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DITERPENES FROM *EUPHORBIA SEGETALIS*

J. JAKUPOVIC,* F. JESKE, T. MORGENSTERN, F. TSICHRITZIS, J. A. MARCO† and W. BERENDSOHN‡

Institute for Organic Chemistry, Technical University of Berlin, Strasse des 17 Juni 135, D-10623 Berlin, Germany; † Departamento de Q. Orgánica, Universidad de Valencia, c/D. Moliner, 50, E-46100 Burjassot, Valencia, Spain; ‡ Botanical Garden and Botanical Museum Berlin-Dahlem, D-14191 Berlin, Koenigin-Luise-Str. 6-8, Germany

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Key Word Index—*Euphorbia segetalis*; Euphorbiaceae; diterpenes; jatrophanes; lathyranes; ingols; bishomojatrophanes; terracinolides: paralianes; pepluane; segetanes; presegetanes; ingenanes; labdane.

Abstract—Numerous new diterpenes including several with new skeletons have been obtained from *Euphorbia segetalis*. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The genus *Euphorbia*, which is the largest in the Spurge family comprising more than 1000 species [1], has been extensively chemically investigated [2–4]. *Euphorbia segetalis* L. belongs to a group of closely related taxa including *E. pinea* L. and *E. portlandica* L., which have been variously treated as subspecies or varieties of *E. segetalis*, and *E. celerieri* (Emberger) J. Vindt, which was originally published as a subspecies of *E. pinea*. The material here analysed belongs to *E. segetalis* in the sense of Valdés *et al.* [5], i.e. including *E. pinea*. It is a common annual (or rarely perennial) nitrophilic herb 10–40 cm high, ranging from the Iberian peninsula throughout the northern Mediterranean to Albania and to Northern Africa and Macaronesia.

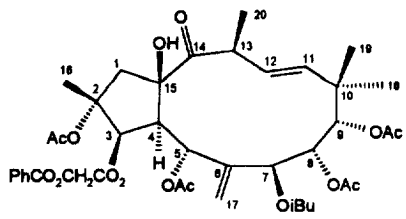
We present our results with a sample collected in Spain, which showed an extraordinary complex composition on secondary metabolites. Further comparative investigations of material from the other members of the group may result in a clarification of the group's taxonomy.

RESULTS AND DISCUSSION

The whole plant extract of *E. segetalis* gave the jatrophanes **1–7**, the lathyrane (ingol derivative) **8**, bishomojatrophanes (terracinolides) **9–16**, the paralianes **17–20**, the pepluane **21**, four diterpenes with new skeletons, i.e. the segetanes **22–24** and the 15-*epi* presegetane **25**, as well as the ingenanes **26–33** and the manoyloxide derivative **34**. With the exception of terracinolides **9–12** [6, 7] and the ingenanes **26** [8], **27** [8], **28** [9], **31** [10], **32** [11], and **33** [12, 13] all other compounds were new. However, the jatrophanes **1–4** are included in the paper on the constituents from *E. terracina* [14] from which they were simultaneously isolated.

The appearance of several methyl doublets and triplets in the high field region of the ^{1}H NMR spectrum of jatrophane **5** (Table 1) pointed to branched ester groups. By spin decoupling, two isobutyrates and a 2-methylbutyrate were established, and confirmed by the ^{13}C NMR spectrum (Table 2). Among the remaining 20 signals recognized were those for four methyl groups (^{1}H NMR spectrum: two secondary and two tertiary), two double bonds (a vicinal disubstituted and an exocyclic), a keto group and six oxygenated sp^3 carbons (five secondary and a tertiary). Three methyne, a methylene and a quartenary carbon accounted for the remaining carbons and supported a jatrophane derivative. Spin decoupling experiments led to two sequences: (i) H-1 to H-5, with a secondary methyl at C-2 and (ii) H-11—H-13 with another secondary methyl group at C-13. Three signals for apparently isolated spin systems were assigned to the consecutive sequence (H-7—H-9) by analogy to the spectra of similar jatrophanes [10, 14, 15] and to those of related jatrophane lactones (see below and [6, 7]). Three out of six oxygenated sp^3 carbons were attached to hydroxy groups. While the tertiary one could only be placed at C-15, the position of the secondary hydroxy groups at C-3 and C-9 followed from the chemical shifts of the corresponding oxymethine proton and from the coupling with the hydroxy group proton. Consequently, the ester groups had to be placed at C-5, C-7 and C-8. The relative position of the ester groups followed from the ^{1}H/^{13}C long range correlations between oxymethine protons and the respec-

* Author to whom correspondence should be addressed.



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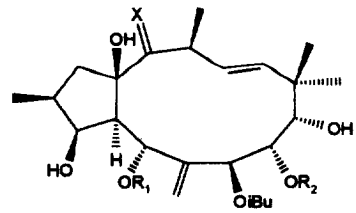
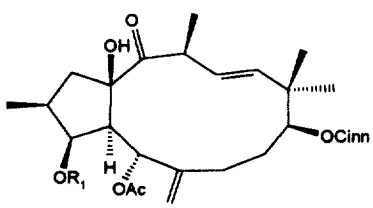
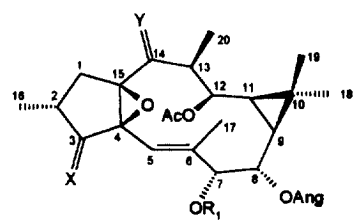


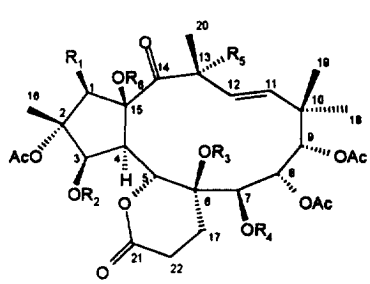
	2	**3**	**4**	**5**
R_1	Mebu	iBu	Mebu	iBu
R_2	Mebu	iBu	Mebu	Mebu
X	β-OAc,H	O	O	O



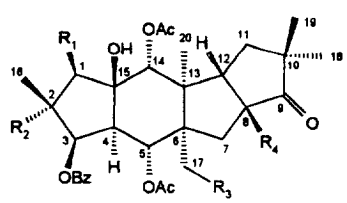
	6	**7**
R_1	Bz	Cinn



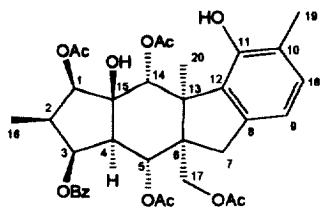
	8	**8a**	**8b**
R_1	Ac	Ac	H
X	O	β-OH,H	β-OH,H
Y	O	α-OH,H	α-OH,H



	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**
R_1	H	H	H	H	H	OAc	H	OAc
R_2	Ac	Ac	H	Ac	H	Ac	Ac	Ac
R_3	Bz	Ac	Ac	Bz	iBu	Ac	Ac	Ac
R_4	iBu	iBu	iBu	Pro	iBu	iBu	iBu	iBu
R_5	H	H	H	H	H	H	OH	OH
R_6	Ac	Ac	Ac	Ac	Ac	H	Ac	H



	17	18	19	20
R_1	OAc	OAc	H	OAc
R_2	H	H	OAc	H
R_3	H	H	H	OAc
R_4	OAc	H	H	H



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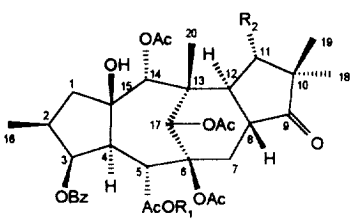
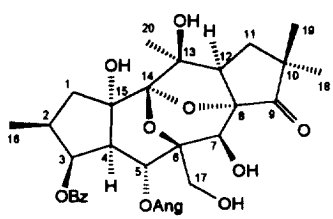


	22	23	24
R_1	Ac	Ac	H
R_2	H	OAc	H



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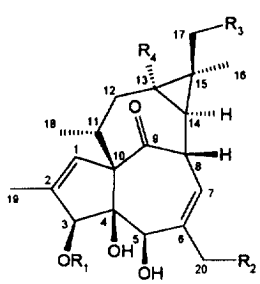

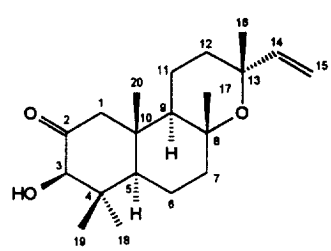

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	26	27	28	29	30	31	32	33
R_1	H	H	Bz	Ang	Ang	Ang	Ang	Ang
R_2	OAc	H	H	OAc	H	H	H	OAc
R_3	H	H	OBz	OAng	OBz	OAng	H	H
R_4	H	H	OAc	H	OAc	H	H	H

Table 1. ^{1}H NMR data of compounds **5–8**, **8a** and **8b** (400 MHz, $CDCl_3$)

H	5	6	7	8	8a	8b
1α	2.45 *dd*	2.42 *dd*	2.39 *dd*	2.31 *dd*	1.79 *dd*	1.81 *dd*
1β	1.50 *dd*	1.90 *dd*	1.86 *dd*	2.40 *dd*	2.02 *dd*	2.03 *dd*
2	2.29 *dddq*	2.34 *dddq*	2.30 *dddq*	2.51 *ddq*	1.66 *m*	1.64 *m*
3	4.19 *ddd*	5.86 *dd*	5.75 *dd*		3.73 *brd*	3.77 *brd*
4	2.76 *brs*	2.82 *dd*	2.79 *dd*			
5	5.23 *brs*	5.73 *d*	5.73 *d*	5.74 *brdq*	5.86 *brs*	6.04 *brdq*
7α	5.38 *s*	1.67 *m*	1.66 *m*			
7β		2.22 *m*	2.23 *m*	5.37 *brd*	5.27 *brs*	4.26 *brs*
8α	4.97 *brs*	1.44 *m*	1.43 *m*			
8β		1.56 *m*	1.56 *m*	4.69 *dd*	4.65 *dd*	4.58 *dd*
9	3.56 *brs*	4.51 *brd*	4.51 *brd*	1.28 *dd*	1.59 *dd*	1.60 *dd*
11	5.97 *d*	5.53 *d*	5.52 *d*	1.09 *dd*	1.46 *dd*	1.56 *dd*
12	5.41 *dd*	5.45 *d*	5.45 *d*	4.89 *dd*	4.85 *dd*	4.85 *dd*
13	3.69 *dq*	3.44 *dq*	3.43 *dq*	2.99 *dq*	2.28 *ddq*	2.24 *ddq*
14					3.95 *brdd*	3.93 *brdd*
16	1.15 *d*	1.07 *d*	1.07 *d*	1.11 *d*	1.10 *d*	1.11 *d*
17	5.24 *brs*	5.15 *brs*	5.16 *brs*	2.17 *d*	2.03 *d*	2.07 *d*
17′	5.06 *brs*	4.71 *brs*	4.71 *brs*			
18	1.08 *s*	1.09 *s*	1.10 *s*	1.08 *s*	1.07 *s*	1.06 *s*
19	1.20 *s*	1.14 *s*	1.14 *s*	0.84 *s*	0.90 *s*	0.91 *s*
20	1.24 *d*	1.36 *d*	1.35 *d*	1.13 d	0.82 *d*	0.83 *d*
5(12)-OR	2.52 *qq*	1.87 *s*	1.95 *s*	2.16 *s*	2.09 *s*	2.09 *s*
	1.14 *d*					
	1.14 *d*					
7(3)-OR	2.62 *qq*	8.12 *m*	6.49 *d*	2.18 *s*	2.14 *s*	
	1.21 *d*	7.45 *m*	7.74 *d*			
	1.21 *d*	7.55 *m*	7.55 *m*			
			7.37 *m*			
8(9)-OR	2.40 *ddq*	6.43 *d*	6.43 *d*	6.11 *qq*	6.11 *qq*	6.15 *qq*
	1.64 *ddq*	7.66 *d*	7.67 *d*	1.97 *dq*	1.99 *dq*	2.04 *dq*
	1.45 *ddq*	7.53 *m*	7.53 *m*	1.83 *dq*	1.85 *dq*	1.97 *dq*
	0.82 *t*	7.38 *m*	7.38 *m*			
	1.12 *d*					
3-OH	3.09 *d*					
9(14)-OH	2.13 *brs*					2.20 *s*
15-OH	4.32 *s*	4.34 *s*	4.31 *s*			

J(Hz): 1α,1β = 14; 2,16 = 13,20 = 6.5; comp. **5**: 1α,2 = 10.5; 1β,2 = 7.5; 2,3 = 3,4 = 4; 3,OH = 8; 11,12 = 16; 12,13 = 9.5; comps. **6** and **7**: 1α,2 = 8.5; 1β,2 = 11; 2,3 = 3.4 = 3.5; 4,5 = 10; 8,9 = 8; 11,12 = 16; 12,13 = 9; comp. **8**: 1α,2 = 9.11 = 9; 1β,2 = 8.5; 5,17 = 5,7 = 1.5; 7,8 = 2; 8,9 = 11,12 = 11; 12,13 = 4; comps. **8a** and **8b**: 1α,2 = 13.14 = 8; 1β,2 = 8,9 = 9.11 = 11,12 = 10; 2,3 = 7; 5,17 = 5,7 = 12,13 = 1.5; 7,8 = 1; 14,OH = 5; OiBu: 2,3 = 2,4 = 7; OMebu: $2,3_1 = 2,3_2 = 3_1,4 = 3_2,4 = 2,5 = 7$; $3_1,3_2 = 14$; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; OCinn: 7,8 = 16.

tive carbonyl group (H-5/C=O_{iBu}, H-7/C=O_{iBu}, H-8/C=O_{MeBu}). The configuration at chiral centres and the conformational behaviour corresponded to that of the co-occurring jatrophanes **2–4** [14] and other similar ones [10, 15].

