Eight New Diterpenoids from *Euphorbia decipiens*

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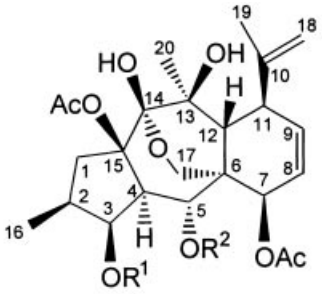
A reinvestigation of *Euphorbia decipiens* with a modified extraction procedure resulted in the isolation and structure elucidation of eight new myrsinane-type diterpene esters (see **3**–**10**). Moreover, revised structures are proposed for decipinone B (**1**) and C (**2**) on the basis of X-ray-diffraction analyses. The structures of the compounds were elucidated by means of different spectroscopic methods, including 1D- and 2D-NMR studies.

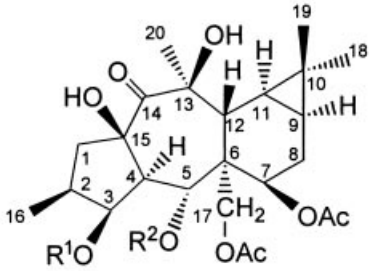
1. Introduction. – Our group has investigated *Euphorbia decipiens* BOISS. et BUHSE previously, and eight new diterpene esters were isolated from it [1–3]. To obtain the minor compounds, the plant was again collected and extracted with acetone [4]. The $CHCl_3$-soluble fraction of the concentrated extract was subjected to different chromatographic procedures to purify compounds **1**–**10** (see *Exper. Part*). Besides the previously isolated compounds, eight new diterpene esters, *i.e.* **3**–**10**, were isolated and their structures elucidated. The fine crystals of compounds **1** and **2** prompted us to subject them to single-crystal X-ray analysis, which resulted in the revised structures for decipinone B and C [3].

2. Results and Discussion. – Decipinone B (**1**) and C(**2**) were purified as described in our previous paper [3] and crystallized from MeOH. The crystals were then subjected to X-ray analysis and 1D and 2D NMR in $CDCl_3$ and also in CD_3OD for **1** [3]. The MS, IR, UV, and ^{1}H-NMR data of **1** were the same as described. The molecular formula $C_{30}H_{42}O_{11}$ was assigned for **2** on the basis of EI-MS (*m*/*z* 578 (M^+)). The ions at *m*/*z* 560 ($[M-H_2O]^+$), 518 ($[M-AcOH]^+$), 490 ($[M-C_3H_7CO_2H]^+$), 458 ($[M-2\ AcOH)]^+$), and 71 ($C_3H_7CO^+$) indicate the presence of OH, acetate, and butanoate moieties in the molecule. In our previous paper [3], the structures of decipinones B and C were derived from NMR studies, and we assumed that the IR absorption of the keto group at C(14)[1]) was masked by the strong absorption of the ester groups, and that this group was also not detected in the ^{13}C-NMR spectrum due to low concentration. However, the structure of decipinones B and C are now revised to **1** and **2**, respectively, on the basis of the results of their X-ray diffraction analyses (*Figs. 1* and *2*).

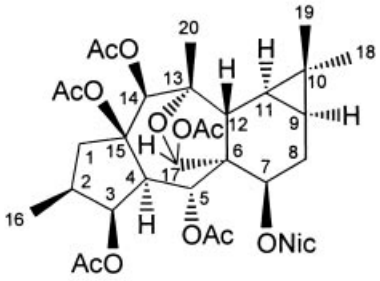
[1]) Arbitrary numbering; for systematic names, see *Exper. Part.*



	R^1	R^2
1	Ac	Bz
2	Ac	Bu
3	Bu	Nic



	R^1	R^2
4	Ac	Bz
5	Ac	Bu



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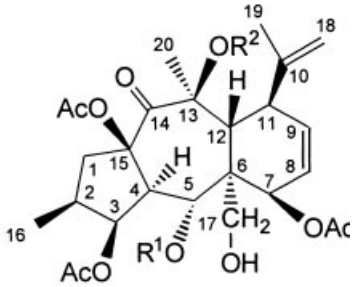
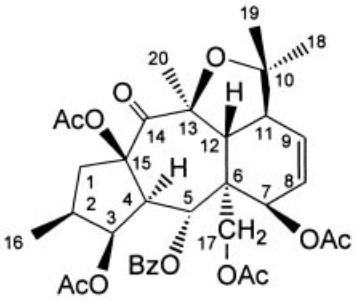


	R^1	R^2
7	Bu	H
8	Bz	H
9	Bu	Ac



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Three *s* at δ 77.8 (C(13)), 100.1 (C(14)), and 98.0 (C(15)) (in CD_3OD) for **1**, and at δ 77.6 (C(13)), 98.6 (C(14)), and 96.8 (C(15)) (in $CDCl_3$) for **1** or **2** clearly confirm the presence of an $H'-$C(17) O-bearing non-carbonyl C-atom C(14)[1]. The cross-peaks $H-$C(12)/C(13), $H'-$C(17)/C(14) and CH_3(20)/C(14) are compatible with the hemiacetal functionality in the HMBC spectrum of **1** (in CD_3OD).

Decipinol ester A (**3**) exhibits a molecular ion at *m/z* 641 in the EI-MS and 642 ($[M+1]^+$) in the CI-MS, consistent with the formula $C_{34}H_{43}NO_{11}$. Besides the ^{1}H- and ^{13}C-NMR spectral data, UV absorptions at 263, 217, and 204 nm confirm the presence of a nicotinic acid ester in the molecule [3]. The IR spectrum shows absorptions at 3480 (OH), 1710, 1725, and 1740 (C=O, esters), and 1640 and 1580 (unsaturation) cm^{-1}. The MS peaks at *m/z* 106 ($C_5H_4NCO^+$) and 124 ($[C_5H_4NCO_2H+H]^+$) in the EI-MS confirm the presence of a nicotinoyl moiety. From the ^{1}H-NMR spectrum of **3**, the pattern of a myrsinane-type skeleton can be deduced.

