Diterpene Polyesters from *Euphorbia seguieriana*

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An Me_2CO extract of *Euphorbia seguieriana* (Euphorbiaceae) afforded seven new diterpene polyesters (**1**−**7**). Five of them (**1**−**5**), having a new parent alcohol that was named 17-hydroxymyrsinol, were structurally related to myrsinol. The other two compounds (**6**, **7**) were new derivatives of the known parent alcohols cyclomyrsinol and lathyrane. The structure elucidations of the new compounds by highfield spectroscopic methods, including 1D and 2D NMR techniques, are described.

Euphorbia seguieriana Necker (Euphorbiaceae) is a glabrous plant widely distributed in the northwest and inner parts of Turkey. In a previous paper on the constituents of *Euphorbia seguieriana* var. *seguieriana*, Jeske et al. reported the presence of new diterpenes in a sample collected from the Botanical Garden in Berlin-Dahlem.[1] In our continuing research on the biologically active compounds from Turkish Euphorbiaceae, we have reported the isolation and structure determination of several new diterpene polyesters from *Euphorbia* species.[2] In this paper, we describe the structures of seven new diterpenes from *Euphorbia seguieriana* collected from Gebze Province near Istanbul (Turkey). The isolated compounds were different from those reported in the literature, thus indicating the ecological importance of a collection site. The structures of the new compounds were elucidated by spectroscopic methods, including 1D and 2D NMR techniques.

Results and Discussion

Spectral properties of compounds **1**−**5** revealed that they possess a new parent diterpene alcohol skeleton and differ in the nature of the ester functions. Compound **1** was obtained as colorless needles and displayed IR absorptions of hydroxyl (3460 cm^{-1}) and carbonyl (1745, 1725 cm^{-1}) groups and unsaturation (1640, 1590 cm^{-1}). The EIMS of **1** established a molecular formula of $C_{40}H_{46}O_{12}N_2$, with a molecular ion peak at *m*/*z* 746. The ^1H and ^{13}C NMR spectra (Table 1) indicated the presence of two acetate groups, two sets of signals of a nicotinoate group, and an isobutyrate group. Excluding the signals of the ester moieties, the ^1H NMR spectrum showed signals for five oxymethine protons at δ 5.45 (t, J = 4 Hz, H-3), 6.08 (d, J = 11 Hz, H-5), 5.24 (d, J = 7 Hz, H-7), 5.26 (s, H-14), and 5.51 (d, J = 5.5 Hz, H-17); a secondary methyl group at δ 0.88 (d, J = 6.8 Hz, H-16); two tertiary methyl groups at δ 1.46 and 1.89; as well as signals for two double bonds: an exocyclic methylene at δ 4.95 (br s) and 5.09 (br s), and a disubstituted double bond at δ 6.15 (ddd, J = 1.5, 7, 10 Hz, H-8) and 5.85 (dd, J = 4, 10 Hz, H-9). A combination of ^{13}C and DEPT NMR spectra showed 40 carbon atoms, including seven CH_3, two CH_2, 20 CH, and 11 quaternary carbons, of which seven are oxygenated (two tertiary alcohols and five ester carbonyls). Based on the molecular ion at *m*/*z* 746 and 19 degrees of unsaturation, of which 13 come from ester residues, 6 degrees of unsaturation for the parent alcohol were revealed, suggesting a tetracyclic skeleton with two double bonds for **1**. A comparison of the data obtained with the parent alcohol myrsinol and its derivatives[3−5] indicated that **1** differs from myrsinol by the presence of a hydroxyl group at C-17 instead of the typical oxymethylene group. In the ^1H NMR spectrum, H-17 was observed at δ 5.51 (δ_C 98.9) as a doublet, transformed to a singlet with D_2O, indicating a free hydroxyl group at C-17. 2D $^1H-^1H$ COSY and $^{13}C-^1H$ HETCOR experiments led to the assignment of all of the vicinal protons and proton-bearing carbons in the molecule. In addition, through spin-decoupling experiments, the sequences H-1 through H-5 and H-7 through H-12 were clearly established. All of the data supported that **1** was a diterpene pentaester of a new parent alcohol structurally related to myrsinol. Assignment of the relative positions of the acyl groups followed from a COLOC spectrum. Cross peaks with the carbonyl carbons and the ester-bearing protons established the locations of the ester groups. The signal at δ 174.9 correlating with the methyl groups at δ 1.03 and 0.98 and the methine proton at δ 5.24 (H-7) indicated attachment of the isobutyryloxy group at C-7. The correlations of the carbonyl carbons of the nicotinoyl groups at δ 165.8 and 164.3 with the protons at δ 5.45 and 5.26, respectively, revealed the substituents at C-3 and C-14 as nicotinoate. The stereochemical features of **1** were assigned by NOE spectroscopy. Irradiation of H-5 increased the intensity of H-12 and H-14, and irradiation of H-4 enhanced the signals of H-3, H-17, and H-7. These results supported the α-configurations for H-17 and H-7. Thus, **1** was assigned to be a new tetracyclic parent alcohol (named 17-hydroxymyrsinol) esterified with an isobutyrate, two nicotinoate, and two acetate groups at C-7, C-3, C-14, C-5, and C-15, respectively.