The NMR spectra of compounds **6** and **7** differed from each other only in the signals for an ester group and exhibited some similarities to those of **5** (Tables 1 and 2). The most striking differences shown were in the C-7—C-9 sequence. Spin decoupling indicated that two out of three functional groups in this fragment were missing. The evidence for the placement of the remaining one at C-9 (benzoate in **6** and cinnamate in **7**) came from the HMBC spectrum of **6** (Table 3) and the observed correlations between the *gem*-dimethyl protons and this oxygenated carbon. Further correlations allowed the placement of the ester groups. The configuration and the preferred conformation were deduced from the results of NOE difference spectroscopy (Table 4). The configuration at all chiral centres but C-9 corresponded to that of jatrophanes **1–5**. The saturation of the H-9 signal caused, *inter alia*, an increase in the intensity of the signals for H-18 and H-11. The latter is only possible with an α-oriented H-9, because of the effects between α-oriented H-4 and H-13 as well as between H-13 and H-11. In contrast, in compounds **1–5** H-18 and H-19 were affected. A further significant difference was the coupling between H-4 and H-5 ($J_{4,5}$ = 0 Hz in **1–5** and $J_{4,5}$ = 10 Hz in **6** and **7**). Based on the NOE results C-5 epimers could be excluded. The compounds are obviously adopting different conformations involving

Table 2. ^{13}C NMR data of compounds **5**, **6** and **8** (100 MHz, $CDCl_3$)

C	5	6	8
1	45.0 *t*	46.8 *t*	29.1 *t*
2	38.1 *d*	38.5 *d*	35.8 *d*
3	75.4 *d*	78.2 *d*	207.9 *s*
4	50.2 *d*	50.5 *d*	68.3 *s*
5	68.7 *d*	73.3 *d*	113.0 *d*
6	145.4 *s*	142.4 *s*	141.4 *s*
7	69.1 *d*	27.0 *t*	76.1 *d*
8	72.1 *d*	27.6 *t*	70.8 *d*
9	81.6 *d*	79.6 *d*	24.9 *d*
10	41.0 *s*	41.0 *s*	19.2 *s*
11	137.8 *d*	137.0 *d*	30.6 *d*
12	128.5 *d*	129.1 *d*	70.5 *d*
13	44.4 *d*	44.3 *d*	43.3 *d*
14	212.7 *s*	212.9 *s*	206.0 *s*
15	88.6 *s*	84.7 *s*	71.5 *s*
16	14.9 *q*	14.1 *q*	13.4 *q*
17	110.7 *t*	114.7 *t*	17.9 *q*
18	26.7 *q*	27.2 *q*	29.0 *q*
19	23.3 *q*	18.2 *q*	16.1 *q*
20	19.9 *q*	21.7 *q*	13.3 *q*
5(12)-OR	174.7 *s*	169.3 *s*	169.4 *s*
	34.1 *d*	20.8 *q*	21.0 *q*
	18.6 *q*		
	18.6 *q*		
7(3)-OR	175.6 *s*	166.1 *s*	170.3 *s*
	34.1 *d*	129.8 *s*	21.0 *q*
	18.7 *q*	129.9 *d*	
	18.9 *q*	128.4 *d*	
		133.1 *d*	
8(9)-OR	175.3 *s*	166.8 *s*	166.9 *s*
	41.0 *d*	118.2 *d*	139.4 *s*
	26.7 *t*	144.9 *d*	127.1 *d*
	11.4 *q*	134.3 *s*	15.7 *q*
	16.6 *q*	128.1 *d*	20.4 *q*
		128.9 *d*	
		130.3 *d*	

mainly the C-5—C-7 segment. As discussed in the paper on the constituents from *E. peplus* [15] and *E. terracina* [14] they are best described in terms of the perpendicular or parallel orientation of the 6,17 exo-methylene group with regard to the mean plane of the macrocyclic ring. The jatrophanes **1**–**5** adopt parallel conformation, characterized by NOEs between H-4 and H-7 and between H-5 and H-8, while **6** and **7** adopt perpendicular conformation indicated by strong interactions between H-17 and H-5 and between H-17′ and H-8 (Table 4). The configuration at C-13 is crucial for the conformation of the northern part of the molecule. The methyl group is always quasi equatorial with H-12 and H-13 being antiperiplanar. This implies that the *trans* double bond and the methyl groups at C-10 are inverted in each of the conformers. A detailed analysis will be published elsewhere. The calculated conformation of **6**, which nicely reflects the described facts, is represented in Fig. 1. The data of compound **6** matched those published for a jatrophane isolated from *E. esula* [16] for which the relative position of the ester residues and the stereochemistry at C-9 were not assigned.

The spectral data of compound **8** (Tables 1 and 2) indicated an ingol derivative. The placement of the ester groups at C-7, C-8 and C-12 was deduced from the results of spin decoupling and HMQC spectra. Their relative positions followed from the $^1H/^{13}C$ long range correlations (Table 3). Two keto groups at C-3 and C-14, already indicated by the chemical shifts and the splitting pattern of the neighbouring protons, i.e. H-2 and H-13 (Table 1) were confirmed by the ^{13}C NMR spectrum (Table 2). The stereochemistry in the macrocyclic part (including cyclopropane moiety) was concluded from observed couplings and the results of the NOE-difference spectra. The starting points for the consideration of dipolar interactions were the geminal methyl groups of the cyclopropane part. In the depicted configuration, the α-oriented H-18 showed effects with H-9 and H-11 and the β-oriented H-19 interacted with H-8 and H-12. An effect between H-8 and H-17 secured the conformation of the Δ^5-double bond with a β-oriented C-17 methyl-group and consequently α-oriented H-5, while the effect between H-17 and H-13 fixed the stereochemistry at C-13. However, the planarity of the cyclopentane part (due to trigonal carbons at C-3 and C-14 and the presence of the epoxide ring between C-4 and C-15) and the missing reference signals in the adjacent ring made the extension of stereochemical assignments to the cyclopentane impossible. To get a reference point in the neighbouring ring, the compound was reduced with $NaBH_4$ in MeOH. Two products were formed, the diol **8a** and, surprisingly, the triol **8b**. NOE experiments with the triol **8b** led to the complete stereochemistry (Table 4). In addition to the effects discussed above, the α-oriented H-5 showed interaction with H-9 and, the most important one, with H-3. The latter required an α-oriented H-3 and, moreover, a β-oriented epoxide ring. Further effects between H-16 and H-3 and between H-16 and H-1α settled the configuration at C-2 and allowed the assignment of each H-1. Finally, the effects between H-20 and H-14 as well as between H-14 and H-1β corroborated the configuration at C-14. The calculated conformations of **8** and **8b** (Fig. 2) agreed well with the spectroscopic results. The first ingols were described from *E. ingens* [17]. So far, all ingols display identical stereochemistry in the B-ring and only recently the first A-ring epimers, i.e. 2-epi and 2,3-bisepi derivatives were reported [18, 19].

The spectra of compounds **9**–**16** (Tables 5 and 6) indicated bishomojatrophanes, a new class of natural products recently reported as constituents of *E. terracina* [6, 7]. In fact, the compounds **9**–**12** were already described (terracinolides A, B, C and E). In the ^1H NMR spectrum of **13** (Table 5) two sets of signals arising from isobutyrates appeared. The chemical shifts indicated a 3-deacyl derivative, i.e. a compound

Table 3. HMBC results for compounds **6**, **8** and **15**

H	6	8	15*
1(1α)	15, 16	2, 15, 16	3, 2, 14
1(β)	2, 3, 14	2, 3, 4, 15	16,15
2		1, 3, 16	
3	1, 15, CO_{OBz}		1, 15, CO_{Ac}
4	5, 14		5, 6
5	4, 7, 17, CO_{Ac}	4, 7, 6, 7, 17	4, 6, 15
7(α)	6, 17	5, 6, 8, 9, 17, CO_{Ac}	17, 5, 6, CO_{iBu}
8		9, CO_{Ang}	CO_{Ac}
9	18, 19, CO_{Cinn}	7, 8, 10, 18	10, 8, 7, 11, CO_{Ac}
11	10, 12, 13, 19		19, 13, 12
12	10, 13	11, 14, CO_{Ac}	10, 13, 11
13	12	14, 20	
16	1, 2, 3	1, 2, 3	1, 2, 3
17	5, 7	6, 7	6, 21
17′	5, 7		21
18	9, 10, 11, 19	9, 10, 11, 19	19, 10, 9, 11
19	9, 10, 11, 18	9, 10, 11, 18	18, 10, 9, 11
20	12, 13, 14	12, 13, 14	13, 12, 14
22α			6, 21
22β			17, 21

* Analogous results were observed with compounds **13**, **14** and **16**.

Table 4. NOE results for compounds **6**, **8b**, **14** and **16**

	6	8b	14	16
1(1α)		3(1), 14(1), 16	13(5), 16, 20	†
1′(1β)		14(2)*		
2				
3	2(4), 4(4), 5(0.5), 16, OBz_{AA}(1)	5(5), 16	4(5), 16, iBu_{Me}	†
4	2(0.3), 3(4), 7α(1), 13(3)		3(5), 13(3), 2-OAc	7(5)
5	17(2), 15-OH(1), OBz_{AA}(1)	3(4), 9(4), 13(2)	22β(5), 15-OH(1)	22(5), 15-OH(1)
7			4(12), 8(3), 11(3)	4(10), 8(3), 11(3)
8			7(3), 9(5), 19	†
9	7α(1), 11(2), 18		8(5), 8-OAc, 18, 19	8(4), 18, 19
11	7α(0.5), 9(2), 13(5), 18, 19		7(5), 13(3), 18	†
12	19, 20		19, 20	
13	4(3), 11(3)		1(4), 4(2), 11(2), 2-OAc	
14		1β(2), 20		
16	1β(2), 3(2), OBz_{AA}(1)	1α(2), 3(4)	1(3), 3(5), 1-OAc, 3-OAc	1(3), 3(5)
17	5(10), 15-OH(3)	7(8), 8(3)		
17′	8β(5)			
18	9(6), 11(5), 12(2), $OCinn_{AA}$(0.5), $OCinn_{BB}$(0.5)	9(9), 11(9), 19	9(7), 11(5), 19, 9-OAc	9(5), 11(5), 19
19	8β(5), 11(2), 12(9), $OCinn_{AA}$(0.5), $OCinn_{BB}$(0.5)	8(6), 12(11), 18	8(7), 9(7), 12(10), 18	8(7), 9(5), 12(10), 18
20	1α(1), 12(2)	12(4), 14(6)	1(5), 12(2)	1(7), 12(4), 13-OH(2)
13-OH				1(3), 4(4), 11(10), 20
15-OH	1β(2), 5(2), 17(2), OBz_{AA}(2)		5(5), 6-OAc	5(2), 1(1)

* Overlapping with the OAng signal.