The ^{1}H-NMR signals of **3** at δ 5.54 (*t*, *J* = 6.5 Hz), 5.53 (*d*, *J* = 10.5 Hz), and 4.48 (*d*, *J* = 6.2 Hz) are typical for the O-bearing methine groups CH(3), CH(5), and CH(7), respectively, and the *AB* pattern at δ 3.95 ('*d*', *J* = 11.4 Hz) and 3.70 ('*dd*', *J* = 11.4, 1.0 Hz) for the OCH_2 group of the myrsinane skeleton (*Table 1*). $H_\alpha-$C(1) (δ 2.44) and H–C(12) (δ 2.93) of **3** appear upfield compared to the corresponding signals of decipinone and myrsinane diterpenoids [1–3][5], which is due to the lack of the keto group at C(14). The C(14)=O and OH–C(17) of the myrsinane skeleton form a hemiacetal function in **3**, exhibiting C(14) at δ 98.6 (*s*) (*Table 2*). The other difference with myrsinane ester is seen in the H–C(8) and H–C(9) signals, which are a couple of unresolved *t*s in **3**. These signals are resolved in the case of **1** when the ^{1}H-NMR is recorded in CD_3OD. The signals at δ 171.4 (*s*, C(1′)), 35.9 (*t*, C(2′)), 18.3 (*t*, C(3′)), and 13.7 (*q*, C(4′)) in the ^{13}C-NMR of **3** and a *t* at δ 0.88 (7.4 Hz) in the ^{1}H-NMR spectrum suggested the presence of a butanoyl group. In the ^{1}H-NMR spectrum (*Table 1*), the characteristic downfield signals of H–C(2″), H–C(4″), H–C(5″), and H–C(6″) establish a nicotinic acid ester in the molecule. The relative positions of the ester groups are deduced from the HMBC and NOESY experiments. Two signals of the protons, geminal to the butanoyl and nicotinoyl groups, are close to each other (H–C(3) and H–C(5)) and resolved by 2D *J*-resolved NMR, so the cross-peaks between $H-$C(3)/C(1′) and $H-$C(5)/C(7″) in the HMBC are not distinguishable. A cross-peak between $H-$C(7)/$COCH_3$ establishes the position of the acetate at C(7). In the NOESY spectrum, the cross-peak between H–C(2″), H–C(17), and H′–C(17′) confirms the position of the nicotinate at C(5).

Kandovanol ester A (**4**) with alcohol functionalities was a colorless oil. The molecular ion at *m/z* 617 in the CI-MS establishes the formula $C_{33}H_{44}O_{11}$. IR Absorptions at 3450, 1740, 1723, and 1650 cm^{-1} and UV maxima at 270.8, 228.2, and 198.6 nm suggest the presence of OH and carbonyl groups and of unsaturation. In the ^{1}H and ^{13}C-NMR spectra (*Tables 1* and *2*), the characteristic signals establish a myrsinane-type diterpene skeleton [1–3][5–10], and the NOESY data confirm the proposed configuration of **4**.

The presence of two upfield-shifted ^{1}H-NMR signals at δ 0.82 (*ddd*, *J* = 3.1, 9.2, 9.2 Hz, H–C(9)), 0.90 (*dd*, *J* = 7.7, 9.3 Hz, H–C(11)) and three ^{13}C-NMR signals at δ 20.1 (*d*, C(9)), 19.3 (*s*, C(10)), and 22.8 (*d*, C(11)) suggest that **4** contains a cyclopropane ring of an aleppicatine or euphoppin skeleton [6][7]. The relative positions of the ester groups are determined by the HMBC data, *i.e.* by the cross-peaks between the $H-$C(3), $H-$C(7), $H-$C(17), and $H'-$C(17) signals and the carbonyl signals of the acetates at δ *ca.* 170. A relatively upfield carbonyl signal at δ 164.9 and its connectivity with $H-$C(5)) (δ 5.99) in the HMBC plot confirm the position of the benzoate moiety. The two quaternary signals at δ 79.6 and 84.3 are assigned to C(13) and C(15), respectively, by comparison with the data of decipinone [1] and confirmed by a HMBC interaction between $H-$C(12)) (δ 2.24)/C(13) (δ 79.6). The NOESY experiment as well as the coupling constants in the ^{1}H-NMR spectrum determine the relative configuration of **4**. The cross-peaks H–C(12)/Me(19), H–C(12)/H–C(5), Me(20)/Me(18), Me(20)/H–C(4) in the NOESY spectrum, together with a relatively large coupling constant of 7.6 Hz between H–C(11)/H–C(12), confirm the presented configuration of **4**.

Table 1. *^{1}H-NMR Data of Compounds* **3**–**10**[1] *in $CDCl_3$. J* in Hz.

