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Three New Diterpene Esters from *Euphorbia decipiens*

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Abstract. Three new diterpene esters, decipinone (**1**), isodecipinone (**2**) and decipidone (**3**), with a tricyclic carbon skeleton have been isolated from *Euphorbia decipiens* Boiss. & Buhse (Euphorbiaceae) and their structures have been elucidated by different spectroscopic methods including HREIMS, EIMS, IR, UV, 1D and 2D NMR techniques. The relative stereochemistry of **1** was established by X-ray crystallography.

INTRODUCTION

Euphorbia decipiens grows wild in different parts of Iran at high altitude.[1] According to the best of our knowledge, the chemical constituents of this plant have not been investigated so far. Some of the plants belonging to the genus *Euphorbia* are used in folk medicine, for instance *E. kansui* is considered as a herbal remedy for edema, ascites and cancer in China and investigation of this plant showed two antileukemic diterpene esters with an ingenane carbon skeleton.[2]

The macrocyclic and polycyclic diterpenes isolated from different species of *Euphorbia* plants with ingenane, tigliane and daphnane skeletons have skin-irritant, tumour-promoting and anti-tumour activities.[3,4,5] Some esters of myrsinol isolated from *E. myrsinites* showed anti-HIV-1 reverse transcriptase (RT) inhibition.[6] The medicinal properties attributed to *Euphorbia* prompted us to investigate *E. decipiens* for its chemical constituents. Now we report the isolation and structure elucidation of three diterpene esters with a tricyclic skeleton by means of different spectroscopic techniques. We are also suggesting a biogenetic pathway for synthesis of this skeleton from a lathyrol derivative precursor.

RESULTS AND DISCUSSION

The chloroform-methanol (1:1) extract of the plant *E. decipiens* was evaporated *in vacuo*. The long chain hydrocarbons and fatty acids were removed (see Experimental) and subjected to column chromatography. The compounds decipinone (**1**), isodecipinone (**2**) and decipidone (**3**) were isolated through repeated column chromatography and PTLC (Fig. 1).

Compound **1** was assigned the molecular formula $C_{35}H_{42}O_{12}$ on the basis of HREIMS

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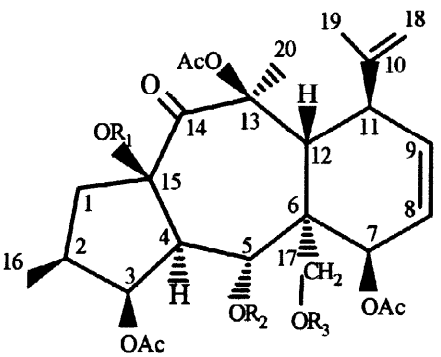
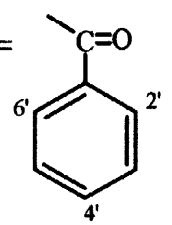
(obsd. 654.2698). Its IR spectra showed characteristic peaks for carbonyl groups at 1700-1730 cm^{-1} and at 1580, 1600 and 710 cm^{-1} for a benzene ring. A sharp peak at 3500 cm^{-1} indicated a non-hydrogen-bonded hydroxyl group in the molecule. In the EIMS spectrum the ions at *m/z*= 594, 534, 474 and 414 indicated the presence of acetate groups which were eliminated from the molecular ion at *m/z*= 654 in the form of acetic acid.

The base peak at *m/z*= 105 (C_6H_5CO), and others at 121 (C_6H_5COO) and 533 (M^+-121) indicated the presence of a benzoate ester group in the molecule.



Compound	R_1	R_2	R_3
1	H	Bz	Ac
2	Ac	Bz	H
3	H	Bu	Ac

Bz = 

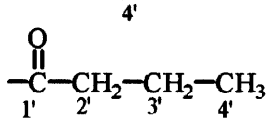
Bu = 

Figure 1. The structure of compounds **1**, **2** and **3** isolated from *Euphorbia decipiens*.

The ^1H NMR of **1** in $CDCl_3$, (Table-1) showed four singlets for acetate methyl groups at δ 2.12, 2.07, 1.94 and 1.73. The high field shift of the last peak may be due to anisotropic effect which has been observed earlier also by other authors e.g. in euphoscopin B,[7] and 7-hydroxy-lathyrol.[8] There were three signals due to protons geminal to ester groups which were observed as a doublet at δ 6.38 (d, *J*=11.5 Hz, H-5), a multiplet at δ 4.87 (H-7, overlapped with 2xH-18 signal) and a triplet at δ 5.3 (t, *J*=3.5 Hz, H-3).

