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ALEPPICATINES A AND B FROM *EUPHORBIA ALEPPICA**

SEVIL ÖKSÜZ,†‡ FALIHA GÜREK,‡ LONG-ZE LIN,§ ROBERTO R. GIL,§ JOHN M. PEZZUTO§ and GEOFFREY A. CORDELL§

†Department of Chemistry, Faculty of Pharmacy, University of Istanbul, 34452 Istanbul, Turkey; ‡TUBITAK Marmara Research Centre, Research Institute for Basic Sciences, Department of Chemistry, P.O. 21, 41470 Gebze, Turkey; §Program for Collaborative Research in the Pharmaceutical Sciences, Department of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, University of Illinois at Chicago, Chicago, IL 60612, U.S.A.

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Key Word Index—*Euphorbia aleppica*; Euphorbiaceae; aleppicatines A and B; pentacyclic diterpene polyesters; cycloartane-type triterpenoids; coumarin; flavone; aromatics.

Abstract—Two new pentacyclic diterpene polyesters, aleppicatine A and B, have been isolated from the acetone extract of the whole plant of *Euphorbia aleppica*, in addition to five known cycloartane-type triterpenes (24-methylenecycloartanol, cyclolaudenol, cycloart-25-en-3β-ol-24-one, cycloart-22-en-3β,25-diol and cycloart-25-en-3β,24-diol), scopoletin, kaempferol and 4-hydroxybenzoic acid and its methyl ether. The structures of the new compounds and their hydrolysis products have been extensively characterized by high-field NMR spectroscopic methods, including 2D NMR techniques.

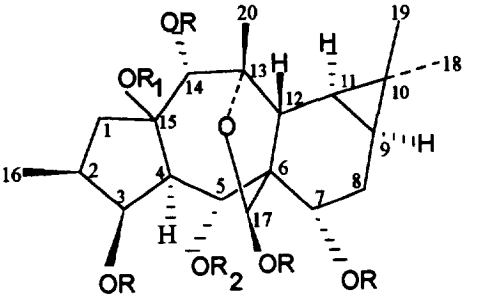
INTRODUCTION

Plants of the genus *Euphorbia* have been the source of a large number of biologically active compounds, and considerable attention has been given to the skin-irritant diterpene esters [2, 3]. As a part of our ongoing search for biologically active diterpenes from the Turkish Euphorbiaceae [1], we have investigated the chemical constituents of *E. aleppica* L., a shrub which is widely distributed in the northwest of Turkey, and which has not been investigated previously. We describe here the isolation, characterization and structural elucidation of two new pentacyclic diterpene polyesters from the whole plant extract of *E. aleppica*.

RESULTS AND DISCUSSION

An acetone extract of *E. aleppica* was partitioned with *n*-hexane. This extract yielded a mixture of triterpenoids by column chromatography on silica gel, from which five known cycloartane-type triterpenoids, namely, 24-methylenecycloartanol, cycloart-22-en-3β,25-diol, cycloart-25-en-3β-ol-24-one, cycloart-25-en-3β,24-diol and cyclolaudenol, were isolated.

The remaining acetone extract afforded two new pentacyclic diterpene polyesters, **1** and **2**. Aleppicatine A (**1**) was obtained as a glassy gum. Its molecular formula was assigned as $C_{35}H_{48}O_{13}$ by CI-mass spectrometry: molecular ion peak at *m/z* 675 $[M-1]^+$ and two prominent peaks at *m/z* 617 $[M-OAc]^+$ and 557 $[M-2\times60]^+$. The IR spectrum showed intense carbonyl absorption bands (1735, 1740, and 1760 cm^{-1}) and unsaturation (1650 cm^{-1}). The ^1H NMR spectrum of **1** in $CHCl_3$ (Table 1) displayed five proton signals geminal to the ester functions at δ 6.58 *s*, 5.85 *d* (J = 11 Hz), 5.69 *s*, 5.03 *dd* (J = 3 and 10 Hz) and 5.12 *t* (J = 4 Hz) for H-17, H-5, H-14, H-7 and H-3, respectively. One secondary methyl doublet at δ 0.83,



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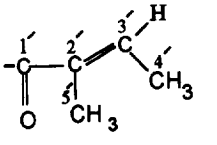
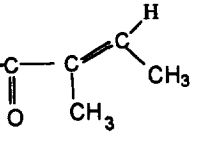


2 R=OAc R_1=R_2=



* Part 4 in the series 'Biologically Active Compounds from the Euphorbiaceae'. For part 3 see ref. [1].

