Determination of Absolute Configuration of Decipinone, a Diterpenoid Ester with a Myrsinane-Type Carbon Skeleton, by NMR Spectroscopy

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The absolute configuration of decipinone (**2**), a myrsinane-type diterpene ester previously isolated from *Euphorbia decipiens*, has been determined by NMR study of its axially chiral derivatives (a*R*)- and (a*S*)-*N*-hydroxy-2′-methoxy-1,1′-binaphthalene-2-carboximidoyl chloride ((a*R*)-MBCC (**3a**) and (a*S*)-MBCC (**3b**)). The absolute configurations at C(7) and C(13) of **2** determined were (*R*) and (*S*), respectively. Therefore, considering the relative configuration of **2**, the absolute configuration determined was (2*S*,3*S*,4*R*,5*R*,6*R*,7*R*,11*S*,12*R*,13*S*,15*R*).

Introduction. – The macro- and polycyclic diterpene esters of plants of the genus *Euphorbia* have different biological activities such as tumor-promoting, anti-tumor, and anti-HIV activities [1–3]. Toxicity of *Euphorbia esula* to cattle, allelopathic activity of *E. esula* to desired forage [4], and high toxicity of the roots of *E. lathyris*, which kills the animals nibbling it, is due to their diterpenes [5].

Lathyrane (**1**; *Fig. 1*) is considered as the precursor of different types of diterpene esters of *Euphorbia* plants, including jatrophane, ingenane, and myrsinol [1][6]. 6,20-Epoxylathyrol was named euphorbiasteroid in the late 19th century, and, in the 1970s, its structure was determined with chemical reactions and X-ray diffraction [7][8]. Different authors have studied the relative and absolute configurations of lathyrane and related skeleta, and some different configurations have been reported [4][8–12]. This might be due to different conformations resulting in various esterifications or to the flexibility of the macrocyclic ring of the diterpenoids, which makes spectroscopic interpretation difficult [13]. The aforementioned biological and ecological importance of the diterpenes isolated from different plants of the genus *Euphorbia* prompted us to investigate the absolute configuration of decipinone (**2**), which has a myrsinane skeleton. *Euphorbia decipiens* is an endemic plant growing wild in Iran. It has been investigated for its novel diterpene esters, and **2** was reported as one of its major constituents [14][15].

To the best of our knowledge, the absolute configuration of the myrsinane-type diterpene esters have not been studied so far. We report the preparation and NMR study of adducts between **2** and (a*R*)- and (a*S*)-*N*-hydroxy-2′-methoxy-1,1′-binaphthalene-2-carboximidoyl chloride ((a*R*)-MBCC (**3a**) and (a*S*)-MBCC (**3b**)), respectively, at the C(10)=C(18) double bond. The absolute configuration was deduced from chemical-shift differences between (a*R*)- and (a*S*)-MBCC derivatives (**4** and **5**) of **2** together with NOE-difference-spectroscopy data.

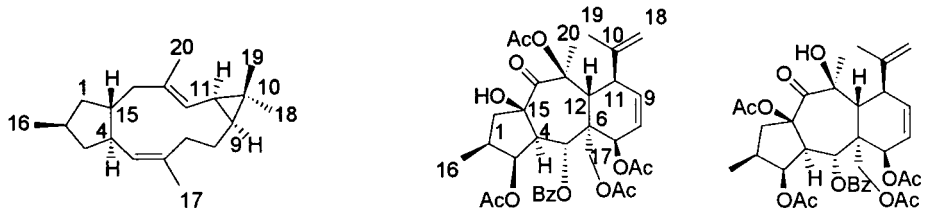


Fig. 1. *Lathyrane* (**1**), *the possible precursor of decipinone* (**2**) *and isodecipinone* (**6**)

Results and Discussion. – Decipinone (**2**) was isolated and purified from *Euphorbia decipiens* as described in [14][15]. The (a*R*)- and (a*S*)-*N*-hydroxy-2′-methoxy-1,1′-binaphthalene-2-carboximidoyl chlorides (**3a**) and (**3b**) were synthesized as described previously [16]. Compound **2** reacted with **3a** and **3b** in $CHCl_3$ in the presence of Et_3N at room temperature to afford **4** and **5**, respectively, which were purified by preparative TLC and HPLC from a mixture of isomers (see *Exper. Part*). Compound **4** showed a molecular ion in HR-FD-MS at *m*/*z* 979.3733, corresponding to the molecular formula $C_{57}H_{57}O_{14}$.