	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
H_α–C(1)	2.44 (*dd*, *J* = 10.8, 14.8)	2.70 (*dd*, *J* = 10.9, 14.8)	2.60 (*dd*, *J* = 10.9, 14.9)	2.72 (*dd*, *J* = 9.8, 16.1)	3.30 (*dd*, *J* = 10.4, 14.8)	3.30 (*dd*, *J* = 10.4, 14.6)	3.34 (*dd*, *J* = 8.8, 14.9)	2.97 (*dd*, *J* = 9.2, 14.5)
H_β–C(1)	2.53 (br. *d*, *J* = 14.4)	1.76 (*dd*, *J* = 6.9, 14.9)	1.81 (*dd*, *J* = 7.3, 14.1)	2.40 (*dd*, *J* = 9.6, 16.1)	1.56 (*dd*, *J* = 6.8, 14.8)	1.58 (*dd*, *J* = 9.6, 15.0)	1.70 (*dd*, *J* = 6.9, 14.9)	1.70 (*dd*, *J* = 9.2, 14.5)
H–C(2)	2.73 (*m*)	2.40 (*m*)	2.35 (*m*)	2.10 (*m*)	2.10 (*m*)	2.10 (*m*)	2.10 (*m*)	2.16 (*m*)
H–C(3)	5.54 (*t*, *J* = 6.5)	5.52 (*t*, *J* = 4.7)	5.48 (*t*, *J* = 4.4)	5.00 (*t*, *J* = 3.9)	5.23 (*t*, *J* = 3.4)	5.23 (*t*, *J* = 3.4)	5.25 (*t*, *J* = 3.6)	5.49 (*t*, *J* = 4.5)
H–C(4)	2.73 (*dd*, *J* = 5.1, 10.5)	2.93 (*dd*, *J* = 4.3, 10.5)	2.93 (*dd*, *J* = 4.0, 10.5)	2.99 (*dd*, *J* = 3.6, 10.7)	2.40 (*dd*, *J* = 3.2, 11.7)	2.45 (*dd*, *J* = 3.1, 11.6)	2.53 (*dd*, *J* = 3.2, 11.6)	2.90 (*dd*, *J* = 4.4, 11.0)
H–C(5)	5.53 (*d*, *J* = 10.5)	5.99 (*d*, *J* = 10.5)	5.72 (*d*, *J* = 10.5)	5.80 (*d*, *J* = 10.7)	5.91 (*d*, *J* = 11.7)	6.18 (*d*, *J* = 11.6)	6.14 (*d*, *J* = 11.6)	6.46 (*d*, *J* = 11.0)
H–C(7)	4.48 (*d*, *J* = 6.2)	4.83 (*dd*, *J* = 3.3, 6.3)	4.77 (*dd*, *J* = 1.6, 7.1)	5.32 (*dd*, *J* = 3.7, 6.3)	4.77 (*d*, *J* = 6.4)	4.80 (*d*, *J* = 6.4)	4.59 (*d*, *J* = 6.4)	5.14 (*d*, *J* = 5.3)
H–C(8) or CH_2(8)	6.26 (br. *t*, *J* = 6.5)	1.62 (*ddd*, *J* = 3.2, 3.2, 6.3) 2.10 (*m*)	1.63 (*ddd*, *J* = 1.8, 1.8, 6.9) 2.24 (*ddd*, *J* = 7.2, 9.5, 14.0)	1.62 (*ddd*, *J* = 2.2, 6.4, 14.3)	6.03 (*ddd*, *J* = 1.6, 6.4, 9.6)	5.99 (*ddd*, *J* = 1.7, 6.4, 9.5)	5.99 (*m*)	6.01 (*ddd*, *J* = 2.8, 5.3, 9.8)
H–C(9)	6.40 (br. *t*, *J* = 7.2)	0.82 (*ddd*, *J* = 3.1, 9.2, 9.2)	0.75 (*ddd*, *J* = 2.0, 9.5, 9.5)	0.93 (*dd*, *J* = 1.8, 9.6)	5.85 (*dd*, *J* = 4.2, 9.4)	5.83 (*dd*, *J* = 4.8, 9.5)	5.76 (br. *d*, *J* = 9.6)	5.85 (*dd*, *J* = 2.0, 9.8)
H–C(11)	3.20 (*d*, *J* = 7.0)	0.90 (*dd*, *J* = 7.7, 9.3)	0.90 (*m*)	0.79 (*dd*, *J* = 6.9, 9.7)	3.46 (*m*)	3.50 (br. *t*, *J* = 5.5)	3.47 (*m*)	2.85 (*td*, *J* = 2.3, 12.7)
