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APIENE ESTERS FROM *FERULA HAUSSKNECHTII*

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Key Word Index—*Ferula haussknechtii*; Apiaceae; sesquiterpene esters; apienes.

Abstract—Ten new apiene-type humulenoid esters were isolated from the root of *Ferula haussknechtii*. The structures were elucidated by spectroscopic methods.

INTRODUCTION

In continuation of our investigation of *Ferula* species which are indigenous to the Anatolia region of Turkey [1–4], we investigated *F. haussknechtii* Wolff. ex Rech. *Ferula* species are known to be a rich source of different classes of sesquiterpenes such as daucanes, germacranes, eudasmanes, guaianes, elemanes, humulenes and himacalenes [5]. Although the occurrence of humulenes is relatively rare in the genus *Ferula*, α-humulenes from *F. juniperina* [6–8], *F. xeromorpha* [9, 10] and *F. tschatcalensis* [11], as well as γ-humulenes from *F. ceratophylla* [12], have been reported previously.

RESULTS AND DISCUSSION

The dichloromethane extract of the root of *F. haussknechtii* afforded ten new sesquiterpene esters in small amounts; their structures were elucidated by spectral techniques, especially stereochemical data obtained with the relatively new techniques such as 2D NMR homo- and heteronuclear COSY and high resolution NOESY experiments.

The IR spectra of the benzoate (1) ($C_{22}H_{28}O_2$), *p*-hydroxybenzoate (2) ($C_{22}H_{28}O_3$) and vanillate (3) ($C_{23}H_{30}O_4$) derivatives of fervanol all exhibited absorptions for an aromatic acyl group. The ^{1}H NMR (Table 1), ^{13}C NMR (Table 2) and MS data for 1, 2 and 3 confirmed the presence of benzoate, *p*-hydroxybenzoate and vanillate acyl groups, respectively, as well as the same sesquiterpene nucleus for all three. A total of four degrees of unsaturation were assigned for this nucleus based on the ^{13}C NMR and mass spectral data. The ^{1}H NMR and ^{13}C NMR spectra of 1–3 indicated the presence of an exocyclic methylene group (δ4.96, 4.90, each 1H, *d* and 148.3, *s*; 114.7, *t*), (a trisubstituted double bond (δ5.32, 1H, *t*; 1.48, 3H, *d* and 126.9, *d*; 135.5, *s*) and a *trans* disubstituted double bond (δ6.04 and 5.59, each 1H, *d*, J = 16.1 Hz; 138.5, *d* and 128.3, *d*), as well as two geminal methyl groups (δ1.16 and 1.07, each 3H, *s*; both at 26.0, *q*). The presence of these three double bonds indicated a monocyclic structure for all three compounds; moreover, the presence of two geminal methyl groups instead of an isopropyl group clearly demonstrated the γ-humulenoid-type structure for 1–3. The location of the aromatic acyl groups and the structural relationship of these three compounds was deduced from 2D NMR homonuclear COSY-45 experiments. Nevertheless, the spectral data did not establish all stereochemical matters. Interestingly, in the ^{1}H NMR spectra of 1–3 the exocyclic methylene proton signals appear as two doublets, whereas the same signals in the spectra of all previously known γ-humulenes except for the compound obtained from *F. ceratophylla*, which probably has the same stereochemical features as 1–3, were reported as broad singlets [13, 14]. The 2D NMR homonuclear COSY-45 experiment confirmed the presence of geminal coupling between the exocyclic methylene protons but no other long range couplings with these protons. This feature is probably indicative of a different conformation of 1–3 relative to previously reported γ-humulenes. Further information regarding the stereochemistry of 1–3 was obtained by a series of NOESY experiments. The ^{1}H NMR NOESY experiments of 3 verified an *s-trans* for the conjugated 4(15),5-diene system and β orientation for the C-7 acyl group.