The spectrum also showed three methyl signals in the molecule which comprised of a secondary methyl at δ 0.89 (d, *J*=6.7 Hz, 3xH-16), one olefinic methyl at δ 1.77 (s, 3xH-19) and one tertiary methyl at δ 1.67 (s, 3xH-20) which seems to be geminal to an oxygen bearing group. This last chemical shift is quite near to that observed for the corresponding methyl (Me-20) in the ^1H NMR spectrum of myrsinol esters at δ 1.58.[6]

The vicinal olefinic protons showing signals at δ 5.72 (dd, *J*=4.5, 9.5 Hz, H-9) and at δ 5.96 (ddd,

J=2.0, 6.5, 9.5 Hz, H-8) are separated by a methine proton at δ 3.28 (br ddd, J=2.0, 4.5, 8.0 Hz, H-11) from the terminal olefinic protons at δ 4.87 in an isopropenyl group, H-18. The downfield chemical shift of H-11 can be considered as a consequence of its location between the two double bonds.[6] H-11 was also coupled with an unusually downfield proton at δ 4.07 (J=8.0 Hz, H-12) which seems to be located in anisotropic field of carbonyl esters or lone pair electron of the free hydroxyl group.[7,9]

A couple of doublets at δ 3.97 (d, J=12.0 Hz) and 4.34 (d, J=12.0 Hz) are also observed in the ^{1}H NMR of compound **1** which represent an oxymethylene group in this molecule, H-17 and H-17'. Besides the ^{1}H-^{1}H COSY for deducing the correlation between protons, we have also examined the vicinal relationships, which were not very clear in ^{1}H NMR because of overlapping of the different protons, by spin decoupling experiment.

Irradiation of the multiplet at δ 2.1 (H-2) collapsed the signals of δ 0.89 (d, J=6.7 Hz, H-16), δ 3.15 (dd, J=9.5, 14.5 Hz, H-1α) and δ 5.3 (t, J=3.5 Hz, H-3) to a singlet and two doublets respectively, on the other hand irradiation at 4.87 changed the proton at δ 5.96 (ddd, J=2.0, 6.5, 9.5 Hz, H-8) to a doublet of doublets indicating the overlapping of H-7, with the olefinic proton, 2xH-18. Irradiation at δ 4.07 collapsed H-11 to a broad doublet indicating the vicinal coupling of H-11 and H-12.

The ^{13}C NMR (BB and DEPT) of **1** showed 33 signals due to 35 carbons including seven CH_3, three CH_2, twelve CH and eleven quaternary carbons of which eight were oxygen bearing (one tertiary alcohol, one tertiary ester, one ketone and five ester carbonyls).

The correlation of protons with the corresponding carbons have been established by HMQC experiments. The location of acetate and benzoate groups were deduced by observing the cross peaks between corresponding protons and carbonyl carbons of ester groups in HMBC, which was in the case of benzoyl carbonyl carbon at δ 165.1 with H-5 and for other acetate groups at about δ 170 and H-3, H-7 and H-17 (Table 1).

With the aid of the above mentioned NMR experiments two partial structures A and B were suggested for this molecule which were connected through fragment C to produce structure E (Fig. 2).

According to the molecular formula $C_{35}H_{42}O_{12}$, **1** contains fifteen degrees of unsaturation. Out of these, twelve are accounted for by the double bond (two), acetyl groups (four), benzoyl group (five) and a ketone (one) group. **1** therefore contains three rings, one of these is six membered as suggested above (Fig. 2). The very close chemical shifts of C-13 (δ 86.5) and C-15 (δ 86.6) indicate that they are part of a seven-membered ring separated by a carbonyl group at C-14. The H-1α signal of **1** (δ 3.15) is shifted downfield due to the anisotropic effect of the carbonyl group at C-14. Such downfield shifts have been observed in other similar compounds e.g. 7-hydroxy-lathyrol,[8] myrsinol esters,[6,10] and esulatins A-C.[11] The chemical shifts of the protons in the ^{1}H NMR spectrum of 7-hydroxy-lathyrol (**4**) (Fig. 3),[8] at positions H-3, H-4 and Me-16 were in a good agreement with the corresponding signals in the ^{1}H NMR spectra of **1**

