33.66*	33.20; 33.65*
31.18*	139.50	29.52*	26.56; 26.20*	28.40; 28.84*	28.49; 28.81*
182.24	125.67	77.69	80.95; 80.20	78.70; 79.89	79.65; 78.78
144.76	70.73	143.55	72.55	73.22	73.14
17.74	29.96	112.46	25.10; 25.03	23.40; 23.33	23.33;23.38
124.05	30.05	18.24	26.70	26.57	26.58
19.33	19.31	19.35	19.35	19.35	19.35
15.18	15.16	15.18	15.17	14.03	15.18
25.47	25.46	25.47	25.46	25.46	25.46
21.32	21.28	21.31 21.24	21.31; 21.07		21.32
170.90	170.89	170.90 170.80	170.90; 171.20		170.94

corresponding to the loss of a side chain that bore the methyl ester group, as in the former case. The properties of **16** were identical with those published for the canaric acid [13] isolated from *Canarium mulleri* resin. We report now its ^{13}C NMR and ^{1}H NMR data (Tables 1 and 2).

From fraction E, sitosterol was isolated and from



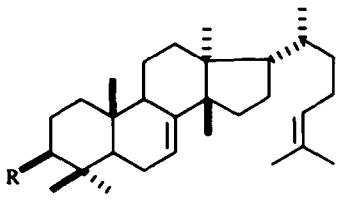


fraction F, after acetylation, were separated betulin diacetate (**14**) [14] and cycloart-23-ene-3β,25-diol monoacetate (**5**) [6].

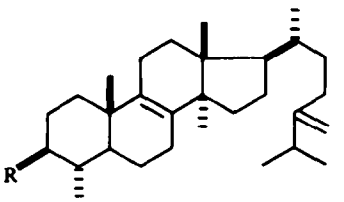
From fraction G, after basic hydrolysis and acetylation, compound **7** was separated. Its IR spectrum showed characteristic bands for hydroxyl and acetoxyl groups. The ^{1}H NMR showed signals corresponding to the following groups: two acetates (4.76, *m*, X ABX), H-24 (4.55, *m* X ABX); H-3 (2.10, *s*, 3H and 2.05, *s*, 3H), a cyclopropane methylene (0.57 and 0.34, *d*, J = 4.4 Hz) and seven methyl groups (four on quaternary carbons, one on a methine and two of them deshielded also on quaternary carbons). The mass spectrum had a parent molecular ion at *m/z* 544 ($C_{34}H_{56}O_5$) corresponding to a cycloartane triterpene with two acetoxyl groups and a tertiary hydroxyl group. The duplicity of the signal at δ 4.76 corresponding to H-24, in addition to the ^{13}C NMR values that can be assigned to the side-chain carbons, led to the conclusion that we had a mixture of C-24 epimers of cycloartane-3β,24,25-triol diacetate (**7**) [15]. Alkaline hydrolysis of **7** led to the triol **7a**, identified as a mixture of C-24 epimers of cycloartane-3β,24,25-triol. The structure was confirmed by the opening of a mixture of C-24 epimers of 3β-acetoxy-24,25-epoxycycloartane (**3a**) isolated as a latex component of the plant. The opening was carried out in acid medium [16] and further acetylation of the product (**7b**) obtained.

From the latex, fractionated as indicated in the Experimental, three fractions were separated and designated. Fraction I was a mixture of four natural acetates separated over silver nitrate–silica gel into euphol acetate (**10**) [4, 17], cycloartenyl acetate (**1**), butyrospermyl 3β-acetate (**12**) and 24-methylenecycloartanyl acetate (**2**).

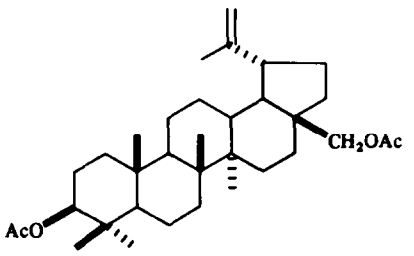
Fraction II was a mixture of four triterpenic alcohols,