† Not evaluated because of overlapping (H-1 with H-11 and H-3 with H-8).

similar to terracinolide C. Obviously the 7-acetate was replaced by an isobutyrate. The ^{13}C NMR spectrum (Table 6) confirmed this assumption. The spectral data of compound **14** were similar to those of terracinolide G [7]. An additional acetate signal and the downfield shift of H-1 indicated 1-acetoxy terracinolide G. The stereochemistry at C-1 followed from a strong NOE effect between H-1, H-20 and H-13. The hydrogen

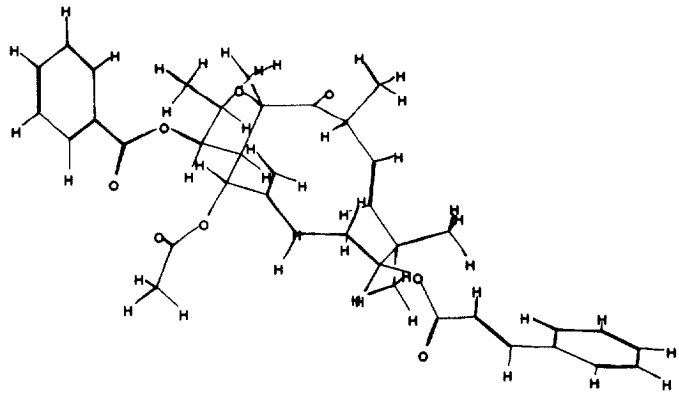


Fig. 1. Calculated conformation of jatrophane **7**; the antiperiplanar orientation of H-4 and H-5 explains the large coupling $J_{4,5} = 10$ Hz.

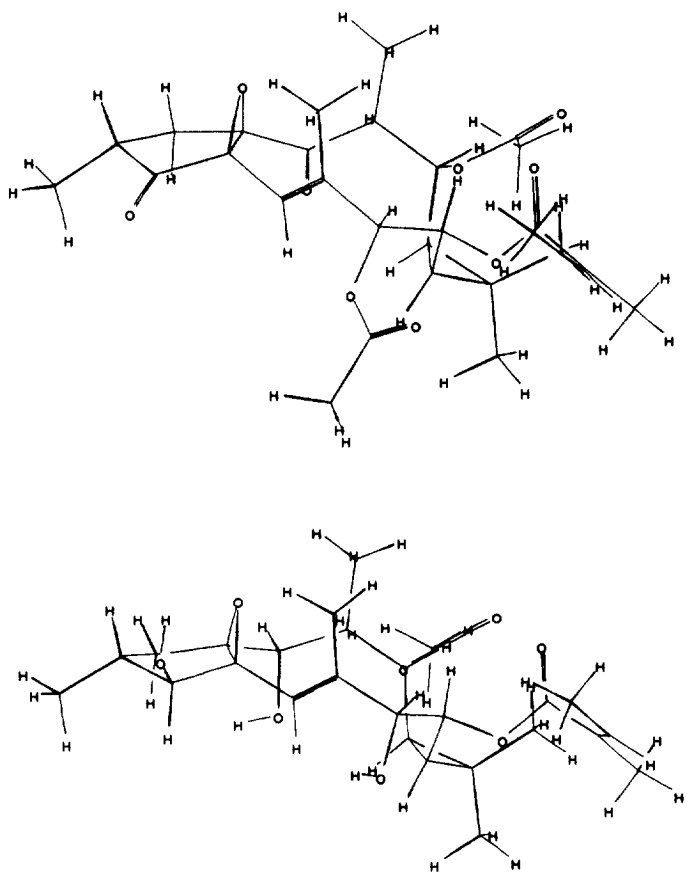


Fig. 2. Calculated conformations of ingols **8** (top) and **8b**.

bonded 15-OH group showed NOEs with H-5 and the acetate at C-6. All other relevant NOEs are listed in Table 4. It is remarkable that several significant interactions between spatially distant groups, e.g. between the methyl groups of isobutyrate and H-3 or between the acetate at C-2 and H-12, indicated that, even in solution, the molecule is adopting a preferred conformation with restricted rotation of ester groups. The most striking difference of the ^{1}H-NMR spectra of compounds **15** and **16** (Table 5) to those of other terracinolides was the missing doublet for H-20, which now appeared as a singlet. The ester groups corresponded to those of terracinolide B (**10**) and **14**, respectively. Their relative positions were deduced from the HMBC spectrum (Table 3). The stereochemistry followed again from the NOE experiments (Table 4). In analogy to previous nomenclature, we have named compounds **13** and **14** as terracinolides

Table 5. ^{1}H NMR data of compounds **13**–**16** (400 MHz, $CDCl_3$)

H	13	14	15	16
1α	2.93 *d*	5.14 *s*	4.01 *d*	6.11 *s*
1β	2.70 *d*		2.83 *d*	
3	4.70 *d*	5.82 *d*	5.47 *d*	5.46 *d*
4	3.58 *dd*	3.80 *dd*	3.85 *dd*	3.85 *dd*
5	5.80 *d*	5.37 *d*	5.49 *d*	5.33 *d*
7	6.12 *s*	6.11 *s*	5.86 *s*	5.95 *s*
8	5.59 *s*	5.53 *s*	5.52 *s*	5.47 *s*
9	4.86 *s*	4.85 *s*	4.91 *s*	4.89 *s*
11	5.90 *d*	6.00 *d*	6.08 *d*	6.13 *d*
12	5.47 *dd*	5.42 *dd*	5.86 *d*	5.77 *d*
13	4.00 *dq*	3.95 *dq*		
16	1.70 *s*	1.53 *s*	1.49 *s*	1.43 *s*
17α	2.45 *m**	2.36 *m**	2.45 *m**	2.39 *m**
17β	1.74 *m**	1.83 *m**	1.85 *m**	1.85 *m**
18	0.91 *s*	0.91 *s*	0.96 *s*	0.96 *s*
19	1.27 *s*	1.24	1.28 *s*	1.27 *s*
20	1.32 *d*	1.40 *d*	1.54 *s*	1.66 *s*
22α	2.45 *m**	2.41 *m**	2.45 *m**	2.39 *m**
22β	3.34 *m**	3.21 *m**	3.31 *m**	3.27 *m**
OAc	2.26 *s*	2.28 *s*	2.19 *s*	2.18 *s*
	2.07 *s*	2.07 *s*	2.16 *s*	2.10 *s*
	2.04 *s*	2.07 *s*	2.06 *s*	2.07 *s*
	2.01 *s*	2.01 *s*	2.05 *s*	2.04 *s*
		2.01	2.02	2.01
		1.99	1.98	2.01
OiBu	2.56 *qq*	2.54 *qq*	2.62 *qq*	2.61 *qq*
	1.26 *d*	1.21 *d*	1.27 *d*	1.26 *d*
	1.20 *d*	1.16 *d*	1.23 *d*	1.20 *d*
OiBu	2.51 *qq*			
	1.20 *d*			
	116 *d*			
13-OH			3.64 *s*	3.73 *s*
15-OH		3.99 *s*		3.98 *s*

* Not of first order.

J(Hz): comp. **13**: 1α,1β = 17; 3,4 = 3; 4,5 = 8.5; 11,12 = 16; 12,13 = 10; 13,20 = 7; comps. **14**–**16**: 3,4 = 4.5; 4,5 = 9.5; comp. **14**: 11,12 = 16; 12,13 = 10; 13,20 = 7; 13,20 = 7; comp. **15**: 1α,1β = 18; comps. **15** and **16**: 11,12 = 17; *i*Bu: 2,3 = 2,4 = 7.

Table 6. ^{13}C NMR data of compounds **10** and **13**–**16** (100 MHz, $CDCl_3$)

C	10*	13	14	15	16
1	49.3 *t*	50.0 *t*	80.2 *d*	45.5 *t*	78.7 *d*
2	86.9 *s*	88.2 *s*	88.0 *s*	86.5 *s*	87.6 *s*
3	78.3 *d*	77.3 *d*	77.8 *d*	81.2 *d*	80.2 *d*
4	45.5 *d*	46.8 *d*	43.6 *d*	46.9 *d*	44.2 *d*
5	71.8 *d*	73.3 *d*	72.3 *d*	72.3 *d*	72.7 *d*
6	80.2 *s*	79.8 *s*	80.8 *s*	81.2 *s*	81.6 *s*
7	66.5 *d*	66.6 *d*	66.6 *d*	68.1 *d*	67.9 *d*
8	67.1 *d*	67.4 *d*	67.2 *d*	67.5 *d*	67.5 *d*
9	81.6 *d*	81.8 *d*	81.4 *d*	81.2 *d*	80.8 *d*
10	39.9 *s*	39.9 *s*	39.9 *s*	39.6 *s*	39.5 *s*
11	134.7 *d*	134.2 *d*	135.8 *d*	131.0 *d*	131.4 *d*
12	130.6 *d*	131.1 *d*	129.4 *d*	133.4 *d*	132.9 *d*
13	43.2 *d*	43.2 *d*	43.9 *d*	82.1 *s*	82.9 *s*
14	204.1 *s*	204.5 *s*	211.0 *s*	204.8 *s*	212.5 *s*
15	90.5 *s*	90.5 *s*	84.6 *s*	92.4 *s*	85.2 *s*
16	18.3 *q*	18.3 *q*	14.7 *q*	19.6 *q*	15.7 *q*
17	25.5 *t*	25.8 *t*	25.3 *t*	26.3 *t*	25.9 *t*
18	26.2 *q*	26.4 *q*	26.0 *q*	26.0 *q*	26.0 *q*
19	22.7 *q*	22.6 *q*	22.5 *q*	22.6 *q*	22.4 *q*
20	20.6 *q*	20.7 *q*	20.7 *q*	29.6 *q*	29.9 *q*
21	172.1 *s*	173.0 *s*	172.4 *s*	172.0 *s*	172.3 *s*
22	28.8 *t*	27.4 *t*	28.7 *t*	28.7 *t*	28.7 *t*
OAc	170.0 *s*	169.9 *s*	170.0 *s*	170.4 *s*	170.3 *s*
	170.0 *s*	169.7 *s*	170.0 *s*	169.9 *s*	169.9 *s*
	169.8 *s*	169.6 *s*	169.8 *s*	169.8 *s*	169.8 *s*
	169.2 *s*	169.2 *s*	169.6 *s*	169.8 *s*	169.7 *s*
	169.0 *s*		169.1 *s*	168.9 *s*	169.5 *s*
	168.5 *s*		169.0 *s*	168.8 *s*	169.2 *s*
	22.7 *q*	22.6 *q*	22.2 *q*	22.4 *q*	22.3 *q*
	22.3 *q*	21.4 *q*	21.0 *q*	22.3 *q*	22.1 *q*
	21.2 *q*	21.0 *q*	20.7 *q*	21.4 *q*	21.0 *q*
	20.9 *q*	20.5 *q*	20.7 *q*	21.0 *q*	20.7 *q*
	20.6 *q*		20.7 *q*	20.7 *q*	20.7 *q*
	20.6 *q*		20.1 *q*	20.5 *q*	20.3 *q*
7-OR	174.6 *s*	174.1 *s*	174.7 *s*	175.5 *s*	175.6 *s*
	34.1 *d*	33.9 *d*	34.1 *d*	34.4 *d*	34.4 *d*
	18.7 *q*	18.5 *q*	18.7 *q*	18.9 *q*	18.9 *q*
	17.9 *q*	17.8 *q*	17.9 *q*	18.3 *q*	18.2 *q*
6-OR		176.7 *s*			
		35.1 *d*			
		19.6 *q*			
		17.8 *q*			

* The data of compound **10** included for reason of comparison.

H and I while **15** and **16** were named 13α-hydroxy terracinolides **B** and I, respectively. The calculated conformation (Fig. 3) perfectly matched the spectroscopic data and is in excellent agreement with the X-ray results [6].

In addition to these macrocyclic diterpenes, eight polycyclic diterpenes, partly with new skeletons, i.e. the paralianes **17**–**20**, the pepluane **21**, the segetanes **22**–**24** and the 15-*epi* presegetanes **25** were obtained. The names are derived from the plants from which each type of these diterpenes was first isolated during the parallel investigation of different Euphorbia species, i.e. paralianes from *E. paralias* [10] and pepluanes from *E. peplus* [15].