Table 1. Spectral data of Compound 1*

H	^{1}H	^{13}C	HMBC
1α	3.15 (dd, J=14.5, 9.5 Hz)	45.2 (t)	C-2, C-3, C-4, C-14, C-15
1β	1.60 (dd, J=14.5, 11.5 Hz)		
2	2.10 (m)	37.7 (d)	
3	5.30 (t, J=3.5 Hz)	79.4 (d)	O*C*OCH$_3$, C-1, C-15
4	2.36 (dd, J=11.5, 3.5 Hz)	53.6 (d)	C-5, C-6, C-14
5	6.38 (d, J=11.5 Hz)	70.8 (d)	O*C*OPh, C-4, C-6, C-7, C-17
6	-	48.3 (s)	
7	4.87 (m)	67.9 (d)	O*C*OCH$_3$, C-5, C-6, C-8, C-9
8	5.96 (ddd, J=2.0, 6.5, 9.5 Hz)	122.2 (d)	C-6, C-7, C-9, C-11
9	5.72 (dd, J=4.5, 9.5 Hz)	136.0 (d)	C-7, C-11, C-12
10	-	147.1 (s)	
11	3.28 (ddd, J=2.0, 4.5, 8.0 Hz)	45.9 (d)	C-6, C-8, C-9, C-10, C-12, C-13, C-18, C-19
12	4.07 (d, J=8.0 Hz)	41.3 (d)	C-5, C-6, C-10, C-11, C-13, C-17
13[a]	-	86.5 (s)	
14	-	205.6 (s)	
15[a]	-	86.6 (s)	
16	0.89 (d, J=6.7 Hz)	14.3 (q)	C-1, C-2, C-3
17	3.97 (d, J=12.0 Hz)	62.3 (t)	O*C*OCH$_3$, C-5, C-6, C-7, C-12
17'	4.34 (d, J=12.0 Hz)		O*C*OCH$_3$, C-5, C-6, C-7
18	4.87 (m, 2H)	113.1 (t)	C-9, C-10, C-11, C-19
19	1.77 (s)	20.0 (q)	C-10, C-11, C-18
20	1.67 (s)	23.3 (q)	C-12, C-13, C-14

$OCOCH_3$[b]	1.73 (s)	20.7 (q)
	1.94 (s)	20.8 (q)
	2.07 (s)	20.9 (q)
	2.12 (s)	21.0 (q)
$OCOCH_3$	-	169.8 (s)
	-	169.9 (s)
	-	170.3 (s)
	-	170.7 (s)
O-B_z		
1'	-	129.9 (s)
2',6'	7.87 (br. dd, J=1.5, 10.0 Hz)	129.7 (d)
3',5'	7.37 (br. t, J=8.0 Hz)	128.3 (d)
4'	7.50 (tt, J=1.0, 8.5 Hz)	133.1 (d)
7'	-	165.1 (s)
OH	4.12 (s)	-

*The ^1H - ^{13}C connectivities were deduced from HMQC; [a,b] The assignments may be interchanged.

(Table 1). Also the ^1H and ^{13}C NMR data recorded for the esters of myrsinols (**5-8**) (Fig. 3),[6,10] the diterpenes isolated from *E. myrsinites* were found to be similar to those recorded for **1**, therefore, the carbon skeleton of **1** was considered as a tricyclic lathyrane skeleton (Fig. 1). Both HMBC and HOHAHA (Fig. 4) experiments confirmed this structure.