Table 1. ^{1}H NMR spectra of compounds **1** and **2** (200 MHz, in $CDCl_3$)

H	**1**	**1** (C_6D_6)	**2**	**1a**	**1b**
1a	2.39 *dd*	2.48 *dd*	2.38 *dd*	2.38 *dd*	3.08 *dd*
1b	1.78 *dd*	1.81 *dd*	1.71 *dd*	1.76 *dd*	1.62 *m*
2	1.97 *m*	1.62 *dddq*	1.92 *m*	1.95 *m*	1.98 *m*
3	5.12 *t*	5.22 *t*	5.08 *t*	5.04 *t*	5.02 *t*
4	3.14 *dd*	3.21 *dd*	3.16 *dd*	3.14 *dd*	2.62 *dd*
5	5.85 *d*	6.11 *d*	5.86 *d*	5.82 *d*	5.81 *d*
7	5.03 *dd*	5.36 *dd*	5.03 *dd*	5.14 *dd*	5.13 *dd*
8a	1.87 *m*	1.95 *ddd*	1.94 *m*	1.95 *m*	1.93 *m*
8b	1.38 *m*	1.32 *ddd*	1.35 *m*	overlapped	1.37 *m*
9	0.98 *ddd*	0.85 *m*	0.98 *m*	0.98 *ddd*	0.97 *ddd*
11	0.87 *dd*	0.85 *m*	0.88 *dd*	0.87 *dd*	0.89 *dd*
12	2.55 *d br*	2.69 *d br*	2.58 *d br*	2.43 *d br*	2.47 *d br*
14	5.69 *s*	6.02 *s*	5.69 *s*	5.63 *s*	4.16 *d*†
16	0.83 *d*	0.78 *d*	0.80 *d*	0.81 *d*	0.81 *d*
17	6.58 *s*	7.11 *s*	6.58 *s*	5.58 *s*	5.57 *s*
18	1.06 *s*	0.84 *s*	1.07 *s*	1.06 *s*	1.05 *s*
19	1.03 *s*	0.82 *s*	1.02 *s*	1.01 *s*	0.99 *s*
20	1.32 *s*	1.48 *s*	1.29 *s*	1.36 *s*	1.53 *s*
$COCH_3$	2.19 *s*	2.04 *s*	2.08 *s*	2.07 *s* (×2)	2.06 *s*
	2.11 *s*	1.79 *s*	2.05 *s*	1.82 *s*	2.04 *s*
	2.05 *s* (×2)	1.78 *s*	1.79 *s*	1.79 *s*	1.81 *s*
	1.79 *s*	1.72 *s*			
		1.58 *s*			
Tigloyl	6.85 *q br*	7.04 *q br*	6.99 *q br*	6.80 *q br*	6.79 *q br*
	—	—	6.85 *dq*	—	—
	1.84 *s br*	1.89 *s br*	1.87 *s br*	1.89 *s br*	1.84 *s br*
	1.78 *d br*	1.42 *d br*	1.82 *s br*	1.80 *d br*	1.79 *d br*
	—	—	1.80 *d br*	—	—
	—	—	—	—	2.94 *d*‡

*500 MHz.

J (Hz, in C_6D_6) for **1** and **2**: 1a,2α = 8; 1b,2α = 11; 1a,1b = 15; 2α,3α = 4; 2α,16 = 7; 3α,4α = 4; 4α,5β = 11; 7β,8α = 10; 7β,8β = 3; 8α,8β = 14; 8β,9α = 3; 8α,9α = 9; 9α,11α = 10; 11α,12β = 9.

†Singlet with D_2O.