The IR spectra of the benzoate (4) ($C_{22}H_{28}O_3$) and vanillate (5) ($C_{23}H_{30}O_5$) of kurubasch aldehyde showed an α,β-unsaturated aldehyde (1695 cm^{-1}) and aromatic acyl group absorptions. The aromatic acyl groups of 4 and 5 were assigned as benzoate and vanillate, respectively, on the basis of their ^{1}H, ^{13}C NMR and mass spectral data. Similarity of their spectra, except for the acyl group signals, confirmed the same sesquiterpene skeleton in both 4 and 5. In addition to the other spectral data, an α-humulenoid structure for 4 and 5 was deduced from the 2D NMR homonuclear COSY-45 experiments. In the ^{1}H NMR spectra of 4 and 5 the downfield position of the H-5 signal (δ6.50, 1H, *d*) and the presence of an aldehyde proton signal (δ9.4, 1H, *d*) instead of a second vinylic methyl signal expected for an α-humulene, clearly indicated that in 4 and 5 the C-4 methyl of α-humulenes had been replaced with an aldehyde group. Furthermore, the doublet at δ5.7 (1H), which coupled with the former H-5 signal, at δ6.50, confirmed the location of the aromatic acyl groups to be C-6 in both compounds. The NOESY experiments of 4 (Table 3) showed that both the $\Delta^{1,10}$ and Δ^4 double bonds had the *E* configuration and that the stereochemistry of the acyl group at C-6 is β.

Kurubaschic acid angelate (6) ($C_{20}H_{30}O_4$) and benzoate (7) ($C_{22}H_{28}O_4$) exhibited similar spectral data to

Table 1. ^{1}H NMR spectra data of compounds 1–10

H	1 (200 MHz)	2 (200 MHz)	3 (500 MHz)	4 (500 MHz)	5 (200 MHz)
1	5.32 *br t*	5.31 *br t*	5.32 *br t*	5.32 *br dd*	5.24 *br t*
	(8.5)	(8.4)	(8.5)	(6.3; 5.8)	(7.6)
2	2.22 *m*	2.21 *m*	2.22 *m*	2.28 *m*	
					2.26 *m*
2′	2.33 *m*	2.32 *m*	2.33 *m*	2.19 *m*	
3				2.61 *td*	
	2.38 *m*	2.36 *m*	2.38 *m*	(4.1; 12.6)	2.60 *m*
3′				2.54 *dt*	
				(3.8; 12.6)	
5	6.04 *d*	6.04 *d*	6.04 *d*	6.49 *d*	6.50 *d*
	(16.1)	(16.1)	(16.1)	(10.3)	(10.3)
6	5.59 *d*	5.58 *d*	5.59 *d*	5.72 *d*	5.70 *d*
	(16.1)	(16.1)	(16.1)	(10.3)	(10.3)
7				1.33 *m*	
	4.68 *br d*	4.68 *br d*	4.68 *br d*		1.38 *m*
7′	(6.9)	(6.8)	(6.9)	1.20 *m*	
8	2.20 *m*	2.19 *m*	2.24 *m*	1.64 *m*	1.60 *m*
8′	1.91 *m*	1.90 *m*	1.92 *m*	1.36 *m*	1.38 *m*
9	2.17 *m*	2.17 *m*	2.17 *m*	2.20 *m*	2.21 *m*
9′	1.58 *m*	1.58 *m*	1.58 *m*	1.46 *dt*	1.48 *dt*
				(2.1; 13)	(2.1; 13)
12	1.16 *s*	1.16 *s*	1.16 *s*	1.20 *s*	1.21 *s*
13	1.07 *s*	1.06 *s*	1.07 *s*	0.96 *s*	0.97 *s*
14	1.48 *d*	1.47 *d*	1.48 *d*	1.55 *br s*	1.57 *br s*
	(1)	(0.9)	(1.1)		
15	4.96 *d*	4.96 *d*	4.96 *d*		
	(2.1)	(2.1)	(2.1)	9.42 *d*	9.44 *d*
15′	4.90 *d*	4.90 *d*	4.90 *d*	(1)	(0.9)
	(2.1)	(2.1)	(2.1)		
3″	8.03 *dd*	7.99 *d*	7.66 *dd*	7.98 *dd*	7.60 *dd*
	(2; 8.9)	(8.8)	(1.8; 8.3)	(1.4; 8.7)	(1.9; 8.4)
4″	7.46 *dt*	6.91 *d*	6.96 *d*	7.41 *dt*	6.93 *d*
	(2; 8.8)	(8.8)	(8.3)	(1.3; 8.6)	(8.4)
5″	7.60 *dt*			7.53 *dt*	
	(2;8.8)			(1.3; 8.6)	
6″	7.46 *dt*	6.91 *d*		7.41 *dt*	
	(2; 8.8)	(8.8)		(1.3; 8.6)	
7″	8.03 *dd*	7.99 *d*	7.62 *d*	7.98 *dd*	7.50 *d*
	(2; 8.9)	(8.8)	(1.8)	(1.4; 8.7)	(1.9)
OCH_3			3.95 *s*		3.93 *s*