Compound **3** was a natural acetyl derivative of **1** at C-17. The ^1H NMR data of the acetylated product of **1** were identical to those of **3** and, therefore, **3** was deduced as 3,-14-*O*-dinicotinoyl-5,15,17-*O*-triacetyl-7-*O*-*iso*-butyryl-17-hydroxymyrsinol.

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Table 1. ^{1}H and ^{13}C NMR Data of Compounds **1**, **6**, and **7** ($CDCl_3$)

H	1	6	7	C[a]	1	6	7
1α	2.81 dd (1.5, 11.5)	2.60 dd (9, 16)	2.61 dd (9, 16)	1	44.2 t	43.3 t	46.5 t
1β	2.33 dd (7.5, 11.5)	2.45 m	1.78 m	2	37.3 d	36.4 d	36.0 d
2	2.35 dq (4, 6.8, 1.5, 7.5)	2.42 m	2.64 m	3	77.9 d	78.4 d	78.0 d
3	5.45 t (4)	5.79 t (4)	5.87 t (3.6)	4	51.6 d	51.7 d	49.6 d
4	3.23 dd (4, 11)	3.14 dd	3.28 dd (3.6, 10.1)	5	69.6 d	68.4 d	69.0 d
5	6.08 d (11)	5.93 d (11)	6.14 d (10.1)	6	56.6 s	62.3 s	48.4 s
7	5.24 d (7)		4.96 dd (1.5, 6.2)	7	81.2 d	204.4 s	69.3 d
8	6.15 ddd (1.5, 10, 7)	5.25 d (6.9)	2.32 ddd (7.1, 2.4, 16)	8	124.4 d	70.7 d	29.7 t
8′			1.75 m	9	134.5 d	30.1 d	19.2 d
9	5.85 dd (4, 10)	2.75 dddd (6, 8, 9, 10.5)	0.82 m	10	147.1 s	78.0 s	19.1 s
11	3.45 ddd (4, 5, 1.5)	2.52 dd (9.6, 2)	0.97 m	11	43.3 d	42.1 d	23.5 d
12	3.37 d (5)	4.27 d (12.4)	2.18 d (7.4)	12	37.6 d	41.9 d	42.1 d
14	5.26 s	5.46 s		13	89.6 s	90.2 s	79.8 s
16	0.88 d (6.8)	0.88 d (7.2)	0.96 m	14	63.4 d	84.1 d	213.2 s
17	5.51 d (5.5)	4.34 d (9.8)	0.99 s	15	90.0 s	90.0 s	82.9 s
17′		3.67 d (9.8)		16	14.2 q	14.1 q	15.2 q
18	4.95 br s	3.03 dd (11.1, 4.9)	5.50 d (12.3)	17	98.9 d	62.3 t	15.8 q
18′	5.09 br s	2.68 m	4.71 d (12.3)	18	113.4 t	34.7 t	62.4 t
19	1.89 s	162.2 s	1.10 s	19	19.4 q	24.6 q	28.7 q
20	1.46 s	1.27 s	1.71 s	20	25.5 q	22.1 q	23.6 q
ONic	9.12 d (2)	9.22	9.18	ONic	164.3 s	166.3	164.4
	8.80 dd (2, 4.8)	8.81	8.71		153.5 d	153.6	153.5
	8.27 dt (2, 8)	8.37	7.93		123.4 d	123.3	123.2
	7.42 dd (8, 4.8)	7.43	7.30		137.5 d	137.0	137.1
ONic	9.08 d	9.12	9.10		127.0 s	126.2	125.4
	8.74 dd	8.81	8.65		150.6 d	150.1	150.9
	8.20 dt	8.23	7.88	O−Nic	165.8 s	166.1	165.3
	7.36 dd	7.43	7.14		152.9 d	153.6	153.5
O-*i*-Bu	0.98 d (7)	0.66 d			123.1 d	123.6	123.3
	1.03 d (7)	1.10 d			137.0 d	137.5	137.1
	2.21 sept. (7)	2.46 m			125.6 s	126.1	126.7
OBz			7.35 dd (7.1, 7.1)		150.0 d	151.0	150.9
			6.89 ddd (7.1, 7.1, 0.5)	OBz	164.3 s		
			7.16 m		129.3 d		
OAc	2.21 s	2.37	1.98		127.7 d		
	1.96 s	1.99			132.7 d		
		1.97			128.2 s		
OH[b]			4.03 br s	O-*i*-Bu	174.9 s	175.2	
			3.92 br s		18.3 q	20.9	
					18.2 q	17.8	
					34.3 d	34.4	
				OAc	168.6 s	168.1	170.1
					22.6 q	29.8	21.5
				OAc	162.8 s	169.0	
					20.8 q	20.1	
				OAc		169.7	
						23.4	