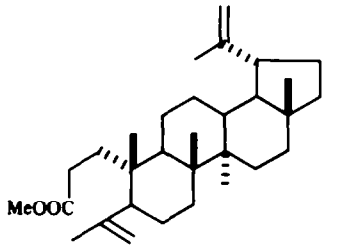
R
12 OAc
12a OH



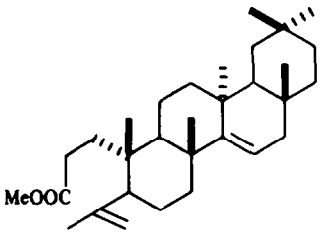
R
13 OH
13a OAc



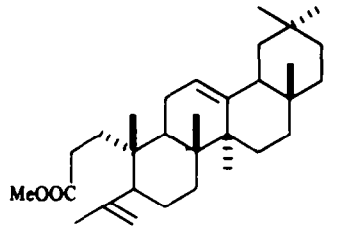
14



16



15



15a

separated as their acetates, which were identical with those isolated from fraction I as the natural acetates. Basic hydrolysis allowed the isolation of euphol (**10a**), cycloartenol (**1a**), butyrospermol (**12a**) and 24-methylenecycloartanol (**2a**) (Tables 1 and 2).

From fraction III, two substances, **13** and **3**, were isolated. Compound **13** was crystalized from methanol and its IR spectrum showed bands for hydroxyl and a terminal double bond. The ^{1}H NMR spectrum showed the peaks corresponding to the terminal methylene group (4.74 and 4.68, *br s*) in addition to a geminal H to an equatorial hydroxyl group (3.12, *dd*, H-3). The presence of four doublet methyl signals between 0.95 and 1.05 and three other singlet methyl peaks allowed the assignment of a noreburicane skeleton for compound **13**, and its identification as obtusifoliol [18].

Compound **3** showed in the IR spectrum the hydroxyl group band (3420 and 1100 cm^{-1}). From the ^{1}H NMR spectrum it was possible to determine the presence of a geminal H to an equatorial hydroxyl group (3.28, *m*, X(ABX), $J_{AX}+J_{BX}$ = 14.6 Hz, H-3), a geminal H to an epoxide (2.70, *dd*, J = 6.6, 5.6 Hz, H-24, a cyclopropane methylene group (0.56, *d*, 0.34, *d*, J = 4.15 Hz) and finally the peaks corresponding to seven methyl groups, two of them deshielded at 1.27 and 1.31 ppm due to the geminal epoxide position. Its mass spectrum with [M]$^+$ at *m/z* 442 ($C_{30}H_{50}O_2$) and its mass fragmentation and the ^{13}C NMR spectrum (Tables 1 and 2) are in agreement with a cycloartane compound with a secondary hydroxyl group at C-3 and an epoxide function in the side chain. The duplicity of the side-chain signals indicated an epimeric mixture at C-24 of 24,25-epoxycycloartane (**3**), which is reported for the first time as a natural product. After acetylation, the mixture of the monoacetate (C-24 epimers, **3a**) was obtained. The structure was confirmed by epoxidation of cycloartenyl acetate (**1**) with *m*-chloroperbenzoic acid to produce the mixture of epoxides epimeric at C-24 (**3a**). The ring opening in acid medium of this mixture [16] leads to **7b** which is acetylated and therefore transformed into the C-24 epimeric mixture of 3β,24-diacetoxy-25-hydroxycycloartane (**7**).

EXPERIMENTAL

Mps (Kofler hot stage apparatus) uncorr.; ^{1}H NMR: 200 MHz TMS as internal standard; ^{13}C NMR: 50.3 MHz; EI mass spectra were measured at 70 eV (temp. 180°).

*Extraction of the triterpenes from the aerial part. Euphorbia broteri** was collected in flower in Béjar (Salamanca). The aerial

*A herbarium sample of the plant is available from the Department of Botany, Faculty of Biology, University of Salamanca.

Table 2.(b) ^{13}C NMR signals compounds **8–16** ($CDCl_3$)