those of **4** and **5**. Indeed, the ^{1}H NMR of **7** was only slightly different to the one recorded for **4**; these differences included the absence of an aldehydic proton signal, a signal for a more deshielded H-5 and a slightly shielded H-6 signal. The IR, ^{13}C NMR and mass spectra of **7** confirmed that the C-4 aldehyde group of **4** had been oxidized to a carboxyl group in **7**. 2D NMR homonuclear (COSY-45) and ^{1}H–^{13}C heteronuclear (HETCOR) shift correlation experiments performed with **7** confirmed the ^{1}H and ^{13}C NMR assignments. Similarity of the chemical shift of H-5 in the ^{1}H NMR of **7** with that exhibited by **13**, a compound which was prepared from its Δ^4 *Z* isomer by photochemical transformation [15], suggested the same Δ^4 *E* configuration for **7**. Not only the Δ^4 *E* configuration but also identical stereochemistry for **4** and **7** was confirmed by correlation of their ^{1}H and ^{13}C NMR data. These assignments were supported by the oxidation of **4** to **7**. The acyl moieties of **6** and **7** were identified as angelate and benzoate, respectively.

The spectral data of the angelate (**8**) ($C_{20}H_{30}O_5$) and benzoate (**9**) ($C_{22}H_{28}O_5$) of 1β,10α-epoxykurubaschic acid as well as the data for 1α,10β-epoxykurubaschic acid benzoate (**10**) ($C_{22}H_{28}O_5$) indicated that all three were 1, 10-epoxy analogues of the kurubaschic acid esters. While spectral similarity suggested the same stereochemistry for **8** and **9**, the spectral comparison indicated different stereochemistry for **10**. An angelate acyl group for **8** and benzoate for both **9** and **10** were assigned on the basis of their IR, MS, ^{1}H and ^{13}C NMR data. To elucidate the stereochemistry of these compounds, all ^{1}H NMR signals of **9** and **10** (diastereomeric pair) were identified by means of 2D NMR homonuclear COSY-45 experiments; then using NOESY experiments (Table 3) their stereochemistries were established as 1α, 10β-epoxy- and 1β, 10α-epoxykurubaschic acid benzoates, respectively. C-4 methyl analogues of these compounds with different acyl groups (**11** and **12**) were reported recently [16, 17], including X-ray crystallographic analysis. The ^{1}H and

($CDCl_3$, TMS as int. standard, J in Hz in parentheses)