The splitting pattern of ^{1}H- and ^{13}C-NMR spectral data of the diterpene moiety of **4** (*Table*) were similar to those recorded for **2**, except for the signals in the aromatic region. However, the H-atoms of the diterpene moiety were highly affected by the anisotropic effect of the naphthalene ring of the MBCC part of the molecule, resulting in some changes in the δ values of the ^{1}H-NMR spectrum.

In the ^{1}H-NMR spectrum of **4**, two signals at δ 2.20 ($d, J = 17.2$) and 2.11 ($d, J = 17.2$) ppm were observed for $H_a-C(18)$ and $H_b-C(18)$ instead of the exomethylene double-bond signals in ^{1}H-NMR spectrum of **2**. This obviously confirmed the formation of a 4,5-dihydroisoxazole ring between the C(10)=C(18) double bond of **2** and the nitrile oxide moiety derived from MBCC. The regioselectivity of this reaction was observed in all of the isomers obtained, which can be explained by there being less hindrance from the C(10)=C(18) double bond than the C(8)=C(9) double bond. The correlation between ^{1}H and ^{13}C and relative positions of the ester groups were determined by HMQC and HMBC experiments, respectively. The assignments of the signals of the Ac groups were deduced by NOESY spectrum. Besides the up-field signals of $H_a-C(18)$ and $H_b-C(18)$ in the ^{1}H-NMR spectrum, the HMBC spectral data confirmed the formation of isoxazoline ring at C(10)=C(18). Two strong cross-peaks between $H_a-C(18)$ and $H_b-C(18)$ and C=N of the isoxazoline ring and no correlation between $H_3C(19)$ and the C=N signal were in agreement with the proposed structure.

In the ^{1}H-NMR spectrum of **4**, the δ values ($\Delta\delta = \delta(\mathbf{4}) - \delta(\mathbf{2})$) of the signals of H–C(5) (−0.51), H–C(8) (−0.19), H–C(9) (−0.69), H–C(11) (−0.60), H–C(12) (−0.22), and H–C(20) (−0.41), were shifted up-field in comparison to those in **2**, which was the result of incorporation of the naphthalene ring in **3** in the molecule (*Fig. 2*).

In order to get more information from the effect of the naphthalene ring of **3** on the chemical shift of the parent molecule, (a*S*)-MBCC derivative **5** was synthesized. The MS and ^{1}H-NMR spectral data were similar to those recorded for **4**, except for

Table. *^{1}H-NMR Data for (a*R*)- and (a*S*)-MBCC Derivatives of Decipinone* (**2**)