H–C(12)	2.93 (br. *s*)	2.24 (*d*, *J* = 7.6)	2.20 (*m*)	2.73 (*d*, *J* = 6.8)	3.46 (*m*)	3.55 (*d*, *J* = 7.0)	3.63 (*d*, *J* = 9.7)	3.46 (*d*, *J* = 12.8)
H–C(14)	–	–	–	4.99 (*s*)				
Me(16)	0.90 (*d*, *J* = 7.5)	0.95 (*d*, *J* = 7.0)	0.97 (*d*, *J* = 7.0)	0.74 (*d*, *J* = 7.8)	0.77 (*d*, *J* = 6.9)	0.94 (*d*, *J* = 6.9)	0.90 (*d*, *J* = 6.8)	0.90 (*d*, *J* = 6.8)
H–C(17)	3.95 (*d*, *J* = 11.4)	4.89 (*d*, *J* = 12.1)	4.85 (*d*, *J* = 12.3)	6.39 (*s*)	3.80 (*d*, *J* = 12.1)	4.03 (*d*, *J* = 12.1)	3.91 (*d*, *J* = 12.0)	4.59 (*d*, *J* = 12.0)
H′–C(17)	3.70 (*dd*, *J* = 1.0, 11.4)	4.33 (*d*, *J* = 12.1)	4.37 (*d*, *J* = 12.3)	–	4.16 (*d*, *J* = 12.1)	4.13 (*d*, *J* = 12.1)	4.07 (*d*, *J* = 12.0)	4.16 (*d*, *J* = 12.0)
H–C(18) or Me(18)	4.81 (br. *s*)	1.07 (*s*)	1.06 (*s*)	1.10 (*s*)	4.93 (br. *s*)	4.90 (br. *s*)	4.96 (br. *s*)	1.41 (*s*)
H′–C(18)	4.57 (br. *s*)			–	4.90 (*m*)	4.94 (br. *s*)	4.86 (br. *s*)	
Me(19)	1.95 (*s*)	0.97 (*s*)	0.92 (*s*)	1.11 (*s*)	1.80 (*s*)	1.80 (*s*)	1.78 (*s*)	1.02 (*s*)
Me(20)	1.33 (*s*)	1.54 (*s*)	1.54 (*s*)	1.28 (*s*)	1.40 (*s*)	1.40 (*s*)	1.56 (*s*)	1.54 (*s*)
Acetyl:								
AcO	2.10 (*s*)	1.89 (*s*)	1.95 (*s*)	1.36 (*s*)	2.14 (*s*)	2.19 (*s*)	2.16 (*s*)	2.21 (*s*)
AcO	1.67 (*s*)	1.87 (*s*)	2.02 (*s*)	1.94 (*s*)	2.00 (*s*)	2.03 (*s*)	2.08 (*s*)	2.19 (*s*)
AcO–C(3)	–	1.86 (*s*)	2.08 (*s*)	2.03 (*s*)	1.98 (*s*)	2.02 (*s*)	2.04 (*s*)	1.86 (*s*)
AcO	–	–	–	2.10 (*s*)	–	–	1.98	1.60 (*s*)
AcO	–	–	–	2.16 (*s*)	–	–	–	–
Benzoyl:								
H–C(2′), H–C(6′)		7.87 (*dd*, *J* = 1.1, 8.1)	–	–	–	7.89 (*dd*, *J* = 1.3, 8.4)	–	7.87 (*dd*, *J* = 1.2, 8.2)
H–C(3′), H–C(5′)		7.38 (br. *t*, *J* = 8.0)	–	–		7.40 (br. *t*, *J* = 8.2)	–	7.39 (br. *t*, *J* = 8.1)
H–C(4′)		7.51 (*dt*, *J* = 1.3, 7.4)	–	–	–	7.50 (*dt*, *J* = 1.4, 7.6)	–	7.53 (*m*)
Butanoyl:								
CH_2(2′)	2.10 (*m*)	–	2.15 (*m*)	–	2.20 (*m*)	–	2.22 (*m*)	–
CH_2(3′)	1.52 (*m*)	–	1.56 (*m*)	–	1.50 (*m*)	–	1.56 (*m*)	–
Me(4′)	0.88 (*t*, *J* = 7.4)	–	0.91 (*t*, *J* = 7.4)	–	0.91 (*t*, *J* = 7.4)	–	0.93 (*d*, *J* = 7.2)	–
Nicotinoyl:								
H–C(2″)	9.30 (br. *s*)	–	–	9.1 (br. *s*)	–	–	–	–
H–C(4″)	8.40 (*dt*, *J* = 1.6, 8.0)	–	–	8.21 (br. *d*, *J* = 7.0)	–	–	–	–
H–C(5″)	7.45 (*dd*, *J* = 4.9, 8.0)	–	–	7.37 (*dd*, *J* = 4.8, 7.4)	–	–	–	–
H–C(6″)	8.79 (br. *d*, *J* = 3.9)	–	–	8.74 (br. *s*)	–	–	–	–