	8	9	10	10a	12	12a	13	14	15	15a	16
C-1	31.68	31.68	35.39	35.70	36.91	37.32	35.09	38.49	25.03	24.66	24.74
C-2	26.87	26.84	24.26	26.60	24.28	27.81	31.26	23.78	33.19	31.53	32.91
C-3	80.75	80.70	81.03	79.08	81.22	79.32	76.61	81.01	174.53	174.54	174.55
C-4	39.52	39.51	37.90	38.96	37.94	39.03	39.32	37.89	147.48	147.58	147.69
C-5	47.25	47.24	50.64	50.54	50.86	50.77	47.19	55.50	40.52	38.03	40.80
C-6	20.96	20.93	18.22	18.37	23.84	24.03	20.81	18.26	28.55	28.59	28.52
C-7	28.14	28.36	26.48	27.94	117.65	117.88	28.24	34.25	33.60	34.18	34.25
C-8	47.84	47.78	134.40	134.57	146.05	145.94	133.73	41.01	40.19	39.68	40.68
C-9	20.23	20.19	134.64	134.57	48.92	49.05	134.77	50.40	50.61	50.60	50.48
C-10	26.10	26.13	37.01	36.33	34.91	35.04	36.43	37.18	38.86	39.27	39.36
C-11	25.85	25.82	21.09	21.10	18.12	18.23	21.85	20.90	17.41	23.83	21.60
C-12	35.57	35.53	28.25	28.28	33.85	33.93	25.64	25.29	33.60	121.77	25.22
C-13	45.38	45.46	44.62	44.63	43.68	43.65	44.65	37.68	37.52	145.16	38.27
C-14	48.90	48.91	49.91	49.93	51.35	51.35	49.96	42.80	157.82	42.41	43.08
C-15	32.94	32.94	31.10	30.95	34.02	34.05	31.39	27.16	117.16	26.23	27.58
C-16	26.58	26.54	30.90	29.74	28.48	28.49	31.19	29.71	35.21	27.09	35.60
C-17	52.17	52.22	50.51	50.54	53.31	53.31	50.52	46.43	35.80	32.58	43.36
C-18	18.00	17.99	15.83	15.84	13.19	13.17	15.81	48.91	48.95	47.40	48.39
C-19	29.77	29.73	19.23	19.20	22.10	22.13	18.79	47.80	39.93	46.93	48.03
C-20	35.89	35.73	36.32	36.33	35.82	35.84	36.55	150.17	28.84	31.11	150.34
C-21	18.32	18.01	18.70	18.72	18.62	18.63	18.26	29.87	36.74	34.85	29.96
C-22	30.92*	41.17*	36.43	35.70	35.26	35.28	35.14	34.62	37.77	37.23	40.06
C-23	29.33*	28.11*	25.01	25.03	25.41	25.42	30.87	28.01	113.55	113.55	113.86
C-24	105.17	182.21	125.34	125.35	125.19	125.22	156.94	16.53	23.53	23.50	23.32
C-25	—	—	130.90	130.88	130.90	130.89	33.91	16.20	19.35	19.53	20.12
C-26	—	—	17.65	17.67	17.68	17.70	21.92	16.12	29.93	16.97	16.06
C-27	—	—	25.72	25.76	25.73	25.73	22.05	14.80	25.27	25.86	14.53
C-28	19.33	19.33	24.30	24.31	27.63	27.67	24.30	62.89	29.97	28.47	18.07
C-29	15.18	15.16	27.98	28.04	27.36	27.37	15.11	109.47	33.52	33.36	109.47
C-30	25.47	25.47	16.57	15.48	15.90	14.77	—	19.18	21.55	23.73	19.40
C-31							106.03				
$\underline{CH_3}$–CO	21.31	21.31	21.31		21.32			21.04			
								21.34			
CH_3–$\underline{CO}$	170.90	170.90	170.94		170.94			171.52			
Others	52.7; 52.4								51.48	51.52	51.52

Multiplicities assigned from DEPT spectrum.
*Assignment of the signal based on literature data [13].
Assignment of the methyl groups in the cycloartane compound (1–9) was based on C/H (HCCORR) two-dimensional correlations.

part was dried and extracted with *n*-hexane in a Soxhlet apparatus for 24 hr. The extract was concentrated *in vacuo*, giving 8.6% of dried plant. The crude extract was chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc and EtOAc, to yield seven fractions: fraction A (20%, *n*-hexane–EtOAc, 9:1), fraction B (3.6%, *n*-hexane–EtOAc, 9:1), fraction C (36.3%, *n*-hexane–EtOAc, 9:1), fraction D (4.3%, *n*-hexane–EtOAc, 9:1), fraction E (3.4%, *n*-hexane–EtOAc, 4:1), fraction F (12.6%, *n*-hexane–EtOAc, 1:1) and fraction G (6.3%, EtOAc).

CC of these fractions on silica gel, $AgNO_2$–silica gel or preparative TLC gave the triterpenes **1, 2, 4, 5, 6, 7, 8, 11, 12, 13a, 14, 15** and **16**.