‡Exchangeable with D_2O.

three tertiary methyl singlets at δ 1.06, 1.03 and 1.32, one olefinic proton at δ 6.85 as a quartet of quartets, a broad singlet at δ 1.84 and acetyl methyl group singlets at δ 2.19, 2.11, 2.05 and 1.79 were observed. Compound **1** afforded a better resolved ^{1}H NMR spectrum in benzene-d_6. In the upfield region, the acetyl methyl group singlets were seen at δ 1.58, 1.72, 1.78, 1.79 and 2.04, an a broad doublet at δ 1.42 for a secondary methyl group and one tertiary methyl singlet at δ 1.89 along with the *br q* at δ 7.04 clearly indicated the presence of one tigloyloxy and five acetoxy groups in the molecule. All of the proton assignments were achieved by extensive spin-decoupling experiments in benzene-d_6 (Table 2). Starting with H_a-1 (*dd*, δ 2.48) and then H-7 (*dd*, δ 5.36), the sequences H_a-1 to H_5 and $H_7$to H_9 were easily deduced. Irradiation of H-7 (*dd*, J = 3, 10 Hz) simplified the signals centred at δ 1.95 and 1.32, suggesting that they were H_a-8 and H_b-8, respectively. Irradiation of the doublet of doublets at δ 3.21 (J = 4 and 11 Hz, H-4) turned the triplet at δ 5.22 (J = 4 Hz, H-3) into a doublet and the doublet at δ 6.11 (J = 11 Hz, H-5) into a singlet, following irradiation of H-3 led to the sequence H-2-H_a-1-H_b-1. Finally, irradiation of the signal at δ 7.04 (*br q* J = 1.5 and 7 Hz, H-3′) collapsed the broad doublet at δ 1.42 (J = 1.5 and 7 Hz, H-4′) to a broad singlet, while the broad singlet at δ 1.89 (H-5′) was sharpened. The ^{13}C NMR (APT) spectrum of **1** displayed 11 CH_3, two CH_2, six CH, five CHO and 11 quaternary carbons. All of the multiplicities were assigned by DEPT spectra. Quaternary carbons of the ester carbonyls were present at δ 165.7 for the tigliate residue and at δ 168.1, 169.6, 170.1 and 170.6 for 'four' acetate moieties. However, in selective INEPT experiments in $CDCl_3$, irradiation of the proton singlets at δ 6.58 and 5.69 enhanced the signals at δ 169.57 and 169.62, respectively. In the BB ^{13}C NMR spectrum, there was one singlet at δ 169.6, which was the average value of the former two resonances. This evidence suggested that the peak at δ 169.59 comes from superposition of *two* carbonyl signals, and was indicative of the presence of five acetoxy and one tigloyloxy groups in the molecule. The latter was also confirmed with the fragments at *m/z* 101 and 83 in its EI-mass spectrum. A quaternary carbon singlet at δ 19.2 with two methyl carbons at δ 27.8 and 15.8 suggested a three-membered ring with a *gem*-dimethyl group [4, 5]. The COSY spectrum (500 MHz, $CDCl_3$) of **1** established the relationships between the

Table 2. ^{1}H NMR spin-decoupling experiments with compounds **1***, **1a** and **1b**†

Compounds	Irradiated H δ (ppm)	Observed H δ (ppm)	Multiplicity changes	
1	3.21 (H-4)	6.11 (H-5)	*d*	*s*
		5.22 (H-3)	*t*	*d* (J = 4 Hz)
	5.22 (H-3)	3.21 (H-4)	*dd*	*d* (J = 11 Hz)
		1.62 (H-2)	*dddq*	*ddq* (J = 8, 11, 7 Hz)
	2.48 (H_a-1)	1.81 (H_b-1)	*dd*	*d* (J = 11 Hz)
		1.62 (H-2)	*dddq*	*ddd* (J = 11, 4, 7 Hz)
	1.62 (H-2)	0.78 (H-16)	*d*	*s*
		3.21 (H-3)	*t*	*d* (J = 4 Hz)
		1.81 (H_b-1)	*dd*	*d* (J = 15 Hz)
		2.48 (H_a-1)	*dd*	*d* (J = 15 Hz)
	7.04 (H-3′)	1.42 (H-4′)	*br d*	*br s*
		1.89 (H-5′)	*br s*	Sharpened
	1.32 (H_b-8)	5.36 (H-7)	*dd*	*d* (J = 10 Hz)
		1.95 (H_a-8)	*ddd*	*br t* (J = 10 Hz)
		0.85 (H-9)	*m*	Simplified
	5.37 (H-7)	1.32 (H_b-8)	*ddd*	*dd* (J = 3, 14 Hz)
		1.95 (H_a-8)	*ddd*	*dd* (J = 10, 14 Hz)
	1.42 (H-4′)	7.04 (H-3′)	*br q*	*br s*
	1.89 (H-5′)	7.04 (H-3′)	*br q*	*q*
1a	*ca* 0.90	1.95 (H_a-8)	*m*	Simplified
	(H-9 and H-11)	2.43 (H-12)	*d*	*s*
	1.90-2.00	2.38 (H-1a)	*dd*	*d* (J = 15 Hz)
	(H-2 and H_a-8)	5.04 (H-3)	*t*	*d* (J = 4 Hz)
		5.14 (H-7)	*dd*	*d* (J = 3 Hz)
		0.81 (H-16)	*d*	*s*
		0.98 (H-9)	*ddd*	*dd* (J = 3, 9 Hz)
1b	1.62 (H_b-1)	3.08 (H_a-1)	*dd*	*d* (J = 8 Hz)
		1.98 (H-2)	*m*	Simplified
	1.98	1.62 (H_b-1)	*m*	Simplified
	(H-2 and H_a-8)	0.81 (H-16)	*d*	*s*
		1.37 (H_b-8)	*m*	Simplified
		5.13 (H-7)	*dd*	*d* (J = 3 Hz)