Kandovanol ester B (**5**) is the 5-*O*-butanoyl analogue of **4** and exhibits a protonated molecular ion at *m*/*z* 581 ($[M+1]^+$; $C_{30}H_{44}O_{11}$) in the CI-MS. The base peak at *m*/*z* 461 $[M-(2\ \mathrm{AcOH})+1]^+$ suggests the presence of acetate moieties in the molecule. In the ^{1}H-NMR spectrum, the signals of the diterpene part of the molecule is very similar to

Table 2. *^{13}C-NMR Data of Compounds* **2**–**8** *and* **10**[1]) *in* $CDCl_3$

	2	**3**	**4**	**5**	**6**	**7**	**8**	**10**
C(1)	38.3	38.4	46.4	46.6	43.8	45.8	45.8	43.1
C(2)	33.2	33.4	35.7	35.8	35.8	37.6	27.6	35.9
C(3)	72.9	74.5	78.3	78.5	76.8	80.1	80.1	77.1
C(4)	54.5	54.8	50.8	50.3	53.3	85.3	55.5	50.7
C(5)	72.3	72.3	69.1	69.9	67.6	70.2	71.0	68.8
C(6)	45.9	45.8	47.5	46.6	55.9	47.9	48.2	47
C(7)	66.2	66.0	70.6	68.2	72.6	67.4	67.7	67.9
C(8)	127.3	127.1	22.9	22.9	25.6	122.7	122.7	126.2
C(9)	137.6	137.9	20.1	19.3	18.6	137.2	137.2	128.9
C(10)	147.6	147.5	19.3	18.8	18.9	147.8	147.9	79.3
C(11)	40.7	40.6	22.8	23.2	23.1	45.4	45.6	47.3
C(12)	40.9	40.6	41.9	41.2	37.4	44.9	45.5	41.8
C(13)	77.6	77.4	79.6	79.9	88.1	81.6	81.5	84.8
C(14)	98.6	98.6	209.9	210.3	79.6	203.0	203.1	200.2
C(15)	96.8	97.2	84.3	83.6	90.0	89.1	89.2	88.8
C(16)	16.1	16.4	15.4	15.1	14.4	14.8	14.8	14.4
C(17)	66.2	66.0	61.7	61.6	97.1	62.0	62.5	61.0
C(18)	110.6	66.0	22.0	22.9	28.2	112.8	112.8	29.7
C(19)	22.2	110.6	20.2	20.1	15.6	18.1	18.3	24.9
C(20)	22.5	22.2	28.5	28.6	24.9	21.1	20.8	26.2
Acetyl:								
*Me*COO	22.1	22.2	21.3	21.3	21.0	20.9	20.3	21.9
*Me*COO	20.8	23.0	21.1	21.2	21.0	20.8	21.2	21.4
*Me*COO–C(3)	20.8	–	20.7	20.7	21.3	20.2	21.1	20.7
*Me*COO	–		–	–	21.4	–	21.0	20.6
*Me*COO	–		–	–	23.0	–	–	–
Me*C*OO	174.2	174.3	170.7	171.9	170.7	170.2	170.2	170.3
Me*C*OO	171.0	170.1	170.5	170.1	170.0	170.0	169.7	170.0
Me*C*OO	170.2	–	169.5	169.7	169.6	169.6	169.2	169.9
Me*C*OO	–	–	–	–	169.1	–	169.0	169.7
Me*C*OO	–	–	–	–	168.2	–	–	–
Benzoyl:								
C(1′)	–	–	129.7	–	–	–	128.4	129.4
C(2′), C(6′)	–	–	129.7	–	–	–	129.2	129.6
C(3′), C(5′)	–	–	128.3	–	–	–	128.4	128.9
C(4′)	–	–	133.3	–	–	–	133.1	133.3
C=O	–	–	164.9	–	–	–	165.0	165.0
Butanoyl:								
C(1′)	171.3	171.4	–	171.1	–	–	–	–
C(2′)	36.1	35.9	–	35.9	–	–	–	–
C(3′)	18.3	18.3	–	17.8	–	–	–	–
C(4′)	13.7	13.7	–	13.7	–	–	–	–
Nicotinoyl:								
C(2″)	–	147.8	–	–	150.7	–	–	–
C(3″)	–	127.4	–	–	126.4	–	–	–
C(4″)	–	140.0	–	–	137.5	–	–	–
C(5″)	–	124.9	–	–	123.2	–	–	–
C(6″)	–	150.3	–	–	153.0	–	–	–
C=O	–	163.1	–	–	164.6	–	–	–

that observed for **4**, but the disappearance of the benzoyl signals and the presence of Me(4′) at δ 0.91 ($t, J = 7.4$ Hz) are in accordance with the corresponding butanoate ester at C(5).

The 3,5,14,15,17-Penta-*O*-acetyl-7-O-nicotinoyleuphoppin (**6**) is obtained as an oil. The molecular formula can be assigned by EI-MS as $C_{36}H_{45}NO_{13}$ (M^+ at m/z 699). The peaks at m/z 639 ($[M - AcOH]^+$), 579 ($[M - (2\ AcOH)]^+$), 519 ($[M - (3\ AcOH)]^+$), 106 ($C_5H_4NCO^+$), and 124 ($[C_4H_5NCO_2H + 1]^+$) indicate acetate and nicotinate moieties to be present in the molecule. The ^{1}H- and ^{13}C-NMR data of **6** are similar to those observed for euphoppines and aleppicatines, except for the data recorded for the ester group [6][7]. The relative configuration of **6** is determined by NOESY and NOE difference data of H−C(14), indicating opposite configuration at C(14) compared to the mentioned compounds (cross-peaks of H_α−C(14) of **6** with H−C(4) and H−C(7)). Besides, the lack of long-range W-coupling between H−C(5) and H−C(17), suggests the orientation of the AcO−C(17) towards the six-membered ring. Compound **6** can be synthesized by oxidation of OH−C(17) to an aldehyde, followed by acetal formation with OH−C(15). The relative positions of the acetates are established by the observed HMBC cross-peaks (*H*−C(3), *H*−C(15), *H*−C(14), *H*−C(15), and *H*−C(17)/carbonyl signals (at δ *ca.* 168–170)), and that of the nicotinate at C(7) by a cross-peak *H*−C(7)/C(7).

The 13-deacetylisodecipidone (**7**) exhibits a protonated molecular ion in the CI-MS at m/z 579 representing the molecular formula $C_{30}H_{42}O_{11}$. The base peak at m/z 519 indicates the loss of an acetate function from M^+. The ^{1}H- and ^{13}C-NMR data are very similar to those recorded for decipidone [1]. The upfield shift for C(13) and downfield shift for C(15) (δ 81.6 (*s*) and 89.1 (*s*), resp.) are the main difference to the ^{13}C-NMR data of decipidone [1]. The above data confirm the position of the OH and AcO at C(13) and C(15), respectively.

The structure of 13-deacetylisodecipinone (**8**), the benzoyl analog of **7**, is elucidated by comparison of its ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) with the spectral data of decipinone [1] and **7**. The main difference is the presence of the signals of a benzoyloxy instead of those of a butanoyloxy group at C(5).

Isodecipidone (**9**), like isodecipinone [1], was obtained as a minor compound, in which the acetate was transesterified from position C(17) in decipidone [1] to position C(15). The CI-MS of **9** shows the molecular ion at m/z 621 ($[M + 1]^+$), indicating the molecular formula $C_{32}H_{42}O_{12}$. In the ^{1}H-NMR spectrum of **9**, there are some differences with respect to those observed for decipidone. The upfield shift of H−C(12) at δ 3.63 ($d, J = 9.7$ Hz) and conversion of the H−C(17), H′−C(17) *d* signals to an *AB* pattern (δ 3.91 ('*d*', $J = 12.0$ Hz), and 4.07 ('*d*', $J = 12.0$ Hz) confirms that the position of the acetate group changed from C(17) in decipidone to C(15) in **9**.