Extraction of the triterpenes from the latex. The latex of *Euphorbia broteri* was collected into MeOH, yielding a solid part that was separated by filtration. The solid was exhaustively extracted with Me_2CO at 40° and the Me_2CO soln together with the originally MeOH soln was evaporated *in vacuo*. After evaporation the residue was dissolved in MeOH–H_2O (1:1) and the triterpene compounds were removed by partition with hexane. The hexane extract (43 g) was chromatographed on silica gel yielding three fractions: I (26.7% hexane–Et_2O, 4:1), II (58.6%, hexane–Et_2O, 1:1) and III (3.9%, Et_2O). By CC of these fractions, the triterpenes **1, 2, 3, 1a, 2a, 10, 10a, 12, 12a** and **13** were isolated.

Isolation of the triterpenes from the aerial part. Fraction A: By saponification of this fraction with KOH–MeOH (10%), acetylation of the neutral part and preparative TLC on $AgNO_3$-silica gel (10%) eluting three times with hexane–C_6H_6, compounds **12** and **2** were isolated. *Fraction B*: The fraction was saponified with KOH–MeOH (10%) and the neutral part was chromatographed on $AgNO_3$–silica gel (10%). The fraction that was eluted with hexane–Et_2O (1:1) was acetylated and afterwards preparative TLC on 5% $AgNO_3$–silica gel, eluting three times with hexane–Et_2O (1:1), gave compounds **6** and **11**. *Fraction C*: By crystalization in MeOH a mixture of the linear alcohols (55.9%) was separated. The mother liquor were acetylated and CC of the acetates afforded compounds **4** and **8** besides **2** and **12** previously isolated from fraction A as esters of the fatty acids. *Fraction D*: After acetylation and CC, two fractions were separated. The less polar fraction (hexane–Et_2O, 9:1) was chromatographed on 10% $AgNO_3$–silica gel yielding **13a**. The more polar fraction (hexane–Et_2O, 4:1) was esterified with CH_2N_2 and CC of the

methyl esters on 10% $AgNO_3$–silica gel (hexane–benzene, 4:1) gave compounds **15** and **16**. *Fraction E*: By acetylation and CC on a silica gel column, sitosterol acetate was isolated. *Fraction F*: The fraction was saponified and the neutral part acetylated at room temp. CC of the mixture of the acetates eluting with *n*-hexane–EtOAc gave two fractions. The less polar fraction (*n*-hexane–EtOAc, 9:1) by CC on 10% $AgNO_3$–silica gel yielded compound **14**. From the more polar fraction (*n*-hexane–EtOAc, 4:1) by preparative TLC (hexane–C_6H_6, 7:3, 3 ×) was isolated compound **5**. *Fraction G*: This was saponified and the neutral part acetylated and chromatographed on a silica gel column (hexane–Et_2O, 1:1). After preparative TLC (hexane–Et_2O 3:7, 3 ×) the epimers at C-24 (**7**) were separated.

Triterpenes from the latex. Fraction I: By careful chromatography on a 20% $AgNO_3$–silica gel column eluting with hexane–Et_2O (19:1) three samples were separated. The first of them was a mixture that was resolved by preparative TLC (hexane–Et_2O 19:1, 3 ×), yielding **10** and **1**. From the other fractions, **12** and **2** were separated. *Fraction II*: By acetylation and chromatography of the acetates on a 15% $AgNO_3$–silica gel column (hexane–Et_2O, 19:1), four compounds were separated. They were the same compounds isolated from fraction I. By saponification of the acetates, compounds **10a**, **1a**, **12a** and **2a** were isolated. *Fraction III*: The fraction was chromatographed on a silica gel column. By preparative TLC (hexane–Et_2O, 4:1, 4 ×) of the fraction that was eluted with hexane–Et_2O (1:1), compounds **13** and **3** were separated.

Butyrospermyl acetate (**12**). Crystallized from Me_2CO: mp 142–144°; $[\alpha]_D^{25}$ +14° ($CHCl_3$; *c* 0.84); IR ν_{max}^{KBr} cm^{-1}: 2940, 1735, 1640, 1470, 1450, 1370, 1250, 1025, 970, 835; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b); MS *m/z* (rel. int.): 468 $[M]^+$ (1.5), 453 (2.5), 175 (2.5), 111 (11), 107 (27), 105 (20.5), 96 (12), 93 (24), 69 (80), 43 (100).