The NMR spectra of **17** (Tables 7 and 8) were similar to those of the first paraliane isolated from *E. paralias* [10]. An additional acetate signal and the downfield shift of H-1 pointed to the corresponding 1-acetoxy derivative. The stereochemistry at all chiral centres was deduced from the NOE results and corresponded to that of known paraliane (Table 9). The configuration at C-1, the only additional asymmetric centre, followed from the NOE between H-1 and H-4. In the spectra of **18** (Tables 7 and 8) the signals for an acetate were missing. By spin decoupling, the sequence H-7—H-8—H-12—H-11 was established, indicating that C-8 acetate was missing. The NMR spectra of **19** (Tables 7 and 8) indicated an isomer of

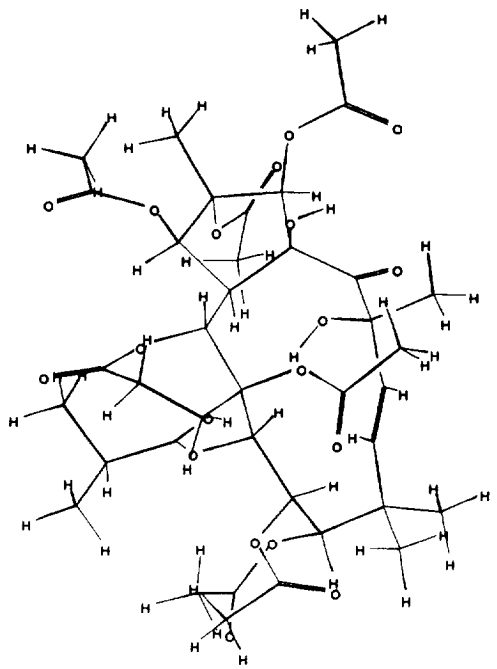


Fig. 3. Calculated conformation of jatrophanelactone **15**.

18 where the C-1 acetate has moved to C-2. Accordingly, the H-16 methyl signal appeared as a singlet while the H-1 signals formed an AB-quartet. Finally, in the ^{1}H NMR spectrum of **20** (Table 7) a methyl singlet was missing. Instead, a downfield shifted AB-quartet together with an additional acetate signal pointed to an acetoxymethyl group. The NOE of the latter with H-4 (Table 9) indicated that the C-17 methyl group was oxidized.

The ^{1}H NMR spectrum of **21** showed similarities to that of **20** (Table 7). However, the signals of the D-ring differed completely. The geminal methyl groups were absent and the ^{13}C NMR data (Table 8) indicated a tetrasubstituted aromatic ring. The 8 Hz vicinal coupling of aromatic signals required their *ortho* position. Obviously a pepluane was present [15]. The HMBC results confirmed the structure (Table 10).

The spectra of compounds **22**–**24** showed similarities to each other and the detailed discussion of the structural elucidation of **22** can stand for the whole group. The presence of four acetates and a benzoate was easily deduced from the typical signals (Tables 11 and 12). An additional ^{13}C NMR signal at δ 166.9 required either a further ester group or a lactone moiety. The fact that 22 signals were counted (after subtraction of those for the acetates and the benzoate) pointed to an ester group, recognized as being part of acetoxyacetate. This is an unusual and, to the best of our knowledge, an unprecedented ester group. The most important information for its structure came from the ^2J- and ^3J- correlations between geminally split proton signals of the $CH_3CO_2\underline{CH_2}CO_2$- group and both carbonyl carbons observed in the HMBC spectrum (Table 7). The structural elements recognized among the remaining 20 ^{13}C NMR signals were four methyl groups (^{1}H NMR: one secondary and three tertiary), a keto group and six sp^3 oxygenated carbons (four secondary and two tertiary). Four methyne groups, three methylene groups and two quartenary carbons accounted for the residual signals. Spin decoupling led to two sequences: (i) H-1 to H-5, with a secondary methyl at C-2 and (ii) H-7—H-8—H-12—H-11. The molecular formula for the parent polyol, $C_{20}H_{32}O_8$, requires 5 $^\circ$ of unsaturation and thus a tetracyclic compound. The presence of four methyl groups (no other methyl group equivalent), and the assumption of a skeleton derived from a common precursor like jatrophane, required that one methyl was incorporated in the ring system. Further information came from the ^{1}H/^{13}C long range correlations extractable from an HMBC spectrum. The *gem*-methyl groups (H-18 and H-19) showed correlations to C-9—C-11. The correlation between H-8 and C-9 completed the D-ring. The third tertiary methyl group, H-20, correlated with C-12, C-13, C-14 and C-17. The correlations between H-17 and C-6, C-7, C-12 and C-13 completed the ring C and indicated C-17 as a methano-bridge between C-6 and C-13. Finally, the correlations starting from H-14 and H-5 (Table 13) connected the interrupted sequences. The stereochemistry was again drawn from the results of NOE experiments which are listed in Table 14. The antiperiplanar oriented H-4 and H-5 ($J_{4,5}$ = 12 Hz) served as reference points. Important effects were observed between H-4 and H-17, between H-5 and H-8, between H-20 and H-12, H-14 and H-17 as well as between 15-OH and H-5, H-14 and the AA′-part of the benzoate. The vicinal coupling $J_{8,12}$ = 16 Hz is noteworthy, indicating a rigid antiperiplanar orientation of the corresponding hydrogens. The calculated conformation is represented in Fig. 4. The spectra of compound **23** (Tables 11 and 12) showed one acetate more which had to be placed at C-11. Accordingly, the spectral data were similar to those of a segetane isolated from *E. paralias*, differing only in the ester residue at C-5 [10]. In contrast, in the spectra of **24** (Tables 11 and 12) the signals for an acetate were missing. In the ^{1}H NMR spectrum, the upfield shift of the oxymethylene signals for the C-5 ester indicated that **24** bears a hydroxyacetate instead of the acetoxyacetate present in **23**. HMBC results (Table 13) confirmed the structure. We have named the basic carbocyclic skeleton without any functional group segetane.

Only a very small amount of the most polar compound **25** was obtained. The ^{1}H NMR spectrum (Table 11) indicated that only two esters, a benzoate and an angelate were present. The ^{13}C NMR spectrum (Table 12) showed in addition to the ester groups signals those for a keto group, an acetal and eight oxy-functions, four tertiary, three secondary and a primary. Furthermore, signals for four methyl, two methylene and three methyne groups as well as a quartenary carbon appeared in the spectrum. Four hydroxy groups, a primary, a secondary and two tertiary

Table 7. ^{1}H NMR data of compounds **17**–**21** (400 MHz, $CDCl_3$)

H	**17**	**18**	**19**	**20**	**21**
1(α)	5.05 *d*	5.04 *d*	2.37 *d*	5.05 *d*	5.02 *d*
1β			2.14 *d*		
2	2.87 *ddq*	2.87 *ddq*		2.87 *ddq*	2.83 *ddq*
3	5.76 *dd*	5.79 *dd*	5.85 *ddd*	5.79 *dd*	5.74 *dd*
4	2.37 *dd*	2.39 *dd*	2.87 *dd*	2.59 *dd*	2.73 *dd*
5	5.98 *d*	5.68 *d*	5.56 *d*	5.77 *d*	5.52 *d*
7α	1.91 *d*	1.81 *dd*	1.79 *dd*	1.77 *m*	2.84 *d*
7β	2.14 *d*	1.46 *dd*	1.46 *dd*	1.77 *m*	2.57 *d*
8		3.21 *ddd*	3.15 *ddd*	3.24 *ddd*	
9					6.81 *d*
11α	1.78 *dd*	1.78 *dd*	1.76 *dd*	1.78 *m*	
11β	2.16 *dd*	1.95 *dd*	1.90 *dd*	1.97 *dd*	
12	4.39 *dd*	4.21 *ddd*	4.19 *ddd*	4.27 *ddd*	
14	4.82 *s*	4.83 *s*	4.87 *s*	4.84 *s*	5.59 *s*
16	0.84 *d*	0.84 *d*	1.57 *s*	0.84 *d*	0.76 *d*
17	1.06 *s*	1.07 *s*	1.12 *s*	4.41 *d*	4.50 *d*
17′				4.23 *d*	4.41 *d*
18	1.11 *s*	1.05 *s*	1.04 *s*	1.06 *s*	7.02 *d*
19	1.27 *s*	1.14 *s*	1.11 *s*	1.16 *s*	2.19 *s*
20	0.70 *s*	0.59 *s*	0.60 *s*	0.62 *s*	1.04 *s*
OAc	2.13 *s*	2.13 *s*	2.08 *s*	2.13 *s*	2.17 *s*
	2.11 *s*	2.09 *s*	2.05 *s*	2.10 *s*	2.15 *s*
	1.90 *s*	1.94 *s*	1.98 *s*	2.06 *s*	2.12 *s*
	1.89 *s*			1.94 *s*	1.94 *s*
OBz	8.03 *AA′*	8.02 *AA′*	7.97 *AA′*	8.01 *AA′*	7.82 *AA′*
	7.42 *BB′*	7.46 *BB′*	7.48 *BB′*	7.46 *BB′*	7.31 *BB′*
	7.56 *C*	7.57 *C*	7.60 *C*	7.57 *C*	7.46 *C*
15-OH	2.86 *s*	2.79 *s*	2.55 *s*	2.82 *s*	

J(Hz): compound **17**: 1,2 = 10; 2,3 = 2,16 = 7; 3,4 = 5; 4,5 = 11β,12 = 12; 7α,7β = 14.5; 11α,11β = 14; 11α,12 = 3; compound **18**: 1,2 = 7α,8 = 10; 2,3 = 2,16 = 7β,8 = 7; 3,4 = 6; 4,5 = 12; 7α,7β = 11α,11β = 14; 8,12 = 13; 11α,12 = 4; 11β,12 = 11; compound **19**: 1α,1β = 15; 3,4 = 6; 4,5 = 8,12 = 12; 7α,7β = 11α,11β = 14; 7α,8 = 11; 7β,8 = 7; 11α,12 = 4; 11β,12 = 10; compound **20**: 1,2 = 10; 2,3 = 2,16 = 7β,8 = 7; 3,4 = 6; 4,5 = 8,12 = 17,17′ = 12; 7α,8 = 9; 11α,11β = 14; 11α,12 = 4; 11β,12 = 10; compound **21**: 1,2 = 10; 2,3 = 2,16 = 7; 3,4 = 6; 4,5 = 17,17′ = 12; 7α,7β = 16; 9,18 = 8.

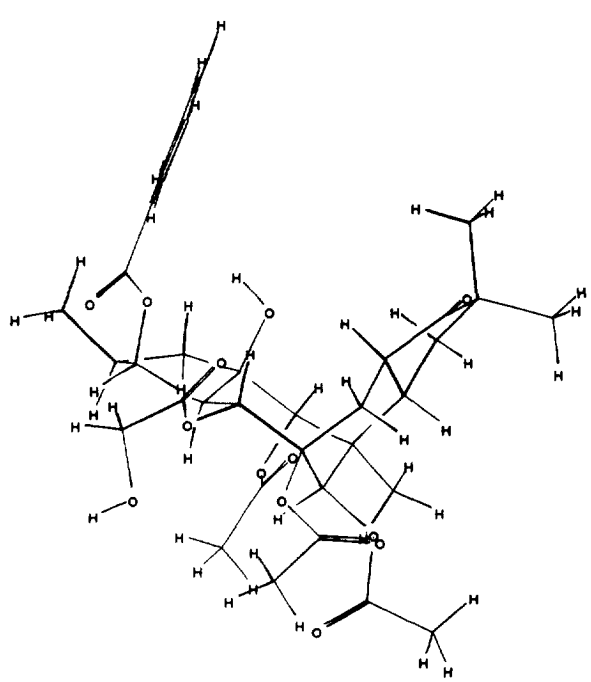


Fig. 4. Calculated conformation of segetane **24**.