[a] Multiplicities were assigned by DEPT (90° and 135°) spectra. [b] D_2O exchangeable.

The relative locations of the acyl groups in compounds **2**, **4**, and **5** were deduced from their COLOC spectra. In each compound cross peaks between the protons adjacent to the ester moieties and the corresponding carbonyl carbons permitted location of the substituents. The five ester residues detected were by 5,15-*O*-diacetate-7-*O*-benzoate-3,14-*O*-dinicotinoate for **2**; 3-*O*-propionate-5,15-*O*-diacetate-7-*O*-benzoate-14-*O*-nicotionate for **4**; and 5,15-*O*-diacetate-3,7,14-*O*-trinicotinoate for **5**.

The EIMS of **6** gave a molecular ion peak at *m*/*z* 804 corresponding to the molecular formula $C_{42}H_{48}O_{14}N_2$. From the ^{1}H and ^{13}C NMR spectra (Table 1) the presence of an isobutyrate, two nicotinoate, and three acetate groups were observed as ester substituents. The ^{13}C NMR spectrum showed that 42 carbon atoms consisted of eight CH_3, three CH_2, 19 CH and, by difference from a broadband spectrum, 12 quaternary carbons. These data were confirmed by ^{1}H−^{13}C COSY correlations between each of the protons and carbons as shown in Table 1. The spectral data of the diterpene skeleton moiety were compatible with the known parent alcohol, cyclomyrsinol, which was previously reported from *Euphorbia* species.[1,6] All of the vicinal protons were deduced by a ^{1}H−^{1}H COSY experiment and by successive spin-decoupling experiments. The partial structures of H-8 through H-12 and H-1 through H-5 were unambiguously assigned. The HMBC spectrum of **6** was very useful for the assignment of the location of acyl substituents (Figure 1). Thus **6** was assigned the structure 5,14-*O*-dinicotinoyl-8-*O*-*iso*-buytryl-3,10,15-*O*-triacetyl-cyclomyrsinol.