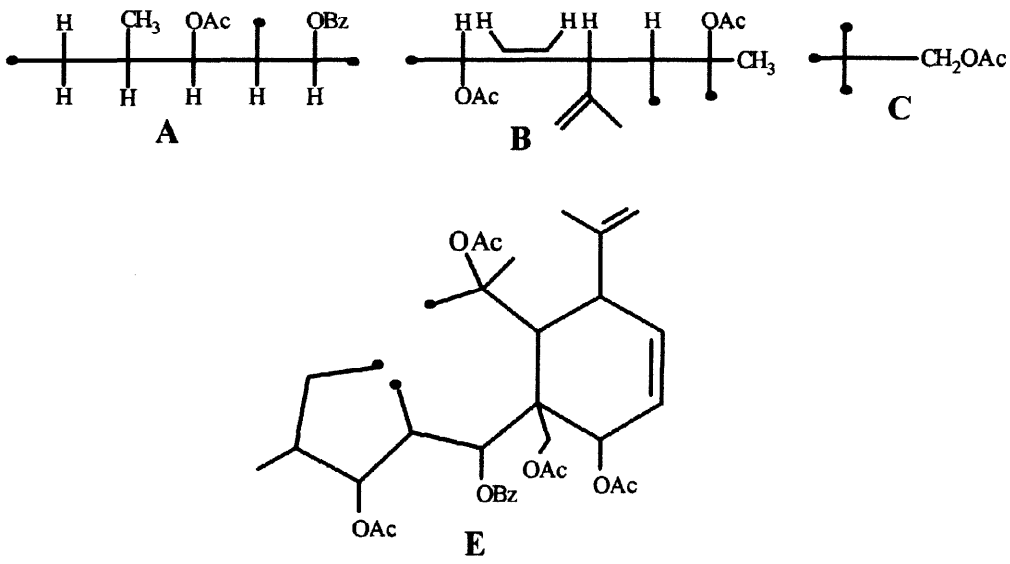
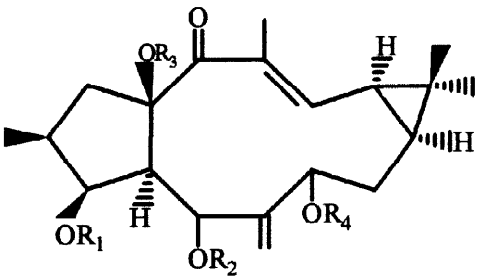
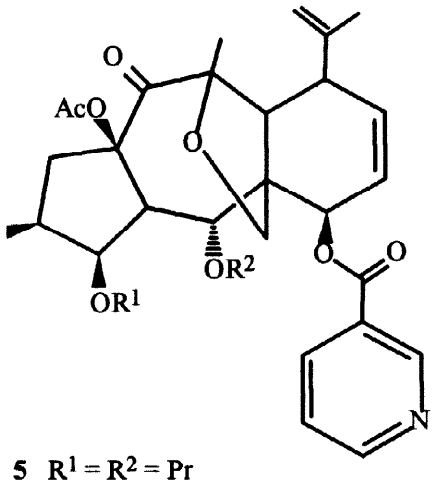


Figure 2. Partial structures suggested by different NMR spectrosocpy techniques for **1**.



4 R_1–R_4 = 2 $COCH_3$, 2 COC_6H_5

Figure 3. 7-hydroxy-lathyrol,**4**,[9] and the myrsinol esters **5-8**.[6]



5 $R^1 = R^2 = Pr$
6 $R^1 = Pr$, $R^2 = Bu$
7 $R^1 = Bu$, $R^2 = Pr$
8 $R^1 = R^2 = Bu$

Pr = Propionyl
Bu = Butanoyl

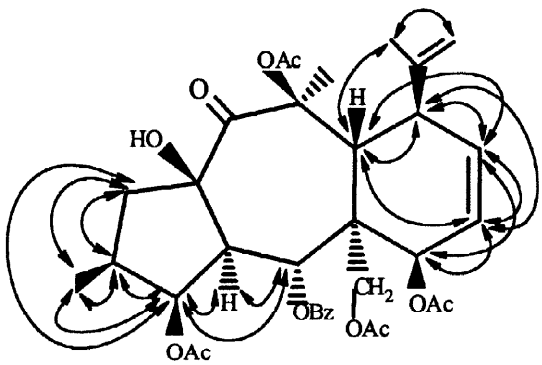


Figure 4. Long-range ^1H - ^1H correlation, HOHAHA for **1**.

To determine the relative stereochemistry at positions 3, 4, 5, 11 and 12 the coupling constants were examined. In the ^1H NMR spectrum, the J value 8.0 Hz for H-12 indicated the trans relationship between H-12 and H-11. The doublet at δ 6.38 with a J value of 11.5 Hz for H-5 and a doublet of doublets at δ 2.36 (J=3.5, 11.5 Hz, H-4) showed that these two protons are again in an anti orientation to each other and a triplet at δ 5.3 (J=3.5 Hz, H-3) confirmed that this proton must be in a similar position with the same dihedral angle to H-2 and H-4, which is consistant with the stereochemistry shown in Fig. 1.

In the NOESY spectrum some cross peaks between δ 4.87 (H-7, H-18) with δ 4.07 (H-12) and δ 3.28 (H-11) were detected, through which we concluded that H-7 and H-11 must be in one face of the molecule and H-12 and H-18 in another. On the other hand, in NOE difference spectroscopy irradiation of Me-20 afforded NOEs at H-1α (4.6%), H-11 (7.3%), H-17 (2%) and H-17' (4.1%) also irradiation of H-12 and hydroxy proton at C-15 gave significant enhancement at H-5 which led us to consider the

stereostructure of **1** as it is shown in Fig. 1.