Position	**4**		**5**	**2**	**6**
	in $CDCl_3$	in C_6D_6	in $CDCl_3$	in $CDCl_3$ [14]	in $CDCl_3$ [14]
H_α–C(1)	3.21 (*dd*, *J* = 10.8, 15.0)	3.40 (*dd*, *J* = 10.8, 14.8)	3.42 (*dd*, *J* = 8.6, 15.0)	3.15 (*dd*, *J* = 9.5, 14.5)	3.34 (*dd*, *J* = 8.8, 14.9)
H_β–C(1)	1.55 (*m*)	1.52 (*dd*, *J* = 8.6, 14.8)	2.00 (*dd*, *J* = 10.8, 15.0)	1.60 (*dd*, *J* = 11.5, 14.5)	1.79 (*dd*, *J* = 10.4, 14.9)
H–C(2)	2.33 (*m*)	1.83 (*m*)	2.15 (*m*)	2.10 (*m*)	2.10 (*m*)
H–C(3)	5.23 (*t*, *J* = 3.0)	5.31 (*t*, *J* = 3.0)	5.20 (br. *s*)	5.30 (*t*, *J* = 3.5)	5.28 (*t*, *J* = 3.5)
H–C(4)	2.41 (*dd*, *J* = 3.0, 11.5)	2.65 (*dd*, *J* = 3.0, 11.5)	2.38 (*dd*, *J* = 3.2, 11.5)	2.36 (*dd*, *J* = 3.5, 11.5)	2.61 (*dd*, *J* = 3.5, 11.6)
H–C(5)	5.87 (*d*, *J* = 11.5)	6.21 (*d*, *J* = 11.5)	6.14 (*d*, *J* = 11.5)	6.38 (*d*, *J* = 11.5)	6.41 (*d*, *J* = 11.6)
H–C(7)	5.02 (*d*, *J* = 6.4)	5.47 (*d*, *J* = 6.5)	4.93 (*d*, *J* = 6.9)	4.87 (*m*)	4.67 (*d*, *J* = 6.4)
H–C(8)	5.77 (br. *dd*, *J* = 7.1, 9.6)	5.94 (br. *dd*, *J* = 6.5, 9.5)	6.03 (br. *t*, *J* = 7.6)	5.96 (*ddd*, *J* = 2.0, 6.5, 9.5)	5.99 (*ddd*, *J* = 2.0, 6.4, 9.5)
H–C(9)	5.03 (*dd*, *J* = 6.4, 9.6)	5.10 (*dd*, *J* = 6.6, 9.5)	5.16 (*dd*, *J* = 6.2, 9.8)	5.72 (*dd*, *J* = 4.5, 9.5)	5.74 (*dd*, *J* = 4.3, 9.5)
H–C(11)	2.68 (*dd*, *J* = 3.4, 6.9)	2.87 (br. *dd*, *J* = 6.6, 3.7)	2.67 (br. *d*)	3.28 (*ddd*, *J* = 2.0, 4.5, 8.0)	3.47 (br. *d*)
H–C(12)	3.85 (*d*, *J* = 3.4)	4.13 (*d*, *J* = 3.7)	3.38 (*d*, *J* = 4.0)	4.07 (*d*, *J* = 8.0)	3.54 (*d*, *J* = 8.1)
H_3C(16)	0.90 (*d*, *J* = 6.9)	0.63 (*d*, *J* = 6.9)	0.84 (*d*, *J* = 6.7)	0.89 (*d*, *J* = 6.7)	0.88 (*d*, *J* = 6.7)
H_a–C(17)	4.13 (*d*, *J* = 12.4)	4.68 (*d*, *J* = 12.3)	4.06 (*d*, *J* = 12.3)	4.34 (*d*, *J* = 12.0)	4.16 (*d*, *J* = 12.0)
H_b–C(17)	3.81 (*d*, *J* = 12.4)	4.00 (*d*, *J* = 12.3)	3.88 (*d*, *J* = 12.3)	3.97 (*d*, *J* = 12.0)	4.09 (*d*, *J* = 12.0)
H_a–C(18)	2.20 (*d*, *J* = 17.2)	2.50 (*d*, *J* = 17.5)	2.43 (*d*, *J* = 17.2)	4.87 (*m*)	4.97 (br. *s*)
H_b–C(18)	2.11 (*d*, *J* = 17.2)	2.23 (*d*, *J* = 17.5)	1.93 (*d*, *J* = 17.2)	4.87 (*m*)	4.87 (br. *d*, *J* = 1.2)
H_3C(19)	1.29 (*s*)	1.37 (*s*)	0.81 (*s*)	1.77 (*s*)	1.80 (*s*)
H_3C(20)	1.26 (*s*)	1.45 (*s*)	1.31 (*s*)	1.67 (*s*)	1.61 (*s*)
MeCOO–C(3)	2.17 (*s*)	1.54 (*s*)	2.08 (*s*)	2.07 (*s*)	2.05 (*s*)
MeCOO–C(7)	1.83 (*s*)	1.82 (*s*)	1.87 (*s*)	1.94 (*s*)	2.15 (*s*)
MeCOO–C(13)	2.01 (*s*)	1.98 (*s*)	–	2.12 (*s*)	–
MeCOO–C(15)	–	–	2.22 (*s*)	–	2.20 (*s*)
MeCOO–C(17)	2.06 (*s*)	1.65 (*s*)	2.05 (*s*)	1.73 (*s*)	1.89 (*s*)
H–C(3″)(MBCC)	7.40 (*d*, *J* = 9.1)	7.01 (*m*)	7.45 (*d*, *J* = 8.9)	–	–
H–C(8″)(MBCC)	7.02 (*d*, *J* = 8.6)	Not assigned	7.01 (*d*, *J* = 8.6)	–	–
MeO	3.76 (*s*)	3.20 (*s*)	3.76 (*s*)	–	–
H–C(2‴,6‴)(BzO)	7.82 (br. *d*, *J* = 7.7)	Not assigned	7.83 (br. *d*, *J* = 7.3)	7.87 *dd*, *J* = 1.5, 10.0)	7.86 (*dd*, *J* = 1.5, 10.0)
H–C(3‴,5‴)(BzO)	7.37 (br. *t*, *J* = 7.6)	Not assigned	7.37 (*m*)	7.37 (br. *t*, *J* = 8.0)	7.39 (br. *t*, *J* = 8.0)
H–C(4‴)(BzO)	7.50 (*m*)	Not assigned	7.52 (*m*)	7.50 (*tt*, *J* = 1.0, 8.5)	7.52 (br. *tt*, *J* = 1.0, 8.5)