Table 8. ^{13}C NMR data of compounds **17**–**21** (100 MHz, $CDCl_3$)

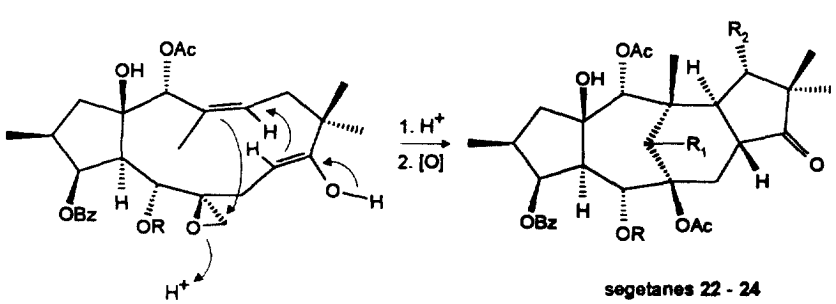
C	17	18	19	20	21
1	74.4 *d*	74.5 *d*	51.2 *t*	74.4 *d*	74.1 *d*
2	37.8 *d*	37.7 *d*	89.9 *s*	37.8 *d*	38.0 *d*
3	73.0 *d*	72.9 *d*	78.5 *d*	72.7 *d*	72.7 *d*
4	43.3 *d*	43.2 *d*	45.2 *d*	43.2 *d*	43.1 *d*
5	68.8 *d*	68.5 *d*	68.5 *d*	68.0 *d*	69.6 *d*
6	52.1 *s*	53.2 *s*	53.1 *s*	55.9 *s*	54.8 *s*
7	40.5 *t*	35.4 *t*	35.4 *t*	29.9 *t*	33.3 *t*
8	90.6 *s*	46.3 *d*	46.3 *d*	45.6 *d*	123.2 *s*
9	216.0 *s*	224.7 *s*	224.9 *s*	224.6 *s*	114.6 *d*
10	46.2 *s*	46.9 *s*	47.0 *s*	46.9 *s*	122.2 *s*
11	33.3 *t*	35.5 *t*	35.5 *t*	35.4 *t*	151.2 *s*
12	49.3 *d*	40.6 *d*	40.8 *d*	41.1 *d*	148.2 *s*
13	51.8 *s*	51.8 *s*	52.1 *s*	52.3 *s*	54.8 *s*
14	72.0 *d*	72.1 *d*	73.3 *d*	71.7 *d*	71.9 *d*
15	82.5 *s*	82.5 *s*	83.9 *s*	82.5 *s*	81.7 *s*
16	10.1 *q*	10.2 *q*	22.4 *q*	10.1 *q*	9.9 *q*
17	16.4 *q*	16.3 *q*	16.5 *q*	63.4 *t*	63.6 *t*
18	28.7 *q*	29.4 *q*	29.4 *q*	29.3 *q*	129.9 *d*
19	25.1 *q*	22.7 *q*	22.7 *q*	22.7 *q*	15.4 *q*
20	16.4 *q*	15.3 *q*	15.5 *q*	15.7 *q*	23.8 *q*
OBz	166.0 *s*	166.6 *s*	165.3 *s*	166.0 *s*	166.2 *s*
	129.8 *s*	129.6 *s*	129.2 *s*	129.5 *s*	129.7 *s*
	129.8 *d*	129.7 *d*	129.6 *d*	129.7 *d*	129.7 *d*
	128.1 *d*	128.4 *d*	128.6 *d*	128.5 *d*	128.2 *d*
	133.1 *d*	133.2 *d*	133.5 *d*	133.3 *d*	133.0 *d*
OAc	170.0 *s*	170.6 *s*	170.8 *s*	170.5 *s*	170.5 *s*
	169.8 *s*	169.9 *s*	170.0 *s*	170.4 *s*	170.3 *s*
	169.7 *s*	169.8 *s*	169.7 *s*	169.8 *s*	170.2 *s*
	169.6 *s*			169.7 *s*	169.7 *s*
	20.9 *q*	20.8 *q*	22.2 *q*	21.3 *q*	21.3 *q*
	20.8 *q*	20.8 *q*	20.9 *q*	20.8 *q*	20.9 *q*
	20.8 *q*	20.6 *q*	20.7 *q*	20.8 *q*	20.7 *q*
	20.6 *q*			20.6 *q*	20.6 *q*

were recognized from the corresponding D_2O exchangeable signals. Two further oxygenated secondary carbons were occupied by the ester groups, while the last two formed an inner acetal. The calculated molecular formula, $C_{32}H_{40}O_{11}$, which was confirmed by the $[M]^+$ peak in the high resolution mass spectrum at *m/z* 600, indicated a pentacyclic compound. By spin decoupling again only short sequences were determined. A possible plane structure which could be deduced on biogenetic grounds was corroborated from the $^1H/^{13}C$ long range correlations extracted from a highly informative HMBC spectrum (Table 13). Again the starting points were the geminal H-18 and H-19 methyl signals which showed cross peaks with the C-9—C-11 signals. The extension of the sequence was achieved because H-20 correlated with C-12—C-14, H-1 with C-2, C-3, C-14 and C-15 and H-17 with C-5—C-7. Finally, correlation starting from hydroxy group signals, i.e. 7-OH with C-8, 13-OH with C-12 and C-14 and 15-OH with C-4, C-13—C-15 incorporated all fragments into the plane structure including the inner acetal between C-14 and C-6 and C-8 respectively. The stereochemistry was deduced by NOE difference spectroscopy (Table 14). In particular, the interaction between H-20, H-1α and H-12, between the methyl groups of the angelate and H-7 and between 17-OH and H-4 and H-7 were conclusive. The calculated conformation (Fig. 5) is in good agreement with the spectroscopic facts. The basic skeleton without any functional group was named presegetan.

From the biogenetic point of view, all compounds are closely related. In each case a jatrophane type precursor is involved in cyclization (rearrangement) and oxidation steps. The formation of paralianes and pepluanes is discussed in the corresponding papers and a possible pathway to segetanes is depicted in Scheme 1. Likewise, the presegetanes could be formed starting with a slightly modified jatrophane.

The structure of two new ingenanes **29** and **30** were easily deduced from their NMR spectra (Tables 15 and 16). The ^1H NMR spectrum (Table 15) of **29** indicated an ingenol derivative with an additional ester group at C-16 or C-17. NOEs between a methyl singlet (H-16) and the upfield shifted cyclopropane signals required the 17-acyloxy derivative. Similar results were observed with ingenols from *E. hermentiana* [20] and *E. kamerunica* [21]. The relative position of the ester groups was deduced from the chemical shifts of proton signals at ester-bearing carbons. The spectra of 20-deoxy ingenol derivative **30** (Tables 15 and 16) were similar to those of **28**. A set of signals for a benzoate was replaced by those for an angelate. The relative position of the ester residues followed from the long range correlations (Table 15).

Finally, a manoyloxid derivative **34** was obtained.



Scheme 1. Proposed biogenesis of segetanes

Table 9. NOE results with compounds **17** and **20***

H	**17**	**20**
1	14(1), 2(4), 4(4), 1-OAc	14(1), 2(2), 4(4)
2	3(4), 1(5), 4(1)	
3	2(6), 4(4), 5-OAc	OBz_{AA}(1), 2(4), 4(5)
4	3(5), 1(3), 17	
5	OBz_{AA}(1), 12(6), OH(1), 7β(1)	OBz_{AA}(1), 12(6), 8(3), OH(1), 7
7α	17, 20	
11α	14(1), 20	
11β	19	
12	5(7), 14(3), OH(1), 11β(5)	5(7), 14(3), 8(4), OH(1)
14	1(2), 12(4), OH(3), 11α(2), 20	1(1), 12(3), OH(3), 11α(1), 20
16	OBz_{AA}(1), 3(1)	OBz_{AA}(1), 1-OAc
17	4(7), 7α(3), 20	4(3), 20
18	11α(4), 19, 20	11α(2), 19, 20
19	11β(3), 8-OAc, 18	8(5), 11β(5), 12(1), 18
20	14(5), 7α(5), 11α(6), 18, 17	14(5), 17(3), 17'(3), 14-OAc, 11α(7), 18
OH	OBz_{AA}(1), 5(2), 14(4), 12(2)	OBz_{AA}(3), 5(2), 14(5), 12(3)
OBz	5(1), OH(1), 8-OAc	
5-OAc	OBz_{AA}(1), 3(1)	
8-OAc	OBz_{AA}(2), OBz_{BB}(1), 11β(3), 19	

* Analogous results were observed wtih compounds **18** and **19**.

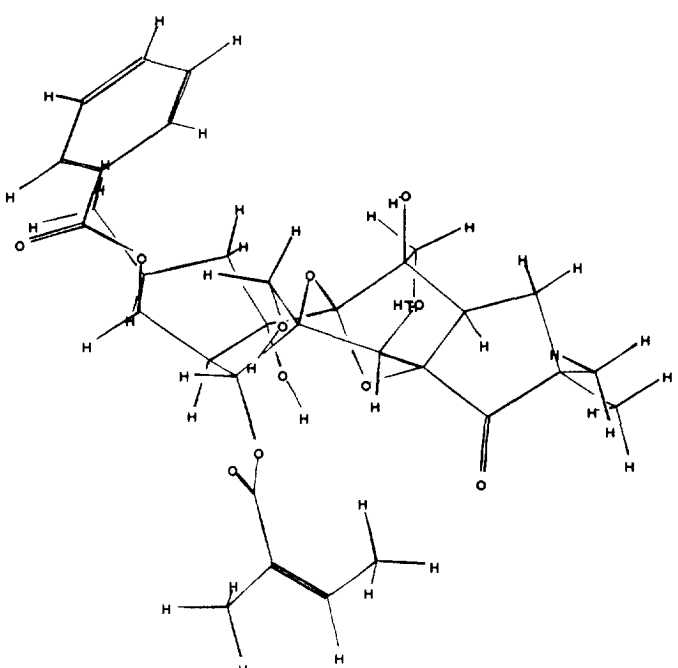


Fig. 5. Calculated conformation of presegetane **25**.

Spin decoupling allowed the assignment of all signals. The substitution in the A-ring was deduced from the long range couplings. W-coupling between H-20 and the axial H-1 excluded a hydroxy group at C-1. The same H-1 was coupled with the signal geminal to hydroxy group. Such ^4J couplings (with a keto group in between) are observed either between two equatorially or two axially oriented hydrogens. Thus, the hydroxy group at C-3 was in an equatorial position. The configuration at C-13 followed from the ^{13}C NMR spectrum. In the epimeric compounds the signal for the equatorial methyl group (C-16) appeared at ca 32 ppm. The axial orientation of this methyl group was further confirmed through the W-coupling with the axial H-16 observable in the ^1H NMR spectrum.

This extraordinary range of secondary metabolites may indicate that other *Euphorbia* species are much richer in secondary metabolites than currently known.

Table 10. HMBC results with compounds **17**, **19** and **21**

H	**17**	**19**	**21**
1(α)	16, CO_{Ac}	15	CO_{Ac}
1β		2	
2	4, 15, 16		16
3	1, 15, CO_{OBz}	1, 2, 15, CO_{OBz}	1, 15, CO_{OBz}
4	5	5, 6	5
5	4, 17, CO_{Ac}	4, 17, CO_{Ac}	4, 7, 15, CO_{Ac}
7α	5, 8, 12, 13	5, 13	5, 8
7β	5, 6, 8, 9, 17	5, 6, 8, 9, 17	5, 6, 8, 12
8	7, 9, 11, 12, 13	9, 11, 13	
9			8, 10, 18
11α	5, 6, 13, 19	12, 13	
11β	19		
12	8, 9, 20	9	
14	4, 6, 13, 15, CO_{Ac}	4, 6, 15, CO_{Ac}	4, 13, 15, CO_{Ac}
16	1, 2, 3	1, 2, 3	1, 2, 3
17	5, 6, 7, 11, 13	6, 13	5, 6, CO_{Ac}
17′			6, CO_{Ac}
18	9, 10, 11, 19	9, 10, 11, 19	11, 12, 19
19	9, 10, 11, 18	10, 11, 18	10, 11, 18
20	6, 12, 13, 14	6, 12, 13, 14	12, 13, 14
OH	4, 14, 15	14	

Most of the previous investigations were bioactivity-guided. As in many other plant families, the taxonomic border at subfamilial level is an unresolved problem to which structural diversity studies could contribute to a better understanding.

EXPERIMENTAL

The plant was collected in June 1994 from an uncultivated field close to the Faculty of Chemistry, University of Valencia, Burjassot, province Valencia, Spain. A herbarium specimen is deposited in the herbarium of the Faculty of Biology, Department for Botany, Dr M. Guara. The air dried material (1.85 kg) was extracted with MeOH (6 l) for 4 days at room temp. to give 170.2 g crude extract. After removal of waxy material by treatment with MeOH at −20°, the filtrate was evpd and sepd by open-column reversed-phase-chromatography (RP2) with mixts comprising MeOH and H_2O into 3 frs. Fr. 1 (MeOH–H_2O, 1:1) contained carbohydrates and other polar compounds and was not further characterized. Fr. 3 (MeOH) gave a mixture of triterpenes which were not further characterized. From fr. 2 (MeOH–H_2O, 7:3, 27.2 g), the methyl-*tert*-butyl ether (MTB)–MeOH (9:1)-soluble part (10.5 g; the gummy residue contained polymeric material and was descarted) was sepd by CC with mixts comprising petrol–MTB–MeOH of increasing polarity. Further separation by TLC and/or HPLC gave 2 mg **1**, 5 mg **2**, 8 mg **3**, 80 mg **4**, 30 mg **5**, 3 mg **6**, 2 mg **7**, 12 mg **8**, 67 mg **9**, 155 mg **10**, 48 mg **11**, 9 mg **12**, 9 mg **13**, 54 mg **14**, 15 mg **15**, 82 mg **16**, 3 mg **17**, 71 mg **18**, 10 mg **19**, 4 mg **20**, 24 mg **21**, 95 mg **22**, 12 mg **23**, 15 mg **24**, 1 mg **25**, 6 mg **26**, 3 mg **27**, 3 mg **28**, 59 mg **29**, 8 mg **30**, 12 mg **31**, 5 mg **32**, 10 mg **33**, 3 mg **34**. The conditions of the final purification step for the new natural products are given with each compound.