In order to firmly establish the structure of the molecule, we examined the molecule by X-ray crystallography which confirmed the structure of **1** as a tricyclic diterpene skeleton. The crystal structure of **1** is shown in Fig. 5; absolute configuration of **1** could not be established due to the poor quality of crystals.

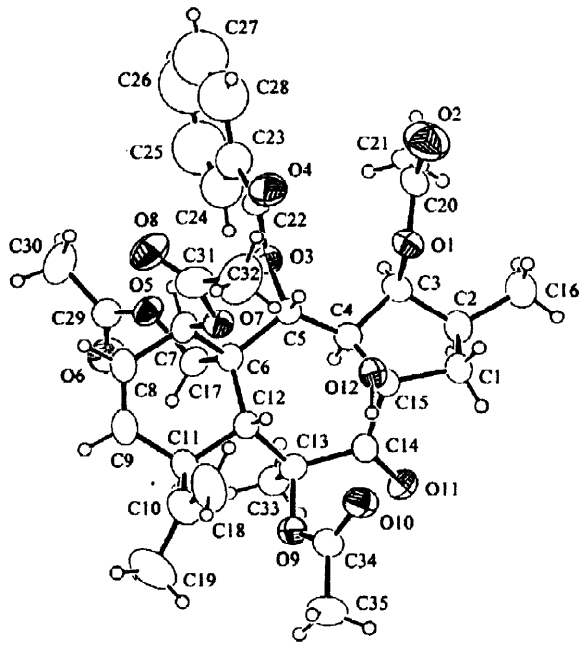


Figure 5. The crystal structure of decipinone (**1**).

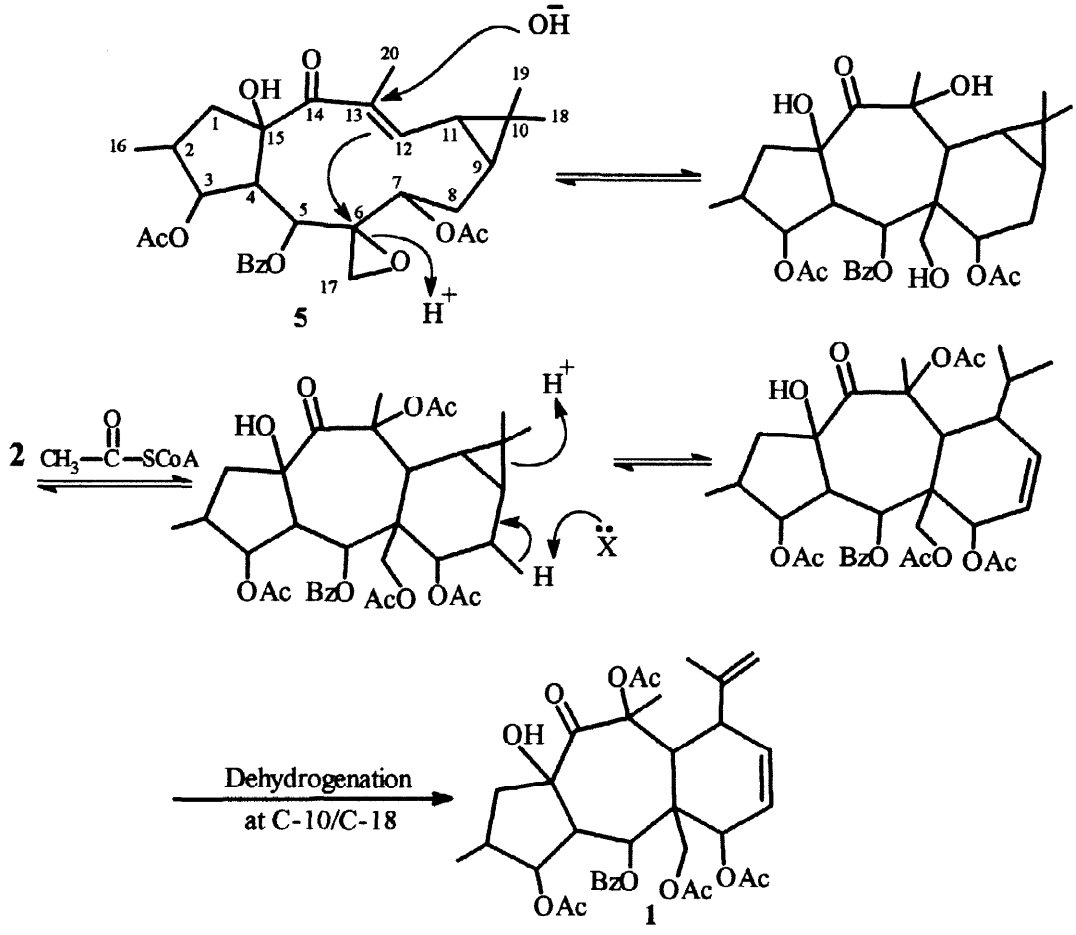
According to Scheme-1, it is suggested that the carbon skeleton of decipinone, **1**, can be produced from a 6,20-epoxy-lathyrol derivative, **5**.[12] Ring closure at position C–6 / C–12 followed by ring opening in cyclopropane between C-9 / C-10 also acetylation of produced hydroxyl groups and finally dehydrogenation at C_{10} / C_{18} , produced the desired structure, **1**.