The molecular formula of **7** was assigned as $C_{41}H_{44}O_{11}N_2$ by EIMS spectrometry, with the molecular ion peak at *m*/*z* 740. The IR spectrum showed the strong absorptions of hydroxyl (3475 cm^{-1}), carbonyl (1735, 1274 cm^{-1}), and ketone (1712 cm^{-1}) groups. The ^{1}H NMR spectrum (Table 1) exhibited a secondary methyl doublet (δ 0.96, J = 6.8 Hz, H-16), three tertiary methyl singlets (δ 0.99, 1.10 and 1.71), three oxymethine protons geminal

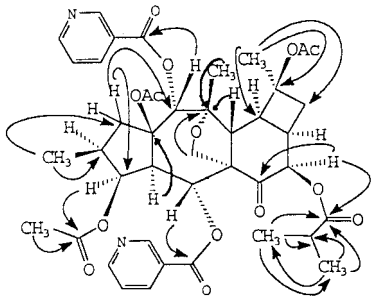


Figure 1. HMBC correlations of compound **6**.

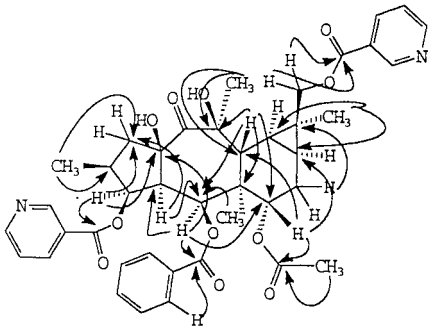
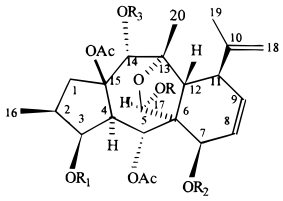
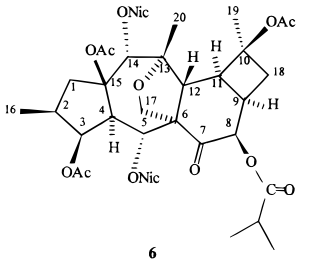


Figure 2. HMBC correlations of compound **7**.

to ester functions (δ 5.87 t, J = 3.6 Hz, H-3; 6.14 d, J = 10.1 Hz, H-5; 4.96 dd, J = 1.5, 6.2 Hz, H-7), and a pair of doublets for an isolated oxymethylene group (δ 5.50 d, J = 12.3 Hz, 4.71 d, J = 12.3 Hz, H-18 and H-18′). Further analysis revealed the presence of two nicotinoyl, one benzoyl, and one acetyl group as ester moieties that were supported by the fragment ions at *m/z* 124 $[C_5H_4NCO_2H+H]^+$, 106 $[C_5H_4NCO]^+$, and 43 $[CH_3CO]^+$. The ^{13}C NMR (APT) spectrum of **7** showed resonances for all 41 carbons in the molecule. The multiplicities were determined by DEPT experiments, which showed the presence of five CH_3, three CH_2, 21 CH, and 12 quaternary carbons. A quaternary carbon resonating at δ 19.0 suggested a three-membered ring system in the molecule.[7] Integration of these data and the observed molecular ion peak at *m/z* 740 and 21 degrees of unsaturation all supported the presence of a tetracyclic diterpene moiety, $C_{20}H_{27}O_7$, esterified with two nicotinic acid, one benzoic acid, and one acetic acid residue. All proton signals were assigned by $^1H-^1H$-COSY and extensive spin-decoupling experiment. Starting with H-5 (δ 6.14) and then H-7 (δ 4.96), the sequences H-1 to H-5 and H-7 to H-9 were unambiguously deduced. Further irradiation of H-9 (δ 0.82) allowed the assignment of H-11 and H-12. The locations of the ester groups were established by an HMBC spectrum. HMBC correlations of δ_C 165.1 to δ_H 5.87 (H-3), of δ_C 164.3 to δ_H 6.14 (H-5) and 7.35 (H-2′,H-6′), and of δ_C 170.1 to δ_H 4.96 (H-7) indicated that nicotinoyl, benzoyl, and acetyl groups were at C-3, C-5, and C-7, respectively (Figure 2). NOESY experiments led to the assignment of stereochemistry of the molecule. Irradiation of H-5, of which the coupling constant indicated a trans A,B ring junction and a β-configuration, caused enhancements of the signals of H-1, H-12, and H-7, thereby supporting a β-configuration for each of these protons. H-2, H-3, and the C-19 methyl were assigned to α-orientations based on the NOE enhancements on irradiation of H-4, and the NOE between one of the methylene protons at C-18 and H-12 was also observed. Consequently, all of the data supported the proposed structure **7** for the isolate, which was identified as 7-*O*-acetyl-5-*O*-benzoyl-13,15-dihydroxy-3,18-*O*-dinicotinoyl-14-oxo-lathyrane.