differences in chemical-shift values of the H-atoms of the 4,5-dihydroisoxazoline ring (*Table*). The position of the free OH group in **5** was determined by HMBC experiment. A cross-peak between H–C(12) and an upfield-shifted ^{13}C-signal at δ 79 ppm (C(13)) suggested the presence of OH at C(13). The parent molecule **6** resulting from the migration of AcO from C(13) to C(15) was also isolated from the plant extract. The ^{1}H-NMR of **6** was previously reported, but, due to insufficient amounts of the compound, the assignment of its ^{13}C-NMR signals by 2D-NMR was not possible [14]. A cross-peak between H_a–C(17), H_b–C(17) and an Me*C*OO signal at δ 170.0 ppm in the HMBC spectrum and the shifts of the C(13) and C(15) signals up- and down-field (δ 81.3 and 90.5 ppm, resp.) confirmed the positions of the free OH group at C(13) and AcO group at C(15) and C(17) in **6** (*Fig. 1*). The $\Delta\delta = \delta(\mathbf{5}) - \delta(\mathbf{2}) = -0.69$ for H–C(12) in comparison to $\Delta\delta = \delta(\mathbf{5}) - \delta(\mathbf{6})$ presented in *Fig. 2* showed an up-field shift for H–C(12) due to the migration of AcO–C(13) to C(15). The most significant differences in the ^{1}H-NMR spectrum of **4** and **5** were the up-field shifts ($\Delta\delta = \delta(\mathbf{5}) -$

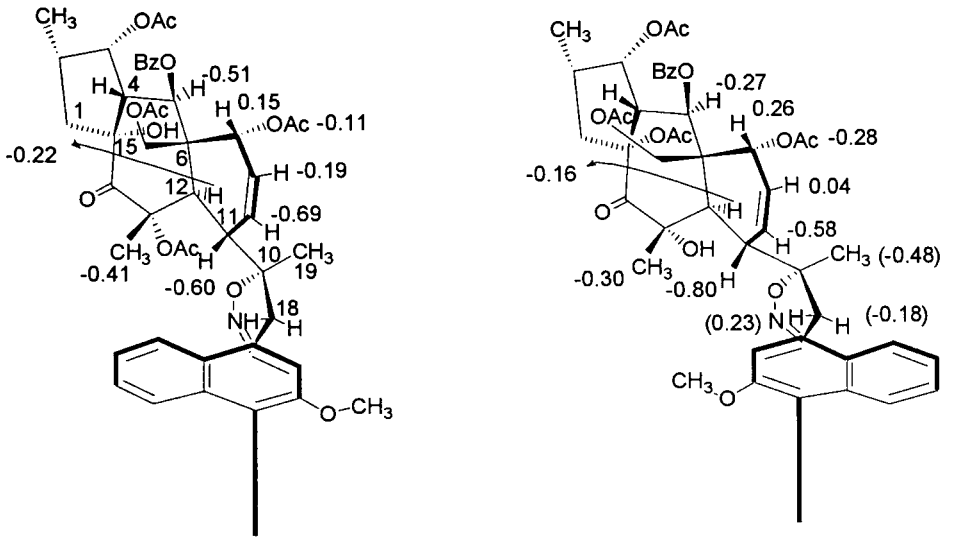


Fig. 2. *Chemical-shift differences for* **4**: $\Delta\delta = \delta(\mathbf{4}) - \delta(\mathbf{2})$, *for* **5**: $\Delta\delta = \delta(\mathbf{5}) - \delta(\mathbf{6})$ *and* $\Delta\delta = \delta(\mathbf{5}) - \delta(\mathbf{4})$ *are presented for H-atoms near the MBCC naphthalene ring*. This figure visualizes the anisotropic effect of MBCC naphthalene ring on the chemical shifts of diterpene moiety of the molecule, for a good imagination of the connectivity of the diterpene to the MBCC part, see *Fig. 3*.