For **2** which can be an intramolecular transesterification product of **1** similar spectra MS, IR, ^{1}H NMR were observed, but in ^{1}H NMR there were some changes which included the upfield shift of H-12 at δ 3.54 (d, J=8.1 Hz) and conversion of H-17, 17' to AB signals at δ 4.09 (d, J=12.0 Hz) and 4.16 (d, J=12.0 Hz) which indicated a migration of an acetyl group from C-17 to free hydroxyl group at C-15, also the broadening of the hydroxyl peak at 3480 cm^{-1} in the IR spectrum of **2** indicated the change of the position of hydroxyl group in this molecule in comparison to **1**.

The molecular formula $C_{32}H_{44}O_{12}$ was obtained for **3** by using HREIMS (obsd. 620.2789). It's IR spectrum is very similar to that recorded for **1** but in this compound there was no indication of benzene ring signals. The absorbtion at λ_{max} (MeOH) 270 nm in the UV spectra of **1**, was not observed in the UV spectrum of this compound.

In the EIMS of **3** the base peak at *m/z* 71 indicated the presence of a C_3H_7CO fragment instead of

benzoyl group in **1**. The ^{1}H- and ^{13}C NMR spectra (see Experimental) of this compound were very similar to those recorded for **1** with the exception of some differences in chemical shifts and also the peaks relating to benzoyl and butanoyl moiety. Instead of phenyl ring signals, we observed a triplet at δ 0.91 (t, J=7.4 Hz, 3xH-4') and signals for H-3' and H-2' which were overlapped with peaks at about δ 1.5 and δ 2.1 in the ^{1}H NMR spectrum of **3**. Their corresponding peaks in ^{13}C NMR (DEPT) at δ 13.7 q, 17.9 t and 36.0 t according to HMQC data together with the cross peaks between H-5 and H-2' with the butanoyl carbonyl carbon at δ 171.8in HMBC suggested a butanoate ester at position 5.



Scheme 1. Proposed biogenesis for synthesis of decipinone (**1**), from a 6,20-epoxy-lathyrol derivative precursor, **5**.

In view of the very similar ^{1}H and ^{13}C NMR data and with the help of other spectroscopic techniques we determined **3** as a *n*-butanoate ester instead of benzoate of **1**.

EXPERIMENTAL

General. Melting points are uncorrected. Mass spectra were recorded on a Finnigan MAT-312 double focusing mass spectrometer. The NMR spectra were recorded in $CDCl_3$ on Bruker AM-400 and

AM-500 NMR Spectrometers with TMS as internal standard. The IR spectra were recorded on a Shimadzu IR-460 spectrophotometer. The UV spectra were recorded on a Hitachi U-3200 instrument and the purity of the samples were checked by TLC on silica gel 60 F_{254} precoated plates, detection under UV light and then by spraying with cerium IV sulfate/H_2SO_4 at 110°C.

Plant Material. Euphorbia decipiens Boiss. & Buhse was collected in July, 1995 from the mountain Kandovan, North of Karaj, Tehran, Iran and identified by Dr. Fereydoon Terme, Center for Plant Research Eveen, Tehran, Iran.

Extraction and Isolation. Air dried whole plant material (2 kg) was powdered and soaked in MeOH:$CHCl_3$ (1:1) at room temperature for 24 hrs. The extract was concentrated under reduced pressure, dissolved in a small amount of methanol and, after keeping in a freezer overnight, was filtered to remove long chain hydrocarbons. The extract, after concentration, (20 g) was chromatographed over a silica gel column (400 g) using hexane with a gradient of chloroform upto 100% and then followed by methanol. The chloroform rich fractions were then subjected to repeated column chromatography (Flash silica gel) and PTLC (silica gel 60 GF_{254}) using EtOAc-hexane (25:75) and $CHCl_3$-Me_2CO (98:2) as eluent and mobile phase respectively for purification of **1**, **2** and **3**.