*In C_6D_6.
†In $CDCl_3$.

signals at δ 0.83 (Me-16) and 1.97 (H-2); δ 2.55 (H-12) and 0.87 (H-11); δ 0.98 (H-9), 1.38 (H_b-8) and 1.87 (H_a-8); and δ 5.03 (H-7), 1.38 (H_b-8) and 1.87 (H_a-8), which allowed the unambiguous assignment of the upperfield protons such as H-9, H-11 and H_2-8 which could not be completely assigned by spin-decoupling experiments due to the proximity of these protons. HETCOR experiments led to the assignment of all of the protons and their respective carbons in the molecule. Of interest was the correlation between the proton singlet at δ 6.58 and the carbon resonance at δ 97.9, which suggested the presence of a secondary carbon between two oxygen atoms.

The ^{1}H NMR spectrum of **1** indicated the nature of the ester functions. The location of the acylating groups could be obtained, in part, by transesterification reactions and through a sequence of selective INEPT experiments [6]. Partial hydrolysis of **1** with 0.1 M sodium methoxide–methanol at room temperature furnished two hydrolysis products, **1a**, and **1b**. The ^{1}H and ^{13}C NMR spectra of **1a** revealed the removal of one acetoxy group from **1** showing a diamagnetic shift for H-17 from δ 6.58 to 5.58 (δ 98.7) and the lack of one of the acetoxy group resonances (δ 2.19, 170.6 and 23.6). The ^{1}H and ^{13}C NMR spectra of **1b** showed the removal of two acetoxy groups from **1**. The singlets at δ 6.58 (δ 98.3) and 5.69 (δ 74.3) were shifted to δ 5.57 and 4.16, respectively, and the acetyl methyl singlets at δ 2.19 (170.6 and 23.6) and δ 1.79 (169.6 and 21.0) disappeared. In addition, the signal of H-4 was diamagnetically shifted to δ 2.62 and H_a-1 was paramagnetically shifted to δ 3.08; this was assignable to the deshielding effect of the OH group at H-14 on C-1. There are also some small shift differences for H-3 and H-7 in both hydrolysis products **1a** and **1b**, as seen in Table 1, while the other protons geminal to the ester functions remained unchanged. The EI-HR mass spectra of **1a** and **1b** gave molecular ion peaks at m/z 634.2986 (cal. 634.2989) and 592.2889 (cal. 592.2883) indicating molecular formulae of $C_{33}H_{46}O_{12}$ and $C_{31}H_{44}O_{11}$, respectively. This evidence also confirmed that the removal of one acetoxy group for **1a** and of two acetoxy groups for **1b** from compound **1** had occurred. However, the precise locations of the acyl groups could not be completely elucidated by transesterification reactions, and the location of each ester group in **1** was established through a sequence of selective INEPT experiments (Table 3). The protons

Table 3. Selective INEPT experiments on **1** ($CDCl_3$ 90.8 MHz)