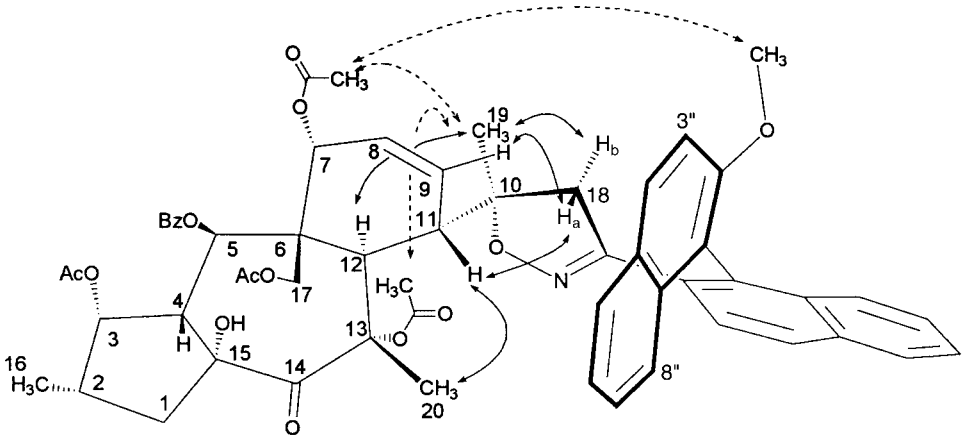
$\delta(\mathbf{4})$) of $H_3C(19)$ (−0.48) and $H_b-C(18)$ (−0.18) and down-field shift of $H_a-C(18)$ (0.23) in **5**, which is consistent with the presented configuration of **2** (*Fig. 2*).

To determine the configuration at C(10) of the isoxazoline ring, the NOE correlations between $H_a-C(18)$, $H_b-C(18)$, $H_3C(19)$, and the H-atoms of the diterpene moiety were very informative in both **4** and **5** (*Fig. 3*). We concluded that the configuration at C(10) is *R* based on the following observations.

The correlations between $H_a-C(18)$ and (H−C(9), H−C(11)); H−C(11) and $H_3C(20)$; and $H_3C(19)$ and (H−C(12), $H_b-C(18)$) in the NOESY spectrum of **4** indicated that $H_a-C(18)$, H−C(9), H−C(11), and $H_3C(20)$ must be on one face and $H_3C(19)$, H−C(12), and $H_b-C(18)$ on the other side of the molecule (*Fig. 3*).

In the NOE-difference-spectroscopy experiments of **4**, irradiation of the signal of $H_a-C(18)$ enhanced the signals of H−C(11) (3.3%) and H−C(9) (4.8%). Irradiation of the signal of $H_3C(20)$ enhanced the signals of H−C(11) (2.5%), $H_a-C(17)$ (0.6%), and $H_b-C(17)$ (1.4%). On the other hand, irradiation of $H_3C(19)$ enhanced the signals of $H_b-C(18)$ (1.1%) and H−C(12) (2.9%), respectively. Finally, H−C(12) showed a NOE with $H_3C(19)$ (4.5%).

The correlation between $H_b-C(18)$, $H_3C(19)$, and MeO of MBCC and *Me*COO at δ 1.82 ppm (AcO−C(7)) suggested that they are on the same side of the molecule in **4** (*Fig. 3*). The NOESY and NOE-difference spectra of **5** showed correlations between $H_b-C(18)$, H−C(19), and H−C(12) on one side and H−C(20), $H_a-C(18)$, H−C(11), and H−C(9) on the other side (*Fig. 3*). The NOE enhancement of $H_3C(20)$ (0.5%) on



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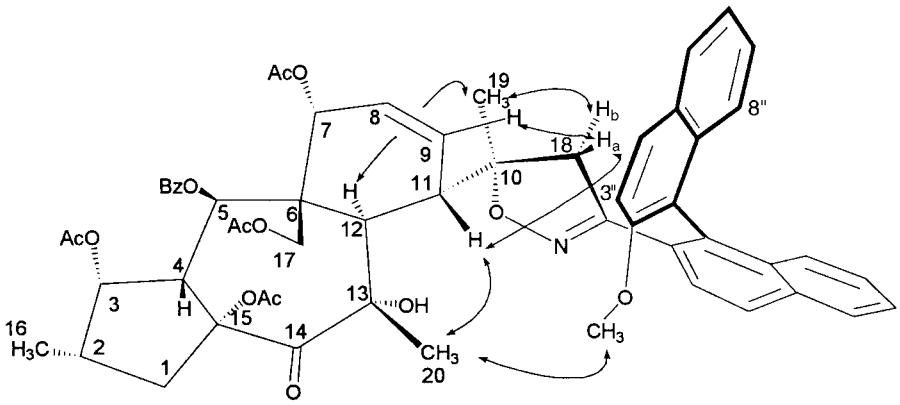


5

Fig. 3. *NOESY Correlations for* **4** and **5**. : in $CDCl_3$; : in C_6D_6.

irradiation of MeO of the MBCC methoxy signal was compatible with the structure of **5**.