	R	R_1	R_2	R_3
1	H	Nic	iBut	Nic
2	H	Nic	Bz	Nic
3	Ac	Nic	iBut	Nic
4	H	Prop	Bz	Nic
5	H	Nic	Nic	Nic



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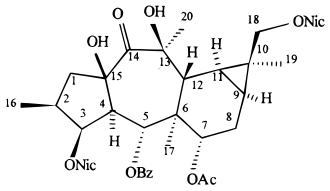

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Experimental Section

General Experimental Procedures. UV spectra were obtained on a Varian DMF 90. IR spectra were recorded on a Perkin−Elmer 983. Optical rotations were measured on an Opt. Act. Ltd. AA-5 model polarimeter. ^1H (200 MHz) and ^{13}C (50.32 MHz) spectra were recorded on a Bruker AC 200 L. HMQC and HMBC spectra were measured on a Varian XL-300 MHz instrument for compounds **6** and **7**. HRMS and LRMS were recorded on a VG analytical Zabspec instrument.

Plant Material. *Euphorbia seguieriana* Necker was collected in July 1995, from Turkey (Gebze). A voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul (ISTE 63003).

Extraction and Isolation. Air-dried, whole plant material (1.45 kg) was macerated with MeOH at room temperature, concentrated in vacuo, dissolved in Me_2CO-H_2O (2:1), and then partitioned with *n*-hexane. The aqueous phase was extracted with $CHCl_3$ and the $CHCl_3$ phase evaporated in vacuo below 40 °C. The crude residue (19.2 g) was subjected to Si gel column chromatography (250 g) using hexane, a gradient of Me_2CO up to 100%, and finally MeOH. Similar fractions were combined and further separated on small Si gel columns as necessary. Fractions were additionally separated on a Chromatotron using a Si gel rotor (hexane−$CHCl_3$−Me_2CO, 40:55:5). Final purification of the isolates was achieved by prepative. TLC on Si gel (hexane−Me_2CO; 9:1 and 4:1). The yields were as follows: **1** (80 mg, 0.006%), **2** (24 mg, 0.002%), **3** (4.1 mg, 0.0003%), **4** (6 mg, 0.0004%), **5** (10 mg, 0.0007%), **6** (7.4 mg, 0.0005%), and **7** (12 mg, 0.0008%).

Compound 1: mp 205−207 °C (uncorrected); UV (EtOH) λ_{max} (log ϵ) nm 260 (0.700), 258 sh, 220 (1.500); IR ($CHCl_3$) ν_{max} 3460, 2980, 2880, 1745, 1725, 1640, 1590, 1470, 1420, 1375, 1279, 1240, 1220, 1160, 1120, 1068, 940, 760 cm^{-1}; $[\alpha]_D$ −0.65° (*c* 10.9, $CHCl_3$); EIMS *m/z* 746 $[M^+, C_{40}H_{46}O_{12}N_2]$ (23), 728 (4), 686 (10), 658 (27), 640 (74), 613 (9), 654 (14), 564 (14), 510 (11), 464 (18), 422 (19), 306 (10), 281 (21), 264 (43), 249 (26), 235 (23), 207 (11), 189 (13), 166 (25), 145 (18), 125 (100), 105 (99), 81 (29), 71 (31); HREIMS *m/z* 746.3058 (calcd for 746.3049); ^1H NMR and ^{13}C NMR, see Table 1.