Known compounds were identified by comparing their spectral data with those of authentic material or with literature data.

*i*Bu = $(CH_3)_2CHCO$; Mebu = $CH_3CH_2CH(CH_3)CO$; Cinn = PhCHCHCO; Ang = $CH_3CHC(CH_3)CO$; AcOAc = CH_3COOCH_2CO; HOAc = $HOCH_2CO$.

(2S*,3S*,4R*,5R*,7S*,8S*,9S*,13S*,15R*)-3,9,15-*Trihydroxy*-5,7-*di*(2-*methylpropyonyloxy*)-8-(2ξ-*methylbutyroyloxy*)-14-*oxo-jatropha*-6(17),11*E*-*diene* (**5**). HPLC: (RP8), MeOH–H_2O (13:7) R_t = 11.7 min; MS *m/z* (rel. int.): 608.356 $[M]^+$ (0.1) (calc. for $C_{33}H_{52}O_{10}$ 608.356), 590 $[M-H_2O]^-$ (0.5), 520 $[M-i\text{BuOH}]^+$ (2), 330 $[520-i\text{BuOH}-\text{MebuOH}]^+$ (2), 302 (23), 284 (10), 206 (23), 96 (52), 71 $[i\text{Bu}]^+$ (60), 57 $[i\text{Bu}-\text{CO}]^+$ (100).

(2S*,3S*,4R*,5R*,9S*,13S*,15R*)-5-*Acetoxy*-3-*benzoyloxy*-9-*cinnamoyloxy*-15-*hydroxy*-14-*oxo-jatropha*-6(17),11*E*-*diene* (**6**). HPLC: RP8, MeOH–H_2O (3:1) R_t = 17.3 min; MS *m/z* (rel. int.): 628.304 $[M]^+$ (2) (calc. for $C_{38}H_{44}O_8$ 628.304), 420 $[M-\text{AcOH}-\text{CinnOH}]^+$ (3), 298 $[420-\text{PhCOOH}]^+$ (8), 131 $[\text{Cinn}]^+$ (100), 105 $[\text{PhCO}]^+$ (56).

(2S*,3S*,4R*,5R*,9S*,13S*,15R*)-5-*Acetoxy*-3,9-*dicinnamoyloxy*-15-*hydroxy*-14-*oxo-jatropha*-6(17),11*E*-*diene* (**7**). TLC: CH_2Cl_2–toluene–MTB (9:9:2) R_f = 0.57; MS *m/z* (rel. int.): 654.319 $[M]^+$ (2) (calc. for $C_{40}H_{46}O_8$ 654.319), 506 $[M-\text{CinnOH}]^+$ (1), 446 $[506-\text{AcOH}]^+$ (1), 298 $[506-\text{CinnOH}]^+$ (8), 219 (8), 131 $[\text{Cinn}]^+$ (100).

Table 11. ^{1}H NMR data of compounds **22**–**25** (400 MHz, $CDCl_3$)

H	22	23	24	25
1α	2.40 *dd*	2.38 *dd*	2.42 *dd*	2.32 *dd*
1β	1.55 *dd*	1.61 *dd*	1.57 *dd*	1.70 *dd*
2	2.08 *m*	2.08 *m*	2.11 *m*	2.43 *m*
3	5.79 *dd*	5.78 *dd*	5.79 *dd*	5.65 *dd*
4	3.42 *dd*	3.42 *dd*	3.44 *dd*	3.55 *dd*
5	5.53 *d*	5.50 *d*	5.62 *d*	5.18 *d*
7α	1.74 *dd*	1.83 *dd*	1.74 *dd*	4.24 *d*
7β	2.34 *m*	2.36 *m*	2.29 *m*	
8	3.64 *ddd*	3.73 *ddd*	3.65 *ddd*	
11α	1.79 *dd*		1.81 *m*	2.08 *dd*
11β	1.98 *dd*	5.57 *d*	1.98 *dd*	1.90 *dd*
12	1.84 *ddd*	2.08 *m*	1.87 *m*	3.52 *dd*
14	5.22 *s*	5.28 *s*	5.23 *s*	
16	0.95 *d*	0.93 *d*	0.94 *d*	0.96 *d*
17	6.43 *s*	6.36 *s*	6.43 *s*	3.85 *dd*
17′				3.65 *dd*
18	1.08 *s*	0.95 *s*	1.08 *s*	1.10 *s*
19	1.15 *s*	1.21 *s*	1.16 *s*	1.23 *s*
20	1.03 *s*	1.06 *s*	1.03 *s*	1.52 *s*
6-Ac	2.08 *s*	2.07 *s*	2.07 *s*	
11-Ac		2.13 *s*		
14-Ac	2.19 *s*	2.17 *s*	2.20 *s*	
17-Ac	2.01 *s*	2.01 *s*	1.95 *s*	
5-OR	4.57 *d*	4.55 *d*	4.17 *dd*	6.31 *qq*
	4.48 *d*	4.47 *d*	3.98 *dd*	2.05 *m*
	2.07 *s*	2.08 *s*		2.05 *m*
OH	2.50 *s*	2.71 *s*	2.45 *s*	
OBz	7.83 *AA′*	7.84 *AA′*	7.83 *AA′*	8.08 *AA′*
	7.60 *BB′*	7.59 *BB′*	7.61 *BB′*	7.50 *BB′*
	7.47 *C*	7.46 *C*	7.48 *C*	7.62 *C*
7-OH				2.99 *d*
13-OH				1.93 *s*
15-OH				4.35 *s*
17-OH				3.93 *dd*

J(Hz): comp. **22**: 1α,1β = 15.5; 1α,2 = 9.5; 1β,2 = 11.5; 2,3 = 3,4 = 7β,8 = 3.5; 2,16 = 7; 4,5 = 11.5; 7α,7β = 13.5; 7α,8 = 11α,11β = 12; 8,12 = 16; 11α,12 = 5; 11β,12 = 10; comp. **23**: 1α,1β = 15; 1α,2 = 9.5; 1β,2 = 11.5; 2,3 = 3,4 = 3; 2,16 = 6.5; 4,5 = 11,12 = 11; 7α,7β = 7α,8 = 12.5; 7β,8 = 4; 8,12 = 16; comp. **24**: 1α,1β = 15; 1α,2 = 9.5; 1β,2 = 11.5; 2,3 = 3,4 = 3.5; 2,16 = 7; 4,5 = 11.5; 7α,7β = 7α,8 = 12.5; 7β,8 = 4; 8,12 = 16; 11α,11β = 11β,12 = 12; comp. **25**: 1α,1β = 1β,2 = 13; 1α,2 = 8; 2,3 = 4,5 = 7,OH = 4; 2,16 = 7; 3,4 = 6; 11α,11β = 9; 11α,12 = 2; 11β,12 = 11; 17,17′ = 10; 17,OH = 12; 17′,OH = 1; Ac(H)OAc: comps. **22** and **23**: $2_1,2_2$ = 16; comp. **24**: $2_1,2_2$ = 17; 2_1,OH = 2_2,OH = 6.5.

Table 12. ^{13}C NMR data of compounds **22**–**25** (100 MHz, $CDCl_3$)

C	22	23	24	25
1	49.6 *t*	49.9 *t*	50.0 *t*	41.3 *t*
2	37.1 *d*	37.3 *d*	37.2 *d*	42.2 *d*
3	80.5 *d*	80.8 *d*	80.8 *d*	76.6 *d*
4	47.3 *d*	47.5 *d*	47.6 *d*	58.2 *d*
5	69.0 *d*	68.8 *d*	68.8 *d*	79.7 *d*
6	83.0 *s*	82.7 *s*	83.4 *s*	92.8 *s*
7	31.8 *t*	30.8 *t*	32.0 *t*	72.4 *d*
8	46.2 *d*	44.7 *d*	46.5 *d*	85.6 *s*
9	219.2 *s*	214.2 *s*	219.3 *s*	221.8 *s*
10	45.3 *s*	49.4 *s*	45.5 *s*	45.1 *s*
11	36.0 *t*	77.3 *d*	36.3 *t*	34.6 *t*
12	42.6 *d*	46.2 *d*	42.8 *d*	47.8 *d*
13	45.8 *s*	45.8 *s*	46.1 *s*	80.3 *s*
14	75.9 *d*	75.4 *d*	75.8 *d*	110.5 *s*
15	81.8 *s*	82.3 *s*	82.5 *s*	96.9 *s*
16	14.1 *q*	14.2 *q*	14.2 *q*	14.0 *q*
17	70.1 *d*	70.6 *d*	70.4 *d*	67.3 *t*
18	24.6 *q*	18.3 *q*	24.8 *q*	26.2 *q*
19	26.4 *q*	25.3 *q*	26.7 *q*	27.2 *q*
20	25.5 *q*	27.1 *q*	25.8 *q*	24.1 *q*
6-OAc	169.8 *s*	170.1 *s*	169.4 *s*	
	20.1 *q*	20.6 *q*	20.7 *q*	
11-OAc		170.5 *s*		
		20.9 *q*		
14-OAc	170.3 *s*	170.2 *s*	170.4 *s*	
	20.9 *q*	21.1 *q*	21.1 *q*	
17-OAc	169.2 *s*	169.3 *s*	169.8 *s*	
	20.5 *q*	21.0 *q*	21.0 *q*	
3-OBz	165.7 *s*	165.8 *s*	166.0 *s*	166.0 *s*
	129.1 *s*	129.4 *s*	129.3 *s*	129.8 *s*
	129.1 *d*	129.2 *d*	129.2 *d*	129.8 *d*
	128.5 *d*	128.8 *d*	128.9 *d*	128.7 *d*
	133.2 *d*	133.5 *d*	133.6 *d*	133.4 *d*
5-OR	166.9 *s*	167.2 *s*	172.2 *s*	169.2 *s*
	60.2 *t*	60.4 *t*	60.9 *t*	126.7 *s*
	169.8 *s*	170.0 *s*		142.9 *d*
	20.9 *q*	20.3 *q*		20.4 *q*
				16.2 *q*

(2R*,4R*,7R*,8S*,9S*,11R*,12S*,13S*,15R*)-7,12-*Diacetoxy*-8-*angeloyloxy*-4,15-*epoxy*-3,14-*dioxo-lathyr*-5*E*-*ene* = 3-*Dehydro*-7,12-*di*-O-*acetyl*-8-O-*angeloyl*-2-*epi*-*ingol* (**8**). TLC: CH_2Cl_2–toluene–MTB (9:9:2) R_f = 0.45; MS *m/z* (rel. int.): 530.252 $[M]^+$ (5.5) (calc. for $C_{29}H_{38}O_9$ 530.252), 488 [M−ketene]$^+$ (1), 470 $[M-AcOH]^+$ (3.5), 388 $[480-AngOH]^+$ (2), 370 $[470-AngOH]^+$ (3), 310 $[370-AcOH]^+$ (5), 179 (10), 83 $[Ang]^+$ (100), 55 $[Ang-CO]^+$ (73).

7 mg **8** were stirred with excess $NaBH_4$ in MeOH for 2 h. After TLC, 3 mg **8a** and 2 mg **8b** were obtained. **8a**: TLC: CH_2Cl_2–toluene–MTB, (7:7:6) R_f = 0.5; MS *m/z* (rel. int.): 534.283 $[M]^+$ (0.1) (calc. for $C_{29}H_{42}O_9$ 534.283), 434 $[M-AngOH]^+$ (1), 374 $[434-AcOH]^+$ (1), 314 $[374-AcOH]^+$ (7), 254 (6), 83 $[Ang]^+$ (100), 55 $[Ang-CO]^+$ (55). **8b**: TLC: CH_2Cl_2–toluene–MTB (7:7:6) R_f = 0.2; MS *m/z* (rel. int.): 492.272 $[M]^+$ (0.1) (calc. for $C_{27}H_{40}O_8$ 492.272), 374 $[M-H_2O-AngOH]^+$ (1), 314 $[374-AcOH]^+$ (3), 256 (3), 83 $[Ang]^+$ (100), 55 $[Ang-CO]^+$ (98). .