24-Methylenecycloartanyl acetate (**2**). Crystallized from MeOH: mp 114–117°; $[\alpha]_D^{25}$ +52° ($CHCl_3$; *c* 0.92); IR ν_{max}^{KBr} cm^{-1}: 3080, 1740, 1650, 1470, 1380, 1250, 1030, 990, 890; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a); MS *m/z* (rel. int.): 482 $[M]^+$ (1.5), 422 (4), 407 (25), 175 (6.5), 125 (6.5), 109 (19), 95 (34), 81 (45), 69 (67), 43 (100).

Cycloart-25-ene-3β,24-diol diacetate (**6**). Crystallized from MeOH: mp 133–135°; $[\alpha]_D^{25}$ +42.8° ($CHCl_3$; *c* 1.3); IR ν_{max} cm^{-1}: 2940, 1740, 1650, 1380, 1250, 1030, 900; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a); MS *m/z* (rel. int.): 526 $[M]^+$ (4), 511 (4.5), 480 (2.5), 466 (13.7), 451 (12.5), 423 (6.6), 406 (3.5), 397 (3.2), 357 (3.7), 354 (4), 302 (3), 297 (6), 203 (19.3), 187 (25), 178 (16), 121 (74), 83 (100).

Euphan-8,25-diene-3β,24-diol diacetate (**11**). $[\alpha]_D^{25}$ +3.7° ($CHCl_3$; *c* 0.87); IR ν_{max} cm^{-1}: 3080, 2980, 1740, 1665, 1470, 1380, 1250, 910; ^1H NMR: see Table 1; MS *m/z* (rel. int.): 526 $[M]^+$ (1.5), 264 (2), 263 (5), 203 (5), 121 (20), 111 (30), 109 (30), 107 (25), 95 (35), 85 (100), 83 (95), 79 (25).

3β-Acetoxycycloart-25-ene-24-one (**4**). MP 129–130° (from MeOH); $[\alpha]_D^{25}$ +55° ($CHCl_3$; *c* 0.81); UV λ_{max}^{EtOH} 219 (ε 8563); IR ν_{max}^{KBr} cm^{-1}: 3080, 2940, 1730, 1640, 1680, 1470, 1375, 1250, 890; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a); MS *m/z* (rel. int.): 482 $[M]^+$ (3), 467 (5), 422 (5), 407 (13), 125 (18), 121 (25), 109 (22), 107 (25), 95 (44), 83 (49), 69 (98), 43 (100).

25,26,27-Trisnor-3β-acetoxy-24-dimethoxycycloartane (**8**). Crystallized from MeOH: mp 98–100° $[\alpha]_D^{25}$ +50.3° ($CHCl_3$; *c* 0.68); IR ν_{max}^{KBr} cm^{-1}: 3040, 2960, 1740, 1480, 1250, 1145, 1080, 1060, 1040. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b); MS *m/z* (rel. int.): 454 $[M]^+$ (4.5), 439 (3), 367 (2), 330 (4), 315 (5), 243 (5), 287 (10), 271 (10), 255 (12), 231 (10), 249 (15), 231 (15), 218 (15), 205 (10), 204 (10), 189 (16), 167 (30), 149 (100), 121 (50), 109 (50), 97 (41), 81 (80).

Isomerization of compound **15**. Compound **15** (43 mg) was isomerized in glacial HOAc (43 ml) by heating with conc HCl (2.5 ml) for 1 hr at 60°. Usual work-up gave a solid which, on crystallization ($CHCl_3$–MeOH), afforded colourless crystals (**15a**, 25 mg) identified as *3,4-seco-4(23),12-oleadien-3-methyl ester*, mp 123–125°; $[\alpha]_D^{25}$ +63.2° ($CHCl_3$; *c* 1.09); IR ν_{max} cm^{-1}: 3060, 2940, 1750, 1640, 1310, 900; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b).

3,4-seco-4(23),20(30)-Lupadien-3-methyl ester (**16**). Mp 96–99°; $[\alpha]_D^{25}$ +37.2° ($CHCl_3$; *c* 0.5); IR ν_{max} cm^{-1}: 3060, 3025, 1740, 1650, 1460, 1380, 890. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b). MS *m/z* (rel. int.): 454 $[M]^+$, 439 (1.5), 411 (2), 373 (4), 367 (4), 235 (10), 218 (6), 149 (12), 135 (7), 107 (19), 85 (60), 83 (100), 81 (25).