Proton H	Irradiated δ (ppm)	Carbons enhanced
9	0.98	19.2 (C-10), 23.6 (C-11)
19	1.03	19.2 (C-10)
12	2.58	19.2 (C-10), 56.8 (C-6)
5	5.85	165.7 ($\underline{C}OCH_3$), 51.5 (C-4), 56.3 (C-6)
17	6.58	169.6 ($\underline{C}OCH_3$), 37.9 (C-12)
7	5.03	170.1 ($\underline{C}OCH_3$), 97.9 (C-17), 66.9 (C-5), 56.3 (C-6)
14	5.69	169.6 ($\underline{C}OCH_3$), 89.5 (C-15), 51.5 (C-4)
3	5.08	170.6 ($\underline{C}OCH_3$), 89.5 (C-15)

H-3, H-5, H-7, H-14 and H-17 were irradiated to establish the three-bond enhancement with the carbonyl carbon of each aliphatic side chain. Irradiation of H-5 (*d*, δ 5.85) and then H-3′ (*br* 9, δ 6.85) enhanced the same carbonyl signal at δ 165.7, corresponding to the carbonyl carbon of the tigloyloxy group and demonstrating that the tigloyl moiety is attached to C-5.

The coupling patterns and NOE difference spectrum of **1b** revealed the stereochemical orientation of the ester groups (Table 4). Thus, irradiation of H-4α (δ 2.62) caused NOEs for H-17, H-3, H-2, H-9 and H-11, indicating that they were α oriented, while irradiation of H-5β (δ 5.86) caused NOE enhancements on H-12, H-7 and H-14, suggesting β orientations for these protons.

All of the spectral data and inspection of a model were in good agreement with the structure proposed for **1** (Fig. 1).

Aleppicatine B **2** was also isolated as a glassy gum and gave very similar spectroscopic data to those of **1**. The IR spectrum showed no hydroxyl group, but intense absorption peaks for carbonyls at 1725, 1730 and 1755 cm^{-1}, and for unsaturation at 1645 cm^{-1}. The

Table 4. Nuclear Overhauser enhancements in the ^1H NMR spectrum of **1b**

Proton	δ_H	Proton	δ H (ppm)
H-5	5.81	H-12	2.47
		H-14	4.16
		H-7	5.13
H-4	2.62	H-17	5.57
		H-3	5.02
		H-2	1.93
		H-9	0.97
		H-11	0.89
H_a-1	3.08	H-14	4.16
		H-8	1.93
		H_b-1	1.65
H-12	2.47	H-5	5.81
		H-14	4.16
		H-19	0.99

^1H and ^{13}C NMR spectra of **2** displayed the presence of two tigloyloxy (δ 165.7 and 165.5) and four acetoxy groups (Tables 1 and 5) as ester functions in the molecule. The ^1H NMR spectrum measured in benzene-d_6 (see Experimental) clearly indicated the methyl group resonances of two tigloyl groups with the singlets at δ 1.92 (13.8) and 1.83 (12.0) and *br* doublets at δ 1.45 (14.7) and 1.39 (14.4). The ^{13}C NMR spectrum showed 38 carbon signals and the CI-mass spectrum gave a molecular ion peak at *m/z* 716, corresponding to a molecular formula $C_{38}H_{52}O_{13}$. The spectral data suggested that the second tigloyloxy group should be at C-15, and the selective INEPT experiments confirmed this hypothesis. Successive irradiation of the signals at δ 6.99 (*br q*, H-3′) and then 6.85 (*br q*, H-3″) enhanced the quaternary carbon resonances at δ 165.7 and 165.5, respectively, indicating that aleppicatine B has the structure **2**. Therefore, **1**

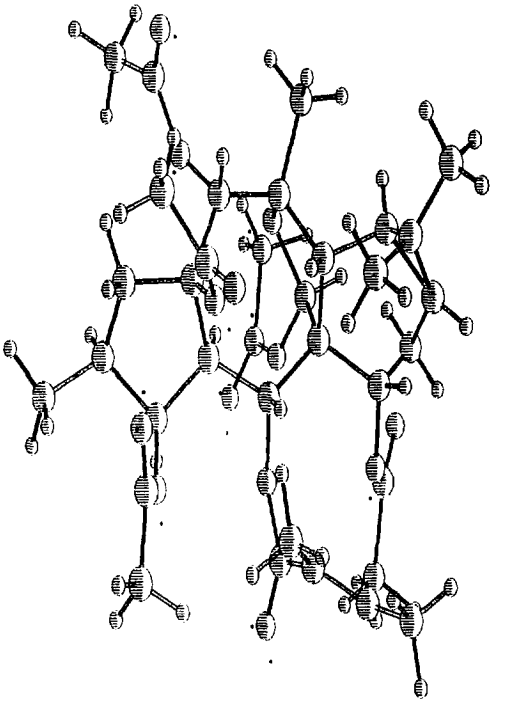


Fig. 1. The molecular structure of aleppicatine A (**1**).