The 15-*O*-acetylcheiradone (**10**) exhibits the molecular-ion peak at m/z 654 in the EI-MS, consistent with the molecular formula $C_{35}H_{42}O_{12}$. The IR spectrum does not show the characteristic absorption of the OH−C(15) of cheiradone [10], but the ^{1}H- and ^{13}C-NMR spectra of **10** are very similar to those of cheiradone, a compound isolated by us from *Euphorbia cheiradenia* [10], except that **10** has one more acetate moiety at C(15). The downfield shift of C(15) to δ 88.8 is compatible with the proposed structure.

Experimental Part

General. Column chromatography (CC): silica gel, 70–230 mesh. Flash chromatography (FC): silica gel 230–400 mesh. TLC: precoated silica gel *G-25-UV$_{254}$* plates: detection at 254 nm, and by ceric sulfate reagent. Optical rotations: *Jasco DIP-360* digital polarimeter. UV and IR Spectra: *Hitachi UV-3200* and *Jasco 320-A* spectrophotometer, resp.; in nm and cm^{-1}, resp. ^{1}H- and ^{13}C-NMR COSY, HMQC, and HMBC: *Bruker* spectrometers operating at 500 and 400 MHz; chemical shifts δ in ppm and coupling constants J in Hz. EI- and CI-MS: *JMS-HX-110* with a data system; *m/z* (rel. %).

Plant Material. The plant *Euphorbia decipiens* BOISS. et BUHSE (Euphorbiaceae) was collected at the mountain Kandovan, north of Karaj, Iran, in 1998, and identified by Mr. *Bahram Zehzad* (plant taxonomist) at the Department of Biological Sciences, Shahid Beheshti University, Eveen, Tehran, Iran. A voucher specimen (no. 98112) has been deposited at the herbarium of the Biology Department of Shahid Beheshti University, Eveen, Tehran, Iran.

Extraction and Isolation. The air-dried ground plant (4 kg) was exhaustively extracted with acetone at r.t. The extract was evaporated to yield the residue (62 g). The defatted extract (51 g) was extracted with $CHCl_3$. The $CHCl_3$ extract (44 g) was subjected to CC (silica gel (880 g), $CHCl_3$/hexane gradient up to 100%, followed by MeOH). Twenty fractions were collected. The $CHCl_3$-rich *Fr. 12* was subjected to repeated CC. The fraction eluted with AcOEt/hexane 20:80, contained compounds **3** and **6**, which were finally purified by prep. TLC (silica gel *60 F$_{254}$*, AcOEt/hexane 1:1, 3 developments). *Fr. 10* of the first column was loaded on $AgNO_3$-impregnated silica gel (flash silica gel, 230–400 mesh) and eluted with pure $CHCl_3$. *Fr. 20* thus obtained was again separated by prep. TLC (hexane/AcOEt 70:30): pure **4**, **5**, and **7**. *Fr. 21* from the same CC contained **9** and **10**, which were purified by prep. TLC ($CHCl_3$/Me_2CO 99:1).

rel-*(2*R*,3*R*,3a*S*,4*S*,4a*S*,5*S*,8*R*,8a*S*,9*R*,10*R*,10a*S*)-2,3,3a,4,5,8,8a,9,10,10a-Decahydro-2,9-dimethyl-8-(methylethenyl)-1*H*-10,4a-(epoxymethano)benz[*f*]azulene-3,4,5,9,10,10a-hexol-3,5,10a-triacetate 4-Benzoate* (= *Decipinone B*; **1**): 10.1 mg (0.0006%). Colorless plate-like crystals (MeOH). M.p. 190–192°. For other data, see [3].

Crystal Data of **1**[2]). $C_{33}H_{40}O_{11}$. Orthorhombic, space group $P2_12_12_1$; $a = 8.893$ (4), $b = 17.509$ (2), and $c = 20.276$ (4), $V = 3157(1)$ Å^3; CuK_α λ 1.54178 Å, $Z = 4$, $D_{calc.} = 1.29$ g/cm^3, $F(000) = 1304.00$, μ(CuK_α) = 8.05 mm^{-1}. Crystal size $0.50 \times 0.48 \times 0.22$ mm^3. X-Ray-diffraction data were collected at 293 (2) K in the range 5.0–68.0° ($0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 24$) with an *Enraf-Nonius CAD-4* diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the program SHELXTL 97. Anistropic thermal parameters were refined for all the non-H-atoms. All the H-atoms were located in the difference *Fourier* maps. Riding models were used to place the H-atoms in their idealized positions. The structure converged with $R_1 = 0.064$, $wR_2 = 0.118$, and g.o.f. = 1.03 for the 1266 reflections with $I > 2.0\sigma(I)$ and 406 parameters. In the final difference *Fourier* synthesis, the electron density fluctuated in the range 0.15 to -0.14 e/Å^3. An absolute structure could not be established in this analysis (*Flack* parameter 0.6 (7)).

Butanoic Acid rel-*(2*R*,3*R*,3a*S*,4a*S*,5*S*,8*R*,8a*S*,9*R*,10*R*,10a*S*)-3,5,10a-Tris(acetyloxy)-2,3,3a,4,5,8,8a,9,10,10a-decahydro-9,10-dihydroxy-2,9-dimethyl-8-(1-methylethenyl)-1*H*-10,4a-(epoxymethano)benz[*f*]azulen-4-yl Ester* (= *Decipinone C*; **2**): 16.4 mg (0.0004%). Colorless prismatic crystals (MeOH). M.p. 232–234°. $[\alpha]_D^{24} = +12.4$ ($c = 0.1$, $CHCl_3$). UV (MeOH): 203.0. IR ($CHCl_3$): 3450, 2900, 2840, 1736, 1728, 1712, 1640, 1450, 1370, 1280, 1150, 1100, 1020, 990, 970, 900, 600. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 578 (0.4, M^+), 560 (1, $[M - H_2O]^+$), 518 (1, $[M - AcOH]^+$), 490 (1, $[M - C_3H_7CO_2H]^+$), 458 (2, $[M - (2\,AcOH)]^+$), 714 (100, $C_3H_7CO^+$).