Betulin diacetate (**14**). Mp 222–224° (from MeOH); $[\alpha]_D^{25}$ +23.4° ($CHCl_3$; *c* 0.61); IR ν_{max}^{KBr} cm^{-1}: 3050, 1740, 1640, 1240, 1020, 890. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b). MS *m/z* (rel. int.): 526 $[M]^+$ (3), 511 (3), 466 (100), 453 (14), 423 (15), 393 (8), 216 (91), 203 (38), 189 (51), 175 (26), 107 (85), 95 (91), 81 (90).

Cycloart-23-ene-3β,25-diol monoacetate (**5**). Colourless crystals, mp 144–145° (from MeOH); $[\alpha]_D^{25}$ +43.6° ($CHCl_3$; *c* 0.22); IR ν_{max}^{KBr} cm^{-1}: 3450, 2980, 1740, 1380, 1250, 1030, 890. ^1H NMR: see Table 1, ^{13}C NMR: see Table 2(a). MS *m/z* (rel. int.): 484 $[M]^+$ (3.5), 451 (7), 425 (8), 424 (12), 410 (8), 392 (10), 382 (10), 255 (15), 203 (25), 187 (20), 175 (25), 161 (38), 149 (35), 109 (95), 95 (100).

C-24 epimers of cycloartane-3β,24,25-triol diacetate (**7**). Mp 160–162°; $[\alpha]_D^{25}$ +39° ($CHCl_3$; *c* 0.72); IR ν_{max} cm^{-1}: 3480, 2960, 2920, 1740, 1470, 1380, 1250, 1030. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a). MS *m/z* (rel. int.): 544 $[M]^+$ ($C_{34}H_{56}O_5$), 529 (4), 526 (4), 485 (6), 484 (13), 469 (6), 423 (5), 363 (6), 357 (3), 330 (5), 297 (8), 270 (10), 255 (12), 203 (18), 175 (20), 109 (61), 95 (90), 69 (100).

Alkaline hydrolysis of compound **7**. Compound **7** (84 mg) in C_6H_6 (10 ml) was hydrolysed with 10% alcoholic KOH for 5 hr at room temp. Usual work-up followed by crystallization (C_6H_6) gave colourless crystals (**7a**, 70 mg), mp 154–156°; $[\alpha]_D^{25}$ ±0 ($CHCl_3$; *c* 1); IR ν_{max} cm^{-1}: 3500, 3040, 2960, 1380, 1030, ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a). Compound **7a** was identified as C-24 epimers of cycloartane-3β,24,25-triol.

Triterpenoids from latex. Euphol acetate (**10**). Mp 107–109° (from MeOH); $[\alpha]_D^{25}$ +38.5° ($CHCl_3$; *c* 0.84); IR ν_{max} cm^{-1}: 1750, 1460, 1380, 1250, 1040, 1025, 1000, 910; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b); MS *m/z* (rel. int.): 468 $[M]^+$ (8.5), 453 (7), 409 (2), 393 (3), 301 (2), 255 (3), 241 (3), 204 (2.5), 187 (3.5), 145 (3), 105 (4.5), 81 (9), 69 (98), 43 (100).

Cycloartenyl acetate (**1**). Crystallized from Me_2CO: mp 117–119°; $[\alpha]_D^{25}$ +54° ($CHCl_3$; *c* 0.30); IR ν_{max}^{KBr} cm^{-1}: 3040, 2930, 1740, 1470, 1450, 1380, 1250, 1040, 1030, 980; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a); MS *m/z* (rel. int.): 468 $[M]^+$ (4), 453 (5), 408 (8), 393 (8), 365 (3), 339 (5), 297 (2), 286 (5), 271 (3), 175 (13.5), 109 (41), 95 (59), 93 (41), 69 (100), 43 (29).

Euphol (**10a**). Mp 115–116° (from MeOH); $[\alpha]_D^{25}$ +31° ($CHCl_3$; *c* 1.3); IR ν_{max} cm^{-1}: 3250, 3010, 2940, 1470, 1455, 1375, 1360, 1220, 1030; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b).