Compound 2: UV (EtOH) λ_{max} (log ϵ) nm 262 (0.730), 251sh, 221 (1.500); IR ($CHCl_3$) ν_{max} 3455, 2982, 2880, 1743, 1727, 1640, 1590, 1472, 1375, 1280, 1238, 1161, 1120, 1068, 940, 760 cm^{-1}; $[\alpha]_D$ −0.45° (*c* 10.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.82 (H-1α), 2.33 (H-1β), 2.35 (H-2), 5.46 (H-3), 3.28 (H-4), 6.27 (H-5), 5.42 (H-7), 6.33 (H-8), 5.88 (H-9), 3.47 (H-11), 3.53 (H-12), 5.31 (H-14), 0.89 (H-16), 5.59 (H-17), 4.93 (H-18), 5.05 (H-18′), 1.89 (H-19), 1.50 (H-20), ONic 9.11, 8.81, 8.28, 7.45, ONic 9.07, 8.68, 8.05, 7.22, OBz 7.89, 7.44, 7.30, OAc 2.33, 1.94; ^{13}C NMR ($CDCl_3$) δ 44.3 (C-1), 37.4 (C-2), 77.9 (C-3), 51.7 (C-4), 69.6 (C-5), 57.0 (C-6), 81.4 (C-7), 124.7 (C-8), 134.9 (C-9), 147.2 (C-10), 43.4 (C-11), 37.9 (C-12), 89.9 (C-13), 64.6 (C-14), 90.1 (C-15), 14.3 (C-16), 98.9 (C-17), 113.5 (C-18), 19.7 (C-19), 25.6

(C-20), ONic 165.4, 153.6, 123.4, 137.5, 126.8, 151.0, ONic 164.4, 152.8, 123.1, 137.0, 124.8, 150.3, OBz 164.5, 129.3, 128.1, 132.6, 130.8, OAc 168.4, 22.7, OAc 168.1, 20.6; EIMS *m/z* 780 [M^+, $C_{43}H_{44}O_{12}N_2$] (3), 762 [$M-H_2O]^+$ (4), 720 (13), 674 (57), 616 (11), 558 (13), 552 (12), 510 (14), 492 (13), 464 (16), 447 (9), 422 (16), 404 (12), 387 (16), 369 (18), 306 (13), 281 (21), 264 (45), 249 (28), 235 (26), 228 (24), 221 (38), 209 (11), 189 (11), 166 (23), 145 (20), 124 (96), 105 (100), 104 (93), 78 (32); HREIMS *m/z* 780.2913 (calcd for 780.2893).

Compound 3: UV (EtOH) λ_{max} (log ϵ) nm 281 sh, 267 sh, 260 (0.730), 222 (1.550); IR ($CHCl_3$) ν_{max} 2980, 2880, 1738, 1725, 1641, 1595, 1470, 1420, 1375, 1279, 1240, 1160, 1120, 1068, 940, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.81 (H-1α), 2.33 (H-1β), 2.34 (H-2), 5.45 (H-3), 3.25 (H-4), 6.12 (H-5), 5.11 (H-7), 5.97 (H-8), 5.74 (H-9), 3.38 (br s, H-11), 3.38 (br s, H-12), 5.30 (H-14), 0.89 (H-16), 6.43 (s, H-17), 4.96 (H-18), 5.09 (H-18′), 1.89 (H-19), 1.45 (H-20), ONic 9.12, 8.79, 8.27, 7.42, ONic 9.07, 8.72, 8.22, 7.36, O-*i*-Bu 0.96, 1.05, OAc 2.20, 2.02, 1.98; EIMS *m/z* 788 [M^+, $C_{42}H_{48}O_{13}N_2$]; (88), 746 (13), 729 (56), 701 (43), 682 (34), 659 (44), 641 (16), 606 (22), 598 (14), 580 (16), 564 (50), 539 (11), 493 (16), 470 (52), 469 (53), 441 (15), 427 (75), 415 (22), 367 (36), 334 (12), 319 (63), 293 (34), 265 (61), 247 (58), 225 (46), 221 (54), 189 (84), 172 (71), 147 (59), 124 (100), 106 (97), 78 (73), 71 (64); HREIMS *m/z* 788.3166 (calcd for 788.3153).