Crystal Data of **2**[2]): $C_{30}H_{42}O_{11}$. Orthorombic, space group $P2_12_12_1$; $a = 8.877$ (2), $b = 15.820$ (2), and $c = 21.696$ (7) Å, $V = 3046.9$ (13) Å^3; CuK_α λ 1.5417 Å; $Z = 4$, $D_{calc.} = 1.261$ Mg/m^3, $F(000) = 1240$, μ(CuK_α) = 0.797 mm^{-1}. Crystal size $0.35 \times 0.30 \times 0.25$ mm^3. X-Ray-diffraction data were collected at 293 (2) K in the range 5.0–68.0° ($0 \leq h \leq 10$, $0 \leq k \leq 18$, $-26 \leq l \leq 26$) on an *Enraf-Nonius CAD-4* diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the program SHELXTL 97. Anistropic thermal parameters were refined for all the non-H-atoms. All the H-atoms were located in the difference *Fourier* maps. Riding models were used to place the H-atoms in their idealized positions. The structure converged with $R_1 = 0.052$, $wR_2 = 0.116$, and g.o.f. = 1.08 for the 3726 reflections with $I > 2.0\sigma(I)$ and

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[2]) Crystallographic data (excluding structure factors) for decipinone B (**1**) and C (**2**) have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC-148205 and 148206, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK.

388 parameters. In the final difference *Fourier* synthesis, the electron density fluctuated in the range 0.19 to -0.17 e/Å^3. An absolute structure was established for this compound (*Flack* parameter 0.0 (3)) with the *Friedel* pairs of reflections, which were not merged (*Fig. 2*).

*Pyridine-3-carboxylic Acid (2*R*,3*R*,3a*S*,4*S*,4a*S*,5*S*,8*R*,8a*S*,9*R*,10*R*,10a*S*)-5,10a-Bis(acetyloxy)-2,3,3a,4,5,8,8a,9,10,10a-decahydro-9,10-dihydroxy-2,9-dimethyl-8-(1-methylethenyl)-3-(1-oxobutoxy)-1*H*-10,4a-(epoxymethano)benz[*f*]azulen-4-yl Ester* (= *Decipinol Ester A*; **3**): 12.5 mg (0.00034%). $[\alpha]_D^{23} = -25.3$ ($c = 0.786$, $CHCl_3$). UV (MeOH): 263.5, 217.3, 204.3. IR ($CHCl_3$): 3480, 1740, 1725, 1710, 1640. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 641 (0.4, M^+, $C_{34}H_{43}NO_{11}^+$, 124 (86, $C_5H_4NCO_2H^+$), 106 (41, $C_5H_4NCO^+$). CI-MS (CH_4): 642 ($[M+1]^+$), 624 ($[M+1-H_2O]^+$), 582 ($[M+1-AcOH]^+$).

rel-(1*a*R,*3*S,*3a*S,*4*S,*4a*S,*5*R,*6*R,*7a*S,*9*R,*9a*S,*9b*R)*-3,5-Bis(acetyloxy)-3a-[(acetyloxy)methyl]-4-(benzoyloxy)-1,1a,2,3,3a,4,4a,5,6,7,7a,9,9a,9b-tetradecahydro-7a,9-dihydroxy-1,1,6,9-tetramethyl-8*H*-cyclopropa[3,4]benzo[1,2-*f*]azulen-8-one* (= *Kandovanol Ester A*; **4**): 17.0 mg (0.00043%). $[\alpha]_D^{23} = +49.07$ ($c = 0.7133$, $CHCl_3$). UV (MeOH): 272.3, 230.3, 199.4. IR ($CHCl_3$): 3450, 1740, 1723, 1650. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 616 (M^+, $C_{33}H_{44}NO_{11}^+$), 496 ($[M-AcOH]^+$), 496 ($[M-2\ AcOH]^+$), 105 ($C_6H_5CO^+$). CI-MS (CH_4). 617 ($[M+1]^+$).

Butanoic Acid rel-*(1a*R,*3*S,*3a*S,*4*S,*4a*S,*5*R,*6*R,*7a*S,*9*R,*9a*S,*9b*R)*-3,5-Bis(acetyloxy)-3a-[(acetyloxy)methyl]-1a,2,3,3a,4,4a,5,6,7,7a,8,9,9a,9b-tetradecahydro-7a,9-dihydroxy-1,1,6,9-tetramethyl-8-oxo-1*H*-cyclopropa[3,4]benzo[1,2-*f*]azulen-4-yl Ester* (= *Kandovanol Ester B*; **5**): 23.3 mg (0.00058%). $[\alpha]_D^{23} = +37.52$ ($c = 0.053$, $CHCl_3$). IR ($CHCl_3$): 3450, 1730, 1640. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. CI-MS (CH_4): 581 ($[M+1]^+$, $C_{30}H_{45}O_{11}^+$), 521 ($[M+1-AcOH]^+$), 503 ($[M+1-AcOH-H_2O]^+$), 461 ($[M-H_2O \times AcOH]^+$.