Cycloartenol (**1a**). Mp 106–107° (from MeOH); $[\alpha]_D^{25}$ +48° ($CHCl_3$; *c* 1); IR ν_{max} cm^{-1}: 3340, 3060, 2960, 2900, 1495, 1470, 1410, 1235, 1130, 1045, 910. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a).

Butyrospermol (**12a**). Mp 108–110° (from MeOH); $[\alpha]_D^{25}$ −12° ($CHCl_3$; *c* 1.2); IR ν_{max} cm^{-1}: 3400, 2980, 1470, 1400, 1390, 1220, 1050, 835. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b).

24-Methylenecycloartanol (**2a**). Mp 120–121° (from MeOH); $[\alpha]_D^{25}$ +41° ($CHCl_3$: *c* 1); IR ν_{max} cm^{-1}: 3400, 3040, 2940, 1660, 1480, 1470, 1400, 1235, 1110, 1070, 1040, 900; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a).

Obtusifoliol (**13**). Crystallized from MeOH as colourless

crystals: mp 142–143°; $[\alpha]_D^{25}$ +73° ($CHCl_3$; *c* 1); IR ν_{max} cm^{-1}: 3400, 3080, 2970, 2880, 1640, 1470, 1380, 1055, 1025, 980, 890; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(b); MS *m/z* (rel. int.): 426 $[M]^+$ (5), 411 (5), 393 (5), 327 (2), 259 (2.5), 245 (1.5), 233 (4), 173 (6), 159 (6), 69 (60), 43 (100).

C-24 *epimers of* 24,25-*epoxycycloartanol* (3). $[\alpha]_D^{25}$ +28.5° ($CHCl_3$; *c* 1); IR ν_{max} cm^{-1}: 3420, 2920, 2860, 1470, 1450, 1380, 1100, 1030. ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a); MS *m/z* (rel. int.): 442 $[M]^+$ (4), 424 (5), 409 (3.5), 315 (1.5), 297 (1.5), 241 (2), 203 (6), 256 (6), 187 (8), 175 (12), 121 (18), 107 (25), 57 (100), 43 (99).

Acetylation of compound 3. Compound 3 (25 mg) was acetylated with Ac_2O–pyridine (2:1, 1.5 ml) at room temp. overnight. The reaction mixture was poured into ice-H_2O and extracted with Et_2O. The Et_2O extract was washed with HCl (2 M), $NaHCO_3$ and H_2O, and dried (dry Na_2SO_4). Removal of the solvent afforded a solid, identified as the C-24 epimers of 3β-acetoxy-24,25-epoxycycloartanol (**3a**), mp: 143–144°; $[\alpha]_D^{25}$ +24° ($CHCl_3$; *c* 0.7); IR ν_{max} cm^{-1}: 2910, 2840, 1740, 1470, 1375, 1250, 1025; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a).

Reaction of cycloartenyl acetate (1) *with* m-*chloroperbenzoic acid*. To a stirred soln of compound 1 (190 mg) in CH_2Cl_2 (1 ml) a soln of *m*-CPBA (10 mg) in CH_2Cl_2 (1 ml) was added as drops. The mixture was stirred at room temp. for 1 hr and then $NaHCO_3$ was added and the product extracted with CH_2Cl_2. The organic phase was washed with Na_2SO_3 (10%), $NaHCO_3$ (5%) and H_2O to neutrality, dried and the solvent removed under vacuum, affording 179 mg of compound **3a**.

Ring opening the epimeric epoxides **3a**. To the mixture of epimers at C-24 of the 3β-acetoxy-24,25-epoxycycloartanol **3a** (130 mg) in 1,2-dimethoxyethane (13 ml), 2.5 ml of a soln of perchloric acid (3 drops) in H_2O (25 ml) was added. The mixture was kept at room temp. overnight. Afterwards an aq. soln of 2 N Na_2CO_3 (5 ml) was added. The product was extracted with Et_2O and purified by preparative TLC (hexane–Et_2O, 1:1) yielding 80 mg (60%) epimers at C-24 of the 3β-acetoxycycloart-24,25-diol (**7b**): $[\alpha]_D^{25}$ +45.3° ($CHCl_3$; *c* 2.6); IR ν_{max} cm^{-1}: 3480, 2960, 2920, 1740, 1470, 1380, 1210, 1030; ^1H NMR: see Table 1; ^{13}C NMR: see Table 2(a).

Acetylation of **7b** afforded the natural product **7**.

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