To get more information from the NOESY spectrum of **4**, NOE experiments were performed in C_6D_6 (*Fig. 3*). In the NOE-difference experiment, irradiation of the MeO group on the aromatic ring enhanced the signals of the MBCC moiety at δ 7.01 (3.6%, H−C(3″)) and an *Me*COO group at δ 1.82 ppm (0.7%, AcO−C(7)). H_b−C(18) (δ

2.23 ppm) showed correlations with H_a–C(18) (12.9%), AcO–C(7) (0.9%), and H_3C(19) (2.7%). Irradiation of H_3C(19) enhanced the signals of H–C(12) (3.2%), H_b–C(18) (1.6%), and two *Me*COO signals at δ 1.98 (0.5%, AcO–C(13)) and 1.82 ppm (1.1%, AcO–C(7)). These correlations of H_b–C(18), H_3C(19), and MeO with *Me*COO–C(7) at δ 1.82 ppm were consistent with the stereochemistry at C(7) as (*R*).

With the above NOE correlations of **4** and **5**, the correct configurations at C(7) and C(13) can be determined as (*R*) and (*S*), respectively. Therefore, considering the relative configuration of **2** [14][15], we can conclude that the absolute configuration of decipinone (**2**) is (2*S*,3*S*,4*R*,5*R*,6*R*,7*R*,11*S*,12*R*,13*S*,15*R*). These findings are supported by the up-field-shifted signals for H_b–C(18) (δ 1.93 ppm and H_3C(19) (δ 0.81 ppm)) in the ^{1}H-NMR spectrum of (a*S*)-MBCC derivative **5**, in comparison to the corresponding signals at δ 2.11 (H_b–C(18)) and 1.29 (H_3C(19)) in **4**.

Experimental Part

General. Column (CC) and flash column chromatography (FC): SiO_2 (63–210 μm) and (40–60 μm), resp. Anal. and prep. TLC: *Merck* silica gel *60 F254* precoated glass plates. HPLC: *Hitachi L-6000* with an *L-4200 H* UV/VIS detector and a *D-2500 Chromato-Integrator* with a semipreparative *RP 18* (*Prep-ODS Inertsil* 6.0 × 250 mm) column. Conformation analysis was assisted by MM2 calculations under the Chem.3D molecular modeling analysis of Chem. Office (*Cambridge Soft*). ^{1}H- and ^{13}C-NMR-Spectral, ^{1}H-^{1}H-COSY, -NOESY, NOE-difference spectroscopy, HMQC and HMBC experiments: *Bruker AMX-500 FT-NMR*, 500 MHz. *FD-MS: Jeol JMS-SX102A* spectrometer.