Compound 4: UV (EtOH) λ_{max} (log ϵ) nm 261 (0.720), 258 sh, 221 (1.550); IR ($CHCl_3$) ν_{max} 3455, 2982, 2875, 1747, 1726, 1641, 1590, 1473, 1420, 1380, 1274, 1245, 1160, 1120, 938, 760 cm^{-1}; $[\alpha]_D$ −0.05° (*c* 2.08, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.74 (H-1α), 2.63 (H-1β), 2.11 (H-2), 5.21 (H-3), 3.08 (H-4), 6.16 (H-5), 5.40 (H-7), 6.36 (H-8), 5.85 (H-9), 3.46 (br s, H-11), 3.46 (br s, H-12), 5.23 (H-14), 0.82 (H-16), 5.56 (H-17), 4.91 (H-18), 5.07 (H-18′), 1.87 (H-19), 1.47 (H-20), ONic 9.09, 8.80, 8.28, 7.43, OBz 8.02, 7.54, 7.38, OProp 0.95 t, 2.13 q, OAc 2.20, 1.95; ^{13}C NMR ($CDCl_3$) δ 44.3 (C-1), 37.4 (C-2), 77.8 (C-3), 51.6 (C-4), 69.5 (C-5), 56.6 (C-6), 81.3 (C-7), 124.5 (C-8), 134.5 (C-9), 147.1 (C-10), 43.4 (C-11), 37.9 (C-12), 89.9 (C-13), 64.3 (C-14), 90.0 (C-15), 14.3 (C-16), 98.9 (C-17), 113.4 (C-18), 19.4 (C-19), 25.5 (C-20), ONic 165.4, 153.5, 123.4, 137.5, 126.8, 151.0, OBz 165.6, 129.4, 127.8, 131.2, 130.8, OProp 174.4, 27.8, 8.8, OAc 168.6, 22.7, OAc 168.4, 20.8; EIMS *m/z* 731.9 [M^+, $C_{40}H_{45}O_{12}N_1$] (100), 713 (14), 703 (84), 685 (17), 671 (27), 660 (10), 644 (12), 625 (76), 610 (27), 582 (15), 565 (28), 549 (27), 503 (84), 491 (18), 479 (14), 472 (23), 443 (54), 421 (32), 415 (60), 369 (18), 293 (16), 281 (29), 264 (45), 249 (30), 239 (33), 221 (47), 189 (20), 162 (21), 145 (21), 131 (18), 124 (100); HREIMS *m/z* 731.2986 (calcd for 731.2936).