Compound **1**. ^1H NMR and ^{13}C NMR data see Table-1; m.p. 246-249°C; $[\alpha]_D^{27}$= -21.3 ($CHCl_3$, c 0.19). IR λ_{max} (KBr) cm^{-1} : 3500, 2950, 2910, 1740, 1720, 1630, 1600, 1450, 1230, 1020, 710, 600; UV λ_{max} (MeOH) nm: 198.4, 227.2, 270.8; HREIMS *m/z* : 654.2698 (calcd. 654.2676), $C_{35}H_{42}O_{12}$; EIMS *m/z* (rel.int.) : 654 [M^+] (1), 594 (1), 534 (1.2), 536 (0.5), 474 (1), 414 (1), 384 (12), 324 (12), 282 (26), 264 (57), 251 (24), 239 (27), 237 (27), 207 (38), 158 (71), 175 (48), 156 (56), 131 (52), 125 (47), 121 (12), 105 (100), 83 (73), 85 (65), 77 (23).

Compound **2**. IR λ_{max} (KBr) cm^{-1} : 3480, 2920, 1740, 1720, 1630, 1600, 1450, 1370, 1270, 1230, 1020, 710, 600; EIMS m/z (rel.int.) : 654 [M^+] (1), $C_{35}H_{42}O_{12}$, 434 (1), 433 (5), 269 (6), 237 (12), 173 (9), 157 (7), 131 (12), 105 (100), 76 (13), ^1H NMR, 400 MHz, (in $CDCl_3$) δ : 1.79 (dd, *J*=10.4, 14.9 Hz, H-1β), 3.34 (dd, *J*=8.8, 14.9 Hz, H-1α), 2.1 (m, H-2), 5.28 (t, *J*=3.5 Hz, H-3), 2.61 (dd, *J*=3.4, 11.6 Hz, H-4), 6.41 (d, *J*=11.6 Hz, H-5), 4.67 (d, *J*=6.4 Hz, H-7), 5.99 (ddd, *J*=2.0, 6.4, 9.5 Hz, H-8), 5.74 (dd, *J*=4.3, 9.5 Hz, H-9), 3.47 (br. d, H-11), 3.54 (d, *J*=8.1 Hz, H-12), 0.88 (d, *J*=6.7 Hz, 3xH-16), 4.09 (d, *J*=12.0 Hz, H-17), 4.16 (d, *J*=12.0 Hz, H-17'), 4.87 (br. s, 2xH-18), 1.89, 1.80 (s, 3xH-19 + OCOC*H*$_3$), 1.61 (s, 3xH-20), 2.20, 2.15, 2.05 (s, 3xOCOC*H*$_3$), 4.97 (s, O*H*), 7.39 (br. t, H-3', H-5'), 7.52 (br. tt, H-4'), 7.86 (br. dd, H-2', H-6'), 7.52 (br. tt, H-4'); ^{13}C NMR (in $CDCl_3$) : δ 200.2, 170.3, 170.0, 169.5, 169.0, 165.0, 133.9, 129.6, 129.4, 129.3, 128.4, 126.6, 112.5, 88.6, 85.6, 80.6, 68.6, 67.8, 61.0, 51.5, 50.7, 44.1, 43.5, 42.0, 35.6, 25.9, 21.5, 21.3, 21.1, 20.8, 20.6, 14.5.