(2R*,3R*,4R*,5R*,6S*,7R*,8S*,9S*,13S*,15R*)-2,8,9,15-*Tetraacetoxy*-5,21-*epoxy*-3-*hydroxy*-6,7-*diisobutyroyloxy*-14,21-*dioxo*-17-*ethyljatropha*-11*E*-*ene* (*Terracinolide H*) (**13**). HPLC: RP8, MeOH–H_2O

Table 13. HMBC results with compounds **22**, **24** and **25**

H	22	24	25
1α	2, 3, 14	2, 3, 14	2, 3, 14
1β	2, 15, 16	2, 15, 16	2, 15
3	1, 15, CO_{OBz}	1, 15, CO_{OBz}	2, CO_{OBz}
4	5, 6	5, 6	
5	4, 7, $CO_{AcO\Delta cO}$	4, 7, 15, $CO_{HO\Delta cO}$	3, 4, 17, CO_{Ang}
7(α)	5, 6, 8	5, 6, 8	8
7β	6, 8, 12, 17		
8	7, 9, 12	7, 9, 12	
11α	9, 10, 12, 18	9, 10, 12, 18	12, 13, 18
11β	12, 18, 19	12, 18, 19	13, 19
12	8, 11, 14	8, 11, 13, 14	8, 9, 20
14	4, 13, 15, 17, CO_{Ac}	4, 13, 15, 17, CO_{Ac}	
16	1, 2, 3	1, 2, 3	2, 3
17	6, 7, 12, 13, CO_{Ac}	6, 7, 12, 13, CO_{Ac}	5, 6
17′			5, 7
18	9, 10, 11, 19	9, 10, 11, 19	9, 10, 11, 19
19	9, 10, 11, 18	9, 10, 11, 18	9, 10, 11, 18
20	12, 13, 14, 17	12, 13, 14, 17	12, 13, 14
7-OH			8
13-OH			12, 14
15-OH	14, 15	14, 15	4, 13, 14, 15
AcOAcO	$CO_{\Delta cOAcO}$, $CO_{AcO\Delta cO}$		
AcOAcO	$CO_{\Delta cOAcO}$, $CO_{AcO\Delta cO}$		

Table 14. NOE results with compounds **22** and **25**

H	22	25
1α		2(3), 20
1β	OBz_{AA}-(1)	16
2		3(5), 4(3), 1α(2)
3	4(3)	5(1), 2(4)
4	17(3), 3(3)	3(3), 5(3)
5	8(3), OH(1), 7β(1)	3(2), 7(1), 17′(5), 4(3)
7		5(1), 17-OH(1), 4(1), 7-OH(6), $OAng_{Me}$
8	5(4), 11β(3), 19	
12		20
14	1α(1), 11β(2), OH(1), 20	
16	OBz_{AA}-(1), 3(1)	OBz_{AA}-(2), 3(2)
17	4(5), 20	
17′		OBz_{AA}-(4), 5(6)
18	11α(3)	11α(2), 19
19	8(2), 11β(2)	11β(5), 18
20	17(3), 14(5), 12(4), 11α(2)	12(7), 1α(5)
OH(17-OH)	OBz_{AA}-(3), 5(2), 14(0.5), 1β(2)	5(3), 7(3)
OAng		7(3)

(7:3) R_t = 12.9 min; MS *m/z* (rel. int.): 766.341 $[M]^+$ (13) (calc. for $C_{38}H_{54}O_{16}$ 766.341), 738 $[M-CO]^+$ (4), 706 $[M-AcOH]^+$ (5), 678 [M – *i*BuOH; 738 – AcOH; 706 – CO]$^+$ (12), 618 $[678-AcOH]^+$ (5), 576 [618 – ketene]$^+$ (6), 558 [618 – AcOH; 576 – H_2O]$^+$ (11), 516 [576 – AcOH; 558 – ketene]$^+$ (18), 428 [516 – *i*BuOH]$^+$ (12), 368 [428 – AcOH]$^+$ (15), 340 [428 – *i*BuOH]$^+$ (24), 322 [340 – H_2O]$^+$ (15), 71 [*i*Bu]$^+$ (*100*).

(1R*, 2S*, 3R*, 4R*, 5R*, 6S*, 7R*, 8S*, 9S*, 13S*, 15S*)-1,2,3,6,8,9-*Hexaacetoxy*-5,21-*epoxy*-15-*hydroxy*-7-*isobutyroyloxy*-14,21-*dioxo*-17-*ethyljatropha*-11*E*-*ene* (*Terracinolide I*) (**14**). HPLC: RP8, MeOH–H_2O (11:9) R_t = 22.2 min; MS *m/z* (rel. int.): 796.315 $[M]^+$ (3) (calc. for $C_{38}H_{52}O_{16}$ 796.315), 778 $[M-H_2O]^+$ (4), 736 [M – AcOH; 778 – ketene]$^+$ (2), 708 [M – *i*BuOH; 736 – CO]$^+$ (34), 676 $[736-AcOH]^+$ (13), 648 $[708-AcOH]^+$ (11), 560

Table 15. ^{1}H NMR data of compounds **29** and **30** and HMBC results with **30** (400 MHz, $CDCl_3$)

H	**29**	**30**	HMBC
1	6.02 *q*	6.06 *q*	3, 4, 10, 19
3	5.57 *brs*	5.46 *brs*	1, 2, 5, 10, CO_{Ang}
5	3.88 *brd*	3.70 *brd*	3, 6, 7
7	6.08 *m*	5.68 *ddq*	5, 20
8	4.24 *brdd*	4.13 *brdd*	6, 9, 14
11	2.51 *ddq*	2.58 *ddq*	
12	2.34 *ddd*	2.78 *dd*	11, 18
12′	1.84 *ddd*	2.41 *dd*	10, 13
13	0.94 *ddd*		
14	1.16 *dd*	1.44 *brd*	13, 16
16	1.15 *s*	1.25 *s*	13, 14, 15
17	4.34 *d*	4.54 *d*	13, 15, 16
17′	4.21 *d*	4.38 *d*	14, 15, 16, CO_{OBz}
18	0.97 *d*	1.01 *d*	10, 11, 12
19	1.79 *d*	1.80 *d*	1, 2, 3
20	4.72 *brd*	1.71 *brs*	5, 6, 7
20′	4.45 *brd*		
4-OH	3.55 *brs*	3.53 *s*	4, 5, 10
5-OH	3.62 *brd*	3.08 *d*	6
3-OAng	6.16 *qq*	6.16 *qq*	
	1.98 *dq*	1.99 *dq*	
	1.88 *dq*	1.89 *qd*	
16-OR	6.06 *qq*	8.12 *AA′*	
	2.00 *dq*	7.47 *BB′*	
	1.91 *dq*	7.57 *C*	
OAc	2.04	2.02 *s*	

J(Hz): 1,19 = 1.5; 7,8 = 11,12′ = 5; 8,14 = 17,17′ = 12.5; 11,12 = 3.5; 11,18 = 7.5; 12,12′ = 16.5; comp. **29**: 5,OH = 5; 12,13 = 9; 12′,13 = 6; 13,14 = 8; 20,20′ = 12.5; comp. **30**: 5,7 = 7,20 = 1; 5,OH = 7; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5.

Table 16. ^{13}C NMR data of compounds **26**, **29** and **30** (100 MHz, $CDCl_3$)

C	**26**	**29**	**30**
1	130.1 *d*	131.6 *d*	131.6 *d*
2	136.7 *s*	136.4 *s*	136.2 *s*
3	80.7 *d*	82.3 *d*	82.8 *d*
4	84.4 *s*	84.9 *s*	84.7 *s*
5	73.7 *d*	74.6 *d*	77.5 *d*
6	138.8 *s*	136.2 *s*	138.3 *s*
7	128.7 *d*	128.1 *d*	122.1 *d*
8	44.1 *d*	43.1 *d*	42.6 *d*
9	206.6 *s*	205.5 *s*	205.1 *s*
10	72.6 *s*	72.0 *s*	72.0 *s*
11	39.8 *d*	38.4 *d*	38.1 *d*
12	31.0 *t*	30.8 *t*	35.2 *t*
13	28.5 *d*	24.2 *d*	68.7 *s*
14	23.1 *d*	23.4 *d*	28.8 *d*
15	23.9 *s*	27.6 *s*	34.1 *s*
16	23.0 *q*	24.5 *q*	18.6 *q*
17	15.4 *q*	65.1 *t*	65.6 *t*
18	17.4 *q*	16.8 *q*	17.8 *q*
19	15.5 *q*	15.5 *q*	15.9 *q*
20	66.6 *t*	66.5 *t*	21.8 *q*
OAc	171.1 *s*	170.9 *s*	170.8 *s*
	21.1 *q*	20.9 *q*	21.2 *q*
OAng		168.2 *s*	168.4 *s*
		127.8 *s*	126.9 *s*
		139.7 *d*	140.2 *d*
		15.8 *q*	15.6 *q*
		20.7 *q*	20.7 *q*
16-OR		168.2 *s*	166.7 *s*
		127.1 *s*	130.2 *s*
		137.8 *d*	129.7 *d*
		15.7 *q*	128.4 *d*
		20.6 *q*	132.9 *d*

$[648-i\text{BuOH}]^+$ (5), 500 $[560-\text{AcOH}]^+$ (7), 458 $[500-\text{ketene}]^+$ (10), 440 $[500-\text{AcOH}]^+$ (9), 398 $[458-\text{AcOH}]^+$ (13), 380 $[440-\text{AcOH}]^+$ (8), 356 $[398-\text{ketene}]^+$ (9), 338 $[398-\text{AcOH}]^+$ (15), 71 $[i\text{Bu}]^+$ (100).

(2R*,3R*,4R*,5R*,6S*,7R*,8S*,9S*,13R*,15R*)-2,3,6,8,9,15-*Hexaacetoxy*-5,21-*epoxy*-13-*hydroxy*-7-*isobutyroyloxy*-14,21-*dioxo*-17-*ethyljatropha*-11*E*-*ene* (13α-*Hydroxyterracinolide B*) (**15**). HPLC: RP8, MeOH–H_2O (11:9) R_t = 14 min; MS *m/z* (rel. int.): 768.320 $[M-CO]^+$ (2) (calc. for $C_{37}H_{52}O_{17}$ 768.320), 726 $[768-\text{ketene}]^+$ (5), 708 $[768-\text{AcOH}]^+$ (18), 666 $[726-\text{AcOH}]^+$ (17), 648 $[708-\text{AcOH}]^-$ (7), 606 $[666-\text{AcOH}; 648-\text{ketene}]^-$ (14), 546 $[606-\text{AcOH}]^-$ (12), 518 $[606-i\text{BuOH}]^+$ (16), 458 $[548-i\text{BuOH}; 518-\text{AcOH}]^+$ (17), 398 $[458-\text{AcOH}]^+$ (6), 356 $[398-\text{ketene}]^+$ (14), 338 $[398-\text{AcOH}]^-$ (8), 71 $[i\text{Bu}]^+$ (100).

(1R*,2S*,3R*,4R*,5R*,6S*,7R*,8S*,9S*,13S*,15S*)-1,2,3,6,8,9-*Hexaacetoxy*-5,21-*epoxy*-13,15-*dihydroxy*-7-*isobutyroyloxy*-14,21-*dioxo*-17-*ethyljatropha*-11*E*-*ene* (13α-*Hydroxyterracinolide I*) (**16**). HPLC: RP8, MeOH–H_2O (11:9) R_t = 9.4 min; MS *m/z* (rel. int.): 812.310 $[M]^+$ (11) (calc. for $C_{38}H_{52}O_{19}$ 812.310), 752 $[M-\text{AcOH}]^+$ (1), 692 $[752-\text{AcOH}]^+$ (7), 664 $[752-i\text{BuOH}; 692-\text{CO}]^+$ (56), 632 $[692-\text{AcOH}]^+$ (13), 622 $[664-\text{ketene}]^+$ (100), 604 $[664-\text{AcOH}]^+$ (22), 562 $[622-\text{AcOH}]^+$ (17), 544 $[604-\text{AcOH}]^+$ (29), 534 $[622-i\text{BuOH}; 562-\text{CO}]^+$ (7), 474 $[534-\text{AcOH}]^+$ (25), 414 $[474-\text{AcOH}]^+$ (24), 354 $[414-\text{AcOH}]^+$ (34), 294 $[354-\text{AcOH}]^+$ (31), 71 $[i\text{Bu}]^+$ (81).