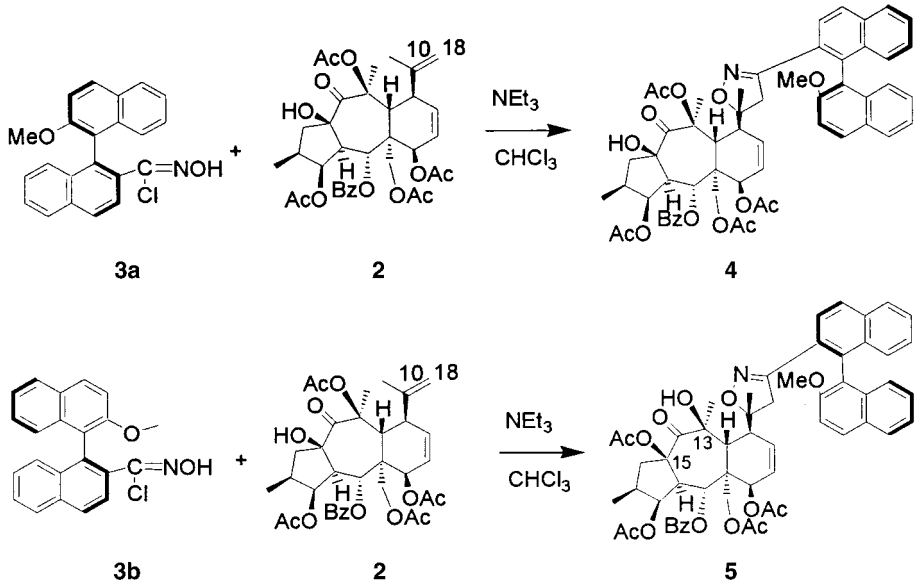
*Extraction and Isolation of (2S,3S,3aR,4R,4aR,5R,8S,8aR,9S,10aR)-3,5,9-Triacetoxy-4a-(acetoxymethyl)-10a-hydroxy-2,9-dimethyl-8-(methylethenyl)-10-oxo-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydrobenzo[*f*]azulen-4-yl Benzoate* (Decipinone; **2**) *and (2S,3S,3aR,4R,4aR,5R,8S,8aR,9S,10aR)-3,5,10a-Triacetoxy-4a-(acetoxymethyl)-9-hydroxy-2,9-dimethyl-8-(methylethenyl)-10-oxo-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydrobenzo[*f*]-azulen-4-yl Benzoate* (Isodecipinone; **6**). Compounds **2** and **6** were extracted and purified from 2 kg of the air-dried aerial parts of *Euphorbia decipiens* Bioss. & Buhse. The plant material was collected from the mountain of Kandovan in north of Karaj, Iran in May 2000. The compounds were purified by CC, FC, and prep. TLC as described previously [14][15]. ^{13}C-NMR ($CDCl_3$, Data of **6**; assigned by HMQC and HMBC experiments): 43.9 (*t*, C(1)); 38.1 (*d*, C(2)); 78.4 (*d*, C(3)); 53.8 (*d*, C(4)); 70.0 (*d*, C(5)); 47.8 (*s*, C(6)); 68.4 (*d*, C(7)); 122.5 (*d*, C(8)); 137.4 (*d*, C(9)); 149.7 (*s*, C(10)); 46.5 (*d*, C(11)); 43.5 (*d*, C(12)); 81.3 (*s*, C(13)); 202.2 (*s*, C(14)); 90.5 (*s*, C(15)); 14.5 (*q*, C(16)); 63.5 (*t*, C(17)); 113.0 (*t*, C(18)); 20.3 (*q*, C(19)); 23.5 (*q*, C(20)); 21.2 (*q*, *Me*COO); 21.3 (*q*, *Me*COO); 21.4 (*q*, *Me*COO); 21.9 (*q*, *Me*COO); 170.7 (*s*, Me*C*OO); 170.5 (*s*, Me*C*OO); 169.9 (*s*, Me*C*OO); 169.9 (*s*, Me*C*OO); 130.0 (*s*, C(1‴)); 129.9 (*d*, C(2‴), C(6‴)); 128.9 (*d*, C(3‴), C(5‴)); 133.6 (*d*, C(4‴)); 165.4 (*s*, C(7‴)).

*Synthesis of (a*R*)- and (a*S*)-*N*-Hydroxy-2′-methoxy-1,1′-binaphthalene-2-carboximidoyl Chloride* (**3a**) *and* (**3b**). Compounds **3a** and **3b** were synthesized as described in [16][17].

Preparation of **5** *and* **6**. To a soln. of **2** (21 mg, 32.1 μmol) and Et_3N (10 μl, 72 μmol) in $CHCl_3$ (200 μl) **3a** (29 mg, 80.2 μmol) was added. The mixture was stirred for two weeks with monitoring of the progress of reaction by TLC. The mixture was separated by prep. TLC (toluene/AcOEt 75:25). The same procedure was applied for preparation and isolation of the (a*S*)-MBCC derivative **5**. The two major bands were separated from each mixture by TLC and subjected to NMR spectroscopy and only one of them in the (a*R*)-MBCC derivatives revealed to be pure enough. The purity of the compound was tested with RP-HPLC (77.5% aq. MeOH). Compound **4** (7 mg) was detected at t_r 16.16 min in 90% purity. Compound **5** was purified (2 mg) from the mixture of (a*S*)-MBCC derivatives with the same method of purification as for **4** and with t_r 17.26 min. yields for **4** and **5** were calc. 22.6% and 6.5%, resp. The different isomers detected in the HPLC experiments may be due to migration of AcO from C(13) to C(15). The *Scheme* represents the pathway of synthesis for **4** and **5**.

*(2S,3S,3aR,4R,4aR,5R,8S,8aR,9S,10aR)-3,5,9-Triacetoxy-4a-(acetoxymethyl)-10a-hydroxy-8-[3-(a*R*)-(2′-methoxy-[1,1′]binaphthalen-2-yl)-5-methyl-4,5-dihydroisoxazol-5-yl]-2,9-dimethyl-10-oxo-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydrobenzo[*f*]azulen-4-yl Benzoate* (**4**): ^{1}H-NMR: see the *Table*. Data of the MBCC moiety

Scheme. *Synthesis of the (a*R*)- and (a*S*)-MBCC Derivatives* (**4** and **5**) *of Decipinone* (**2**) *and Isodecipinone* (**6**)