Compound **3**. m.p. 186-188°C; IR λ_{max} (KBr) cm^{-1}; 3500, 2980, 2950, 1730, 1450, 1370, 1250, 1170, 1140, 1020, 750, 620; UV λ_{max} (MeOH) nm : 198.5; HREIMS *m/z* 620.2789 (calcd. 620.2833), $C_{32}H_{44}O_{12}$; EIMS *m/z* (rel.int.) : 620 [M^+] (1), 560 (1), 500 (1), 384 (3), 282 (13), 264 (27), 239 (11), 228 (8), 185 (18), 175 (22), 158 (40), 156 (37), 132 (20), 131 (40), 125 (46), 71 (100), 69 (17), 60 (23); ^{1}H NMR, 400 MHz (in $CDCl_3$) δ : 1.55 (m, H-1β), 3.15 (dd, *J*=9.5, 14.5 Hz, H-1α), 2.10 (m, H-2), 5.26 (t, *J*=3.4 Hz, H-3), 2.30 (dd, *J*=3.4, 11.7 Hz, H-4), 6.07 (d, *J*=11.7 Hz, H-5), 4.80 (d, *J*=6.4 Hz, H-7), 5.99 (ddd, *J*=1.9, 6.4, 9.6 Hz, H-8), 5.75 (dd, *J*=4.6, 9.6 Hz, H-9), 3.32 (br. t, *J*=6.0 Hz, H-11), 3.88 (d, *J*=8.0 Hz, H-12), 0.92 (d, *J*=6.7 Hz, 3xH-16), 3.90 (d, *J*=12.0 Hz, H-17), 4.21 (d, *J*=12.0 Hz, H-17'), 4.86 (br. s, H-18), 4.87 (br. s, H-18'), 1.76 (s, 3H-19), 1.64 (s, 3xH-20), 1.93, 2.01, 2.03, 2.09 (s, 4xOCOC*H*$_3$), 3.82 (s, OH), 0.91 (t, *J*=7.4 Hz, 3xH-4'), 1.50 (m, 2xH-3'), 2.10 (m, 2xH-2'); ^{13}C NMR (in $CDCl_3$) δ : 45.8 (C-1), 37.6 (C-2), 79.6 (C-3), 54.1 (C-4), 70.1 (C-5), 48.1 (C-6), 67.8 (C-7), 122.1 (C-8), 136.5 (C-9), 147.0 (C-10), 45.9 (C-11), 41.8 (C-12), 86.8, 86.9 (C-13, C-15), 205.9 (C-14), 14.4 (C-16), 61.8 (C-17), 113.0 (C-18), 19.7 (C-19), 22.6 (C-20), 171.8, ($OCOC_3H_7$), 170.3, 170.1, 2x169.9 (4xO*C*OCH$_3$), 21.1, 21.0, 20.9, 20.7 (4xOCOC*H*$_3$), 36.0 (C-2'), 17.9 (C-3'), 13.7 (C-4').

X-Ray Structure Analysis of (1) :

Crystal Data : $C_{35}H_{42}O_{12}$, F.W.=654.69, orthorhombic, space group $P2_12_12$ (#18), lattice parameters : a=15.574(3), b=19.620(4), c=11.314(2) Å, V=3457.1(11) $Å^3$; D_{calc}=1.258 g cm^{-3}, Z=4, λ (Cu Kα)=1.5418 Å, μ=0.789 mm^{-1}, F(000)=1392, T=295(1) K.

Data Collection : Colourless plate-like crystals of **1** having approximate dimensions of 0.60 x 0.50 x 0.04 mm, were grown from methanol and mounted on a glass fiber. All measurements were made on an Enraf Nonius CAD-4 diffractometer with Cu-Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20.0 < \theta < 30.0^\circ$ corresponded to a primitive orthorhombic cell. Based on the systematic absences of : h00, h=2n+1, the space group was uniquely determined to be : $P2_12_12$ (#18). The data were collected at a temperature of 295(1) K using the ω-2θ scan technique to a maximum 2θ value of 60.0° with indices : h=0 to 17, k=-21 to 22 and l=0 to 12; Friedel pairs were not merged.

Data Reduction : Of the 5619 reflections which were collected, 5134 were unique (Rint=0.047). The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards did not show any sign of decay. The linear absorption coefficient, μ, for Cu-Kα radiation is 0.79 mm^{-1} which is sufficiently small, therefore, absorption correction was deemed unnecessary. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement : The structure was solved by direct methods,[13] and expanded using Fourier techniques.[14] The non-hydrogen atoms except phenyl C-atoms were refined anisotropically. The phenyl ring was disordered and its atoms were refined as constrained hexagons over two sites with partial occupancies and isotropic temperature factors. Hydrogen atoms were included at geometrically idealized positions with C-H and O-H 0.95 Å and were not refined. The final cycle of full-matrix least-squares refinement using F^2 was based on 4257 observed reflections ($I>2.0\sigma$ (I)) and 379 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors : R=0.076 (R=0.096 for all data) and wR=0.202, respectively, and goodness of fit, S=1.119. The weighting scheme was based on counting statistics. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.30 and -0.34 e^- $Å^{-3}$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in Fcalc,[16] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[17] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[18] All calculations for data reduction were performed using the TEXSAN,[19] crystallographic software package of Molecular Structure Corporation and the refinement was carried out with the aid of SHELX93.[20] The absolute configuration could not be established by Flack[21] method; the Flack parameter was 0.3(4). A full details on the XRD analysis of **1** have been submitted as supplementary material.

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