(1R*,2R*,3S*,4R*,5R*,6R*,8S*,12S*,13S*,14R*,15R*)-1,5,8,14-*Tetraacetoxy*-3-*benzoyloxy*-15-*hydroxy*-9-*oxo*-*paraliane* (**17**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 21.2 min; MS *m/z* (rel. int.): 656.283 $[M]^+$ (0.1) (calc. for $C_{35}H_{44}O_{12}$ 656.283), 596 $[M-\text{AcOH}]^+$ (46), 554 $[596-\text{ketene}]^+$ (9), 536 $[596-\text{AcOH}]^-$ (12), 476 $[536-\text{AcOH}]^+$ (7), 416 $[476-\text{AcOH}]^+$ (3), 354 $[476-\text{PhCOOH}]^+$ (3), 294 $[416-\text{PhCOOH}; 354-\text{AcOH}]^+$ (9), 105 $[\text{PhCO}]^+$ (100).

(1R*,2R*,3S*,4R*,5R*,6R*,8R*,12R*,13S*,14R*,15R*)-1,5,14-*Triacetoxy*-3-*benzoyloxy*-15-*hydroxy*-9-*oxo*-*paraliane* (**18**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 27.4 min; MS *m/z* (rel. int.): 598.278 $[M]^+$ (2) (calc. for $C_{33}H_{42}O_{10}$ 598.278), 538 $[M-\text{AcOH}]^+$ (7), 478 $[538-\text{AcOH}]^+$ (12), 418 $[478-\text{AcOH}]^+$ (2), 416 $[538-\text{PhCOOH}]^+$ (6), 356 $[478-\text{PhCOOH};$

Table 17. ^{1}H NMR and ^{13}C NMR data of compound **34**

H		C	
1α	2.10 *brdd*	1	52.1 *t*
1β	2.47 *d*	2	210.9 *s*
3	3.89 *dd*	3	82.9 *d*
5	1.64 *brd*	4	45.2 *s*
6α	1.81 *m*	6	19.6 *t*
6β	1.41 *dddd*	5	54.5 *d*
7α	1.55 *m*	7	42.6 *t*
7β	1.92 *ddd*	8	74.6 *s*
9	1.64 *brd*	9	54.9 *d*
11α	1.48 *m*	11	15.6 *t*
11β	1.60 *m*	10	43.1 *s*
12α	1.67 *m*	12	35.5 *t*
12β	1.81 *m*	13	73.5 *s*
14	5.86 *dd*	14	147.5 *d*
15c	4.95 *dd*	15	110.6 *t*
15t	5.17 *dd*	16	28.3 *q*
16	1.30 *s*	17	24.9 *q*
17	1.30 *s*	18	29.3 *q*
18	1.18 *s*	19	16.2 *q*
19	0.69 *s*	20	16.3 *q*
20	0.77 *brs*		
OH	3.44 *d*		

J(Hz): 1α,1β = 5,6β = 6β,7α = 7α,7β = 9,11β = 12.5; 1α,3 = 1.5; 3,OH = 5; 6α,6β = 13; 6β,7β = 6α,7β = 3; 14,15c = 11.0; 14,15t = 17.5; 15c,15t = 1.5.

416−AcOH]$^+$ (20), 338 [356−H_2O]$^+$ (4), 314 [356−ketene]$^+$ (16), 296 [356−AcOH]$^+$ (17), 105 [PhCO]$^+$ (100).

(2R*,3R*,4S*,5R*,6R*,8R*,12R*,13S*,14R*,15R*)-2,5,14-*Triacetoxy*-3-*benzoyloxy*-15-*hydroxy*-9-*oxo-paraliane* (**19**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 25.1 min; MS *m/z* (rel. int.): 598.278 [M]$^+$ (7) (calc. for $C_{33}H_{42}O_{10}$ 598.278), 538 [M−AcOH]$^+$ (6), 478 [538−AcOH]$^+$ (9), 418 [478−AcOH]$^+$ (11), 416 [538−PhCOOH]$^+$ (9), 400 [418−H_2O]$^+$ (13), 356 [478−PhCOOH; 416−AcOH]$^+$, 338 [356−H_2O]$^+$ (19), 314 [356−ketene]$^+$ (19), 296 [356−AcOH]$^+$ (56), 105 [PhCO]$^+$ (100), 77 [Ph]$^+$ (36).

(1R*,2R*,3S*,4R*,5R*,6R*,8R*,12R*,13S*,14R*,15R*)-1,5,14,17-*Tetraacetoxy*-3-*benzoyloxy*-15-*hydroxy*-9-*oxo-paraliane* (**20**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 12.7 min; MS *m/z* (rel. int.): 656.283 [M]$^+$ (1) (calc. for $C_{35}H_{44}O_{12}$ 656.283), 596 [M−AcOH]$^+$ (7), 536 [596−PhCOOH]$^+$ (17), 476 [536−AcOH]$^+$ (8), 414 [536−PhCOOH]$^+$ (39), 372 [414−ketene]$^+$ (27), 354 [414−AcOH; 372−H_2O]$^+$ (26), 312 [372−AcOH]$^+$ (28), 294 [354−AcOH]$^+$ (36), 105 [PhCO]$^+$ (100).

(1R*,2R*,3S*,4R*,5R*,6R*,13S*,14R*,15R*)-8,10(18)11-*Hexadehydro*-1,5,14,17-*tetraacetoxy*-3-*benzoyloxy*-11,15-*dihydroxy-pepluane* (**21**). TLC: petrol–MTB (11:9) R_f = 0.41; MS *m/z* (rel. int.): 652.252 [M]$^+$ (9) (calc. for $C_{35}H_{40}O_{12}$ 652.252), 610 [M−ketene]$^+$ (4), 592 [M−AcOH]$^+$ (2), 532 [592−AcOH]$^+$ (3), 410 [532−PhCOOH]$^+$ (5), 368 [410−ketene]$^+$ (5), 350 [410−AcOH]$^+$ (5), 308 [368−AcOH]$^+$ (8), 290 [350−AcOH]$^+$ (12), 105 [PhCO]$^+$ (100).

(2S*,3S*,4R*,5R*,6R*,8R*,12S*,13R*,14R*,15R*)-6,14,17-*Triacetoxy*-5-(2-*acetoxyacetoxy*)-3-*benzoyloxy*-15-*hydroxy*-9-*oxo-segetane* (**22**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 8.6 min; MS *m/z* (rel. int.): 654.268 [M−AcOH]$^+$ (37) (calc. for $C_{35}H_{42}O_{12}$ 654.268), 612 [654−ketene]$^+$ (7), 536 [654−AcOAcOH]$^+$ (40), 432 (38), 414 [536−PhCOOH; 432−H_2O]$^+$ (17), 372 [432−AcOH; 414−ketene]$^+$ (18), 354 [414−AcOH; 372−H_2O]$^+$ (22), 312 [372−AcOH; 354−ketene]$^+$ (71), 294 [354−AcOH; 312−H_2O]$^+$ (100), 276 [294−H_2O]$^+$ (41), 105 [PhCO]$^+$ (35).

(2S*,3S*,4R*,5R*,6R*,8R*,11S*,12S*,13R*,14R*,15R*)-6,11,14,17-*Tetraacetoxy*-5-(2-*acetoxyacetoxy*)-3-*benzoyloxy*-15-*hydroxy*-9-*oxo-segetane* (**23**). TLC: toluene–CH_2Cl_2–MTB (4:4:1 3×), R_f = 0.33; MS *m/z* (rel. int.): 712.273 [M−AcOH]$^+$ (37) (calc. for $C_{37}H_{44}O_{14}$ 712.273), 652 [712−AcOH]$^+$ (87), 594 [712−AcOAcOH]$^+$ (12), 534 [652−AcOAcOH; 594−AcOH]$^+$ (19), 530 [652−PhCOOH]$^+$ (13), 472 [594−PhCOOH]$^+$ (11), 430 [472−ketene]$^+$ (20), 412 [534−PhCOOH; 530−AcOAcOH; 472−AcOH]$^+$ (22), 370 [430−AcOH; 412−ketene]$^+$ (42), 352 [412−AcOH; 370−H_2O]$^+$ (20), 310 [370−AcOH; 352−ketene]$^+$ (100), 292 [352−AcOH; 310−H_2O]$^+$ (83), 105 [PhCO]$^+$ (65), 101 [AcOAc]$^+$ (17).

(2S*,3S*,4R*,5R*,6R*,8R*,12S*,13R*,14R*,15R*)-6,14,17-*Triacetoxy*-5-(2-*hydroxyacetoxy*)-3-*benzoyloxy*-15-*hydroxy*-9-*oxo-segetane* (**24**). HPLC: RP8, MeOH–H_2O (3:2) R_t = 6.1 min; MS *m/z* (rel. int.): 612.257 [M−AcOH]$^+$ (24) (calc. for $C_{33}H_{40}O_{11}$ 612.257) 596 [M−HOAcOH]$^+$ (0.5), 536 [612−HOAcOH]$^+$ (5), 490 [612−PhCOOH]$^+$ (1), 474 [596−PhCOOH]$^+$ (0.5), 432 [474−ketene]$^+$ (13), 414 [490−HOAcOH]$^+$ (3), 372 [432−AcOH]$^+$ (5), 354 [414−AcOH]$^+$ (5), 312 [372−AcOH]$^+$ (20), 294 [354−AcOH]$^+$ (28), 266 [294−CO]$^+$ (17), 105 [PhCO]$^+$ (100).

(2S*,3S*,4R*,5R*,6R*,7S*,8R*,12R*,13S*,14R*,15R*)-5-*Angeloyloxy*-3-*benzoyloxy*-6,14:8,14-*diepoxy*-7,13,15,17-*tetrahydroxy*-9-*oxo*-15-*epi preseg-etane* (**25**). TLC: petrol–MTB (3:7) R_f = 0.43; MS *m/z* (rel. int.): 600.257 [M]$^+$ (3) (calc. for $C_{32}H_{40}O_{11}$ 600.257), 582 [M−H_2O]$^+$ (16), 500 [M−AngOH]$^+$ (70), 378 [500−PhCOOH]$^+$, 105 [PhCO]$^+$ (67), 83 [Ang]$^+$ (46), 55 [Ang−CO]$^+$ (100).

20-O-*Acetyl*-3-O-*angeloyl*-17-*angeloyloxyingenol* (**29**). HPLC: RP8, MeOH–H_2O (3:1) R_t = 8.3 min; MS *m/z* (rel. int.): 570.283 [M]$^+$ (0.5) (calc. for $C_{32}H_{42}O_9$ 570.283), 470 [M−AngOH]$^+$ (0.5), 410 [470−AcOH]$^+$ (0.5), 370 [470−AngOH]$^+$ (0.5), 310 [410−AngOH]$^+$ (2), 282 [310−CO]$^+$ (2), 83 [Ang]$^+$ (98), 55 [Ang−CO]$^+$ (100).

13α-*Acetoxy*-3-O-*angeloyl*-17-*benzoyloxyingenol* (**30**). TLC: CH_2Cl_2–toluene–MTB (2:2:1) R_f = 0.73; MS *m/z* (rel. int.): 492.215 [M−AngOH]$^+$ (1.5) (calc.

for $C_{29}H_{32}O_7$: 492.215), 432 $[492-AcOH]^+$ (5.5), 310 $[432-PhCOOH]^+$ (18), 241 (16), 164 (28), 122 $[PhCOOH]^+$ (50); 105 $[PhCO]^+$ (100), 83 $[Ang]^+$ (64).

3β-Hydroxy-2-oxo-manoyloxid (**34**). TLC: CH_2Cl_2–toluene–MTB (2:2:1) $R_f = 0.79$; MS *m/z* (rel. int.): 320.235 $[M]^+$ (2.5) (calc. for $C_{20}H_{32}O_3$ 320.135), 305 $[M-Me]^+$ (72), 287 $[305-H_2O]^+$ (17), 222 (26), 135 (35), 55 (100).

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