Compound 5: UV (EtOH) λ_{max} (log ϵ) nm 280 sh, 258 sh, 260 (0.700), 222 (1.500); IR ($CHCl_3$) ν_{max} 3460, 2980, 2880, 1748, 1725, 1645, 1590, 1470, 1425, 1377, 1275, 1240, 1162, 1068, 940, 762 cm^{-1}; $[\alpha]_D$ −0.1° (*c* 3.72, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.82 (H-1α), 2.31 (H-2), 5.45 (H-3), 3.31 (H-4), 6.25 (H-5), 5.38 (H-7), 6.28 (H-8), 5.90 (H-9), 3.49 (br s, H-11), 3.49 (br s, H-12), 5.31 (H-14), 0.89 (H-16), 5.49 (H-17), 4.96 (H-18), 5.09 (H-18′), 1.89 (H-19), 1.48 (H-20), ONic 9.12, 8.81, 8.28, 7.44, ONic 9.10, 8.69, 8.12, 7.30, ONic 9.02, 8.67, 8.05, 7.27, OAc 2.32, 1.94. ^{13}C NMR ($CDCl_3$) δ 44.2 (C-1), 37.4 (C-2), 77.9 (C-3), 51.5 (C-4), 69.5 (C-5), 56.6 (C-6), 81.3 (C-7), 124.5 (C-8), 134.4 (C-9), 147.1 (C-10), 43.5 (C-11), 37.6(C-12), 89.5 (C-13), 63.5 (C-14), 90.0 (C-15), 14.2 (C-16), 98.9 (C-17), 113.4 (C-18), 19.4 (C-19), 25.5 (C-20), ONic 164.3, 153.7, 136.8, 128.5, 123.2, 150.8, ONic 166.5, 153.7, 137.5, 129.5, 150.8, 123.2, ONic 164.3, 152.9, 136.8, 128.6, 122.5, 150.3, OAc 168.6, 22.6, OAc 168.2, 24.9; EIMS *m/z* 781 [M^+, $C_{42}H_{43}O_{12}N_3$] (12), 764 (78), 735 (10), 717 (59), 702 (29), 675 (14), 659 (64), 641 (31), 615 (22), 599 (60), 582 (18), 539 (21), 522 (16), 492 (46), 470 (73), 427 (79), 416 (32), 386 (31), 296 (40), 263 (52), 247 (63), 229 (83), 222 (46), 189 (46), 175 (83), 166 (84), 145 (52), 124 (99), 106 (100), 79 (70); HREIMS *m/z* 781.2801 (calcd for 781.2845).

Compound 6: Mp 255 °C (uncorr.); UV (EtOH) λ_{max} (log ϵ) nm 260 (1.300), 255 (1.130), 230 (1.500); IR ($CHCl_3$) ν_{max} 3071, 2988, 2980, 1739, 1721, 1604, 1595, 1371, 1280, 1225, 1140, 1110, 1020, 720 cm^{-1}; $[\alpha]_D$ +10° (*c* 2.87, $CHCl_3$); EIMS *m/z* 804 [M^+, $C_{42}H_{48}O_{14}N_2$] (44), 762 (30), 745 (40), 698 (36), 674 (9), 659 (16), 638 (10), 580 (13), 469 (30), 446 (21), 427 (66), 336 (14), 296 (19), 279 (28), 247 (21), 235 (55), 205 (16), 191 (35), 166 (18), 149 (36), 124 (100), 106 (87), 97 (23), 80 (25), 71 (46), 57 (35), 43 (34); HREIMS *m/z* 804.3102 (calcd for 804.3103); ^1H NMR and ^{13}C NMR, see Table 1.

Compound 7: Mp 178 °C; UV (EtOH) λ_{max} (log ϵ) nm 260 (0.700), 253 (0.630), 220 (1.500); IR ($CHCl_3$) ν_{max} 3475, 3071, 2981, 1735, 1712 1600, 1585, 1380, 1274, 1120, 740, 720 cm^{-1}; $[\alpha]_D$ −0.15° (*c* 10.5, $CHCl_3$); EIMS *m/z* 740 [M^+, $C_{41}H_{44}O_{11}N_2$] (14), 697 (21), 680 (63), 665 (10), 637 (10), 435 (6), 417 (11), 393 (17), 374 (18), 312 (14), 294 (10), 281 (13), 269 (27), 251 (46), 239 (48), 223 (16), 221 (9), 175 (19), 124 (100), 104 (96), 77 (9); HREIMS *m/z* 740.2938 (calcd for 740.2946); ^1H NMR and ^{13}C NMR, see Table 1.

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