Pyridine-3-carboxylic acid rel-*(1a*R,*3*S,*3a*S,*4*S,*4a*S,*5*R,*6*R,*7a*S,*8*R,*9*S,*9a*S,*9b*R,*11*R)*-4,5,7a,8,11-Pentakis(acetyloxy)-1,1a,2,3,4,4a,5,6,7,7a,8,9,9a,9b-tetradecahydro-1,1,6,9-tetramethyl-9,3a-(epoxymethano)-3a*H*-cyclopropa[3,4]benzo[1,2-*f*]azulen-3-yl Ester (= 3,5,14,15,17-Penta-*O*-acetyl-7-*O*-nicotinoyleuphoppin*; **6**): 19.4 mg (0.00048%). $[\alpha]_D^{23} = -19.75$ ($c = 6.666$, $CHCl_3$). UV (MeOH): 264.5, 220.3, 200.1. IR ($CHCl_3$): 3650, 3500, 1760, 1725, 1710, 1695. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 699 (12, M^+, $C_{36}H_{45}NO_{13}^+$), 639 (21), 579 (4), 537 (61), 519 (3), 484 (15), 414 (5), 308 (6), 325 (6), 294 (8), 265 (9), 266 (10), 238 (7), 223 (12), 191 (11), 174 (13), 166 (18), 133 (9), 124 (100), 106 (28), 79 (6), 69 (7), 55 (5). CI-MS (CH_4). 700 ($[M+1]^+$), 640 $[M+1-AcOH]^+$), 580 $[M+1-(2\ AcOH)]^+$, 520, 415, 285.

Butanoic Acid rel-*(2*R,*3*R,*3a*S,*4*S,*4a*S,*5*S,*8*R,*8a*S,*9*R,*10a*S)*-3,5,10a-Tris(acetyloxy)-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydro-9-hydroxy-4a-(hydroxymethyl)-2,9-dimethyl-8-(1-methylethenyl)-10-oxobenz[*f*]azulen-4-yl Ester* (= *13-Deacetylisodecipidone*; **7**): 12.1 mg (0.0003%). $[\alpha]_D^{23} = -15.61$ ($c = 0.448$, $CHCl_3$). ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. IR ($CHCl_3$): 3450, 1730, 1640. CI-MS (CH_4): 579 ($[M+1]^+$ $C_{30}H_{43}O_{11}^+$), 519 ($[M+1-AcOH]^+$).

rel-*(2*R,*3*R,*3a*S,*4*S,*4a*S,*5*S,*8*R,*8a*S,*9*R,*10a*S)*-3,5,10a-Tris(acetyloxy)-4-(benzoyloxy)-2,3,3a,4,4a,5,8,8a,9,10a-decahydro-9-hydroxy-4a-(hydroxymethyl)-2,9-dimethyl-8-(1-methylethenyl)benz[*f*]azulen-10(1*H*)-one* (= *13-Deacetylisodecipinone*; **8**): 4.5 mg (0.00011%). $[\alpha]_D^{23} = +15.35$ ($c = 0.717$, $CHCl_3$). UV (MeOH): 272.3, 228.3, 198.1. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. IR ($CHCl_3$): 3500, 2950, 1740, 1720, 1630, 1600. EI-MS: 612 (12, M^+, $C_{33}H_{40}O_{11}^+$), 491 (23, $[M-121]^+$), 121 (10, $C_6H_5CO_2^+$), 105 (100, $C_6H_5CO^+$). CI-MS (CH_4): 613 ($[M+1]^+$).

Butanoic Acid rel-*(2*R,*3*R,*3a*S,*4*S,*4a*S,*5*S,*8*R,*8a*S,*9*R,*10a*S)*-3,5,9,10a-Tetrakis(acetyloxy)-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydro-4a-(hydroxymethyl)-2,9-dimethyl-8-(1-methylethenyl)-10-oxobenz[*f*]azulen-4-yl Ester* (= *Isodecipidone*; **9**): 2.8 mg (0.00007%). M.p. 187–189°. $[\alpha]_D^{23} = -22.8$ ($c = 0.48$, $CHCl_3$). UV (MeOH): 264.5, 220.3, 200.1. IR ($CHCl_3$): 3650, 3500, 1760, 1725, 1710, 1695. ^{1}H-NMR: *Table 1*. CI-MS (CH_4): 621 ($[M+1]^+$, $C_{32}H_{45}O_{12}^+$), 561, 533, 519, 501, 473, 459, 441, 413,371, 353, 293, 311, 89, 61.

rel-*(2a*R,*5*S,*5a*S,*6*S,*6a*S,*7*R,*8*R,*9a*S,*10a*R,*10b*S)*-5,7,9a-tris(acetyloxy)-5a-[(acetyloxy)methyl]-6-(benzoyloxy)-2,2a,5,5a,6,6a,7,8,9,9a,10a,10b-dodecahydro-2,2,8,10a-tetramethyl-10*H*-azuleno[5,6,7-cd]isobenzofuran-10-one* (= *15-O-Acetylcheiradone*; **10**): 28.1 mg (0.0007%). M.p. 170–172°. $[\alpha]_D^{23} = +15.15$ ($c = 0.066$, $CHCl_3$). UV (MeOH): 274.0, 230.6, 201.7, 193.2. IR ($CHCl_3$): 3350, 3100–3000, 1730, 1600. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 654 (3, M^+, $C_{35}H_{42}O_{12}^+$), 626 (7), 566 (4), 293 (73), 233 (93), 191 (73), 105 (100). CI-MS (CH_4): 700 ($[M+1]^+$), 640 ($[M+1-AcOH]^+$), 580 ($[M+1-(2\ AcOH)]^+$), 520, 415, 285.

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