Table 5. ^{13}C NMR spectra of **1** and **2** (50.32 MHz, $CDCl_3$)

C	1*		2	1a	1b
1	44.8	(45.5)	44.7	44.8	44.9
2	36.5	(37.0)	36.8	36.5	37.5
3	76.8	(77.0)	76.9	76.4	76.4
4	51.5	(51.6)	51.5	51.6	49.6
5	66.9	(67.4)	66.9	67.1	67.2
6	56.3	(57.0)	56.3	56.9	57.4
7	71.7	(71.8)	71.7	73.4	72.3
8	25.1	(25.6)	25.1	25.1	25.2
9	18.3	(18.9)	18.3	18.8	18.8
10	19.2	(19.2)	19.1	19.3	19.2
11	23.6	(23.9)	23.5	24.0	24.0
12	37.9	(37.0)	37.9	38.4	38.4
13	88.2	(88.4)	88.4	86.7	88.6
14	73.1	(73.4)	72.3	73.9	74.3
15	89.5	(89.5)	89.5	89.5	91.1
16	14.6	(14.4)	14.5	14.5	14.6
17	97.9	(98.3)	97.8	98.7	98.3
18	27.8	(27.7)	27.8	28.0	27.6
19	15.8	(15.7)	15.8	15.9	15.9
20	25.2	(25.8)	25.1	25.6	25.8
1′	165.7	(165.7)	165.7	165.5	165.5
2′	128.8	(129.6)	128.5	129.1	129.0
3′	138.3	(137.7)	138.2	138.1	138.1
4′	11.9	(12.2)	11.9	11.9	11.9
5′	14.3	(14.1)	14.3	14.5	14.6
1″	—	—	165.6	—	—
2″	—	—	128.8	—	—
3″	—	—	139.0	—	—
4″	—	—	12.3	—	—
5″	—	—	14.5	—	—
$COCH_3$	169.1	(169.4)	168.9	169.6	169.6
	169.6 × 2	(169.1) × 2	169.6	169.1 × 2	170.7
	170.1	(169.8)	170.1	171.3	171.7
	170.6	(170.1)	170.6	—	—
	20.7	(20.3)	18.3	20.9 × 2	21.1
	21.0 × 2	(20.9) × 2	21.0	21.3	21.4
	21.3	(20.9)	21.0	22.7	22.9
	23.6	(21.0)	21.4	—	

*90.8 MHz; values in parentheses in C_6D_6.
Assignments were made with DEPT and HETCOR experiments.

and **2** differed solely in the nature of the C-15 acyl groups; **1** has an acetoxy group at C-15 while **2** has a tigloyloxy group.

Compounds **1** and **2** showed no activity at 20 $\mu g\,ml^{-1}$ against human lung carcinoma, hormone-dependent human prostate and hormone-dependent breast cancer cell lines [7].

EXPERIMENTAL

Instruments. ^1H and ^{13}C NMR: (200 and 50.32 MHz), respectively (compound **1** 360 and 90.8, respectively); ^1H–^1H COSY spectrum of **1**: GE Omega 500 MHz NMR spectrometer; 200 MHz Varian-Gemini Instrument was used for the NOE spectra of **1b**; MS: Vg Zabspec. for **1a** and **1b**; Varian MAT-112S double-focusing instrument for **1** and **2**.

Plant material. Euphorbia aleppica L. was collected in July, 1991, from Istanbul, Turkey. A voucher is deposited in the herbarium of the Faculty of Pharmacy, University of Istanbul (ISTE: 63453).

Extraction and isolation. Air-dried whole plant material (1 kg) was macerated with Me_2CO and after filtration this procedure was repeated twice. All of the filtrates were combined and concd *in vacuo*, dissolved in MeOH–H_2O (1:1) and partitioned against *n*-hexane. From the *n*-hexane extract (11.84 g) triterpenes were isolated. The Me_2CO–H_2O phase was further extracted with $CHCl_3$ and the $CHCl_3$ phase was evapd *in vacuo* below 40°. The crude extract (5.5 g) was subjected to CC on silica gel using a gradient of petrol–EtOAc.