($CDCl_3$): 8.02 (*d*, *J* = 9.1); 7.97 (br. *d*, *J* = 6.9, 2 H); 7.92 (*d*, *J* = 8.1); 7.88 (*d*, *J* = 8.1); 7.48 (*m*); 7.35–7.40 (*m*, 4 H); 7.25 (*m*). Data of the MBCC and the benzoyl moieties (C_6D_6): 8.32 (*d*, *J* = 8.6); 8.07 (br. *d*, *J* = 6.6, 2 H); 7.72 (br. *t*, *J* = 7.4, 2 H); 7.65 (br. *t*, *J* = 7.0, 2 H); 7.39 (*d*, *J* = 8.4); 7.22 (*d*, *J* = 8.1); 7.18 (br. *t*, *J* = 6.9); 7.08 (br. *t*, *J* = 7.4); 7.02 (*dd*, *J* = 5.4, 9.1); 7.01 (*m*, 3 H); 6.93 (br. *t*, *J* = 8.1). HR-FD-MS: *m*/*z* 979.3779 (calc. for $C_{57}H_{57}O_{14}N$; found: *m*/*z* 979.3733. ^{13}C-NMR ($CDCl_3$): 47.0 (*t*, C(1)); 37.3 (*d*, C(2)); 79.9 (*d*, C(3)); 56.9 (*d*, C(4)); 71.9 (*d*, C(5)); 49.1 (*s*, C(6)); 66.3 (*d*, C(7)); 126.7* (*d*, C(8)); 133.8* (*d*, C(9)); 90.7 (*s*, C(10)); 44.3 (*d*, C(11)); 41.9 (*d*, C(12); 85.9 (*s*, C(13)); 207.2 (*s*, C(14)); 88.9 (*s*, C(15)); 14.9 (*q*, C(16)); 61.5 (*t*, C(17)); 48.2 (*t*, C(18)); 24.6 (*q*, C(19)); 20.5* (*q*, C(20)); 21.18 (*q*, *Me*COO); 21.16 (*q*, *Me*COO); 21.13 (*q*, *Me*COO); 20.5* (*q*, *Me*COO); 170.1 (*s*, Me*C*OO); 169.9 (*s*, Me*C*OO); 169.8 (*s*, Me*C*OO); 169.4 (*s*, Me*C*OO); 129.8 (*s*, C(1‴)); 129.4 (*d*, C(2‴), C(6‴)); 128.3 (*d*, C(3‴), C(5‴)); 133.1* (*d*, C(4‴)); 165.0 (*s*, C(7‴)); 154.6 (*s*, C(1″)(MBCC)); 157.8 (*s*, C=N); 34.0 (*s*, MBCC); 133.9 (*s*, MBCC); 133.3 (*s*, MBCC); 132.9 (*s*, MBCC); 130.6 (*d*, MBCC); 128.9 (*s*, MBCC); 128.2 (*d*, MBCC); 128.1 (*d*, MBCC); 128.0 (*d*, MBCC); 127.3 (*d*, MBCC); 126.6 (*d*, MBCC); 126.5 (*d*, MBCC); 126.4 (*d*, MBCC); 126.0 (*d*, MBCC); 124.9 (*d*, C(8″)(MBCC)); 124.2 (*d*, MBCC); 120.9 (*s*, MBCC); 113.4 (*d*, C(3″)(MBCC)); 56.5 (*q*, MeO). *: Assignments may be interchanged.

*(2*S*,3*S*,3a*R*,4*R*,4a*R*,5*R*,8*S*,8a*R*,9*S*,10a*R*)-3,5,10a-Triacetoxy-4a-(acetoxymethyl)-9-hydroxy-8-[3-(a*S*)-(2′-methoxy-[1,1′]binaphthalen-2-yl)-5-methyl-4,5-dihydroisoxazol-5-yl]-2,9-dimethyl-10-oxo-1,2,3,3a,4,4a,5,8,8a,9,10,10a-dodecahydrobenzo[*f*]azulen-4-yl Benzoate* (**5**). ^{1}H-NMR: see the *Table*. Data of the MBCC moiety ($CDCl_3$): 8.04 (*d*, *J* = 9.1); 7.98 (br. *d*, *J* = 8.8); 7.94 (*d*, *J* = 8.4); 7.89 (*d*, *J* = 8.6), 7.87 (*d*, *J* = 8.1); 7.52 (*m*); 7.24–7.38 (*m*, 4 H). HR-FD-MS: *m*/*z* 979.3779 (calc. for $C_{57}H_{57}O_{14}N$; found: *m*/*z* 979.3746).

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