Similar frs were combined and further purified by prep. TLC using toluene–Me_2CO (9:1, 4:1) as developing solvents to afford the diterpenes **1** (28 mg, 0.5%) and **2** (19 mg, 0.3%).

Transesterification of aleppicatine A (**1**). Compound **1** (12 mg) was treated with 0.1 M NaOMe–MeOH (4 ml) for 5 hr. The reaction mixt. was neutralized with phosphate buffer to pH 6.8. After evapn, the aq. phase was extracted with EtOAc, to afford, after prep. TLC, the products **1a** and **1b**.

Aleppicatine A (**1**). CIMS *m/z* (rel. int.): $C_{35}H_{48}O_{13}$, 675 $(M-1]^+$ (4), 633 $[M-COCH_3]^+$ (8), 617 (100), 577 (22), 557 (89), 517 (18), 499 (5), 472 (8), 457 (10), 415 (8), 397 (6), 355 (5), 309 (22), 267 (12), 249 (4), 175 (4), 101 (34), 83 (75), 60 (89); FABMS *m/z*; 699 $[M+Na]^+$ positive ion, 646, 617, 557, 517, 430, 309, 286, 249, 238, 158; ^1H and ^{13}C NMR: Tables 1 and 5.

Hydrolysis product of **1** (**1a**). CIMS *m/z* (rel. int): 633 $(M-1]^+$ (6), 617 (89), 575 (71), 557 (84), 535 (62), 517 (74), 497 (23), 475 (51), 457 (36), 415 (70), 397 (24), 369 (57), 355 (69), 309 (100), 295 (61), 267 (73), 249 (49), 235 (15), 175 (8), 101 (7), 83 (4); ^1H and ^{13}C NMR: Tables 1 and 5.

Hydrolysis product of **1** (**1b**). EIMS *m/z* (rel. int.): 592 $[M]^+$ (21), 574 (13), 532 (13), 514 (7), 492 (11), 475 (15), 432 (46), 403 (43), 372 (50), 344 (59), 312 (45), 283 (84), 266 (100), 251 (58), 237 (75), 223 (89), 191 (73), 175 (60), 149 (75), 133 (44), 109 (43); ^1H and ^{13}C NMR: Tables 1 and 5.

Aleppicatine B (**2**). ^1H NMR (in C_6D_6): δ 2.73 (*dd*, $J=8$, 14 Hz, Ha-1), 5.38 (*t*, $J=4$ Hz, H-3), 3.42 (*dd*, $J=4$, 11 Hz, H-4), 6.21 (*d*, $J=11$ Hz, H-5), 5.41 (*dd*, $J=3$, 9 Hz, H-7), 2.80 (*d*, $J=9$ Hz, H-12), 6.25 (*s*, H-14), 7.19 (*s*, H-17), 0.81 (*d*, $J=7$ Hz, H-16), 0.89 (*s*, H-18), 0.89 (*s*, *H*-19), 1.53 (*s*, H-20), 7.09 (*br q*, $J=1.5$, 7 Hz, H-3′), 1.39 (*br d*, $J=1.5$, 7 Hz, H-4′), 1.83 (*br s*, H-5′), 7.11 (*br q*, $J=1.5$, 7 Hz, H-3″), 1.45 (*br d*, $J=1.5$, 7 Hz, H-4″), 1.92 (*br s*, H-5″), 2.18, 1.84, 1.82, 1.78 (4 × OAc); EIMS *m/z* (rel. int.): $C_{38}H_{52}O_{13}$, 716 $[M]^+$ (2), 679 (5), 674 (4), 662 (4), 657 (28), 617 (6), 597 (15), 573 (8), 557 (34), 515 (17), 497 (12), 475 (15), 455 (13), 415 (18), 409 (13), 355 (49), 349 (24), 309 (21), 295 (61), 277 (22), 267 (100), 253 (23), 249 (73), 223 (54), 209 (33), 207 (45), 195 (37), 191 (49), 175 (50), 105 (37); ^1H and ^{13}C NMR: Tables 1 and 5.

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