	6 (200 MHz)	7 (500 MHz)	8 (200 MHz)	9 (500 MHz)	10 (500 MHz)
H-1	5.25 *br t*	5.27 *br t*	2.98 *dd*	2.98 *dd*	2.89 *dd*
	(7.6)	(7.4)	(3.4; 11.3)	(3.4; 11.4)	(4; 10.9)
H-2			2.25 *ddd*	2.24 *ddd*	2.45 *tt*
	2.30 *m*	2.28 *m*	(1.5; 6.5; 14.4)	(3.1; 6.4; 14.1)	(3.7; 13.7)
H-2′			1.58 *br q*	1.57 *ddt*	1.47 *m*
			(14.4)	(1.5; 13; 14.4)	
H-3		2.68 *ddd*	2.96 *dt*	2.97 *dt*	2.77 *dt*
	2.63 *m*	(5.3; 10; 12.6)	(1.4; 14.2)	(1.4; 14.2)	(3.3; 14.1)
H-3′		2.61 *td*	2.70 *br dd*	2.71 *br dd*	2.69 *td*
		(4.1; 12.6)	(6.3; 14.2)	(6.4; 14.2)	(3.7; 14.1)
H-5	6.93 *d*	6.98 *d*	6.88 *d*	6.94 *d*	6.88 *d*
	(10.6)	(10.6)	(10.6)	(10.9)	(10.5)
H-6	5.45 *d*	5.58 *d*	5.53 *d*	5.66 *d*	5.73 *d*
	(10.6)	(10.6)	(10.6)	(10.9)	(10.5)
H-7		1.31 *m*			1.47 *m*
	1.25 *m*		1.38 *m*	1.41 *m*	
H-7′		1.18 *m*			1.22 *m*
H-8		1.63 *m*		1.41 *m*	1.68 *m*
	1.48 *m*		1.38 *m*		
H-8′		1.32 *m*		1.34 *m*	1.28 *m*
H-9	2.21 *br d*	2.19 *br d*	1.82 *br dd*	1.81 *br dd*	2.07 *dd*
	(12.6)	(12.6)	(11.6; 14.3)	(11.7; 12.4)	(8.1; 12.7)
H-9′	1.48 *dt*	1.47 *dt*	1.25 *m*	1.22 *dd*	0.83 *b dd*
	(2.1; 12.6)	(2.1; 12.6)		(8.1; 12.4)	(11.6; 12.7)
H-12	1.07 *s*	1.17 *s*	1.10 *s*	1.19 *s*	1.16 *s*
H-13	0.89 *s*	0.93 *s*	0.95 *s*	0.98 *s*	0.98 *s*
H-14	1.61 *br s*	1.61 *s*	1.18 *s*	1.17 *s*	1.39 *s*
H-15					
H-15′					
H-3″	6.06 *qq*	7.98 *dd*	6.10 *qq*	7.99 *dd*	7.99 *dd*
	(1.4; 7.2)	(1.4; 8.7)	(1.4; 7.2)	(1.4; 8.1)	(1.3; 8.1)
H-4″	1.96 *dq*	7.41 *dt*	1.98 *dq*	7.42 *dt*	7.43 *dt*
	(1.4; 7.2)	(1.3; 8.6)	(1.4; 7.2)	(1.3; 8.1)	(1.3; 8.2)
H-5″	1.86 *t*	7.53 *dt*	1.88 *t*	7.54 *dt*	7.54 *dt*
	(1.4)	(1.3; 8.6)	(1.4)	(1.3; 8.1)	(1.3; 8.2)
H-6″		7.41 *dt*		7.42 *dt*	7.43 *dt*
		(1.3; 8.6)		(1.3; 8.1)	(1.3; 8.2)
H-7″		7.98 *dd*		7.99 *dt*	7.99 *dd*
		(1.4; 8.7)		(1.4; 8.1)	(1.3; 8.1)
OCH_3					

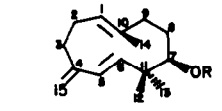
^{13}C NMR data correlation of **9** with that of **11** and **10** with that of **12**, especially for their similar structural fragments, clearly supported these assignments.

Humulenoid sesquiterpenes are relatively rare compounds in nature and the *cis* Δ^4 double bond conformational feature in the compounds described here distinguishes these compounds from the common type of all-*trans*-humulenes. Apparently, these *cis* Δ^4 double bond-containing compounds (α-apienes) are derived from *cis,trans*-farnesyl pyrophosphate [18] in contrast to the *trans,trans*-farnesyl pyrophosphate precursor of the latter type. Due to their *cis,trans*-farnesyl pyrophosphate precursor the *s-trans* 4(15), 5-diene conformation of fervanol esters (**1**–**3**) (γ-apienes) is formed instead of *s-cis* 4(15),5-diene conformation of common all-*trans*-humulene analogue γ-humulenes. It is of interest that to date all humulenoids containing *cis* Δ^4 double bonds or *s-trans* 4(15),5-dienes were isolated from the Apiaceae; therefore, we named this subclass as apienes (similar to the germacrane–heliangene relationship).

EXPERIMENTAL

Plant material. The plant material was collected from the Kurubaş Pass area between Van-Gürpınar (Eastern Anatolia) in June 1983. A voucher specimen is deposited in the Herbarium of Dicle University (DUF) (Herb. no. SAYA 83–167).

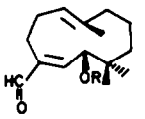
Isolation of compounds. Air-dried and finely cut root pieces of *F. haussknechtii* (13 g) were extracted with CH_2Cl_2 (100 ml) at room temp. for 20 min. Concentration of the CH_2Cl_2 extract *in vacuo* provided 1.1 g of a crude viscous oil. This oil was dissolved in Me_2CO (50 ml) and left overnight in a refrigerator. Following the removal of precipitated hydrocarbon mixtures by filtration, the solvent was removed *in vacuo* to yield 980 mg of a light yellow viscous oil. This material was chromatographed on a Sephadex LH-20 column (3 × 50 cm) packed in cyclohexane



1 R = Benzoate

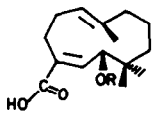
2 R = p-Hydroxybenzoate

3 R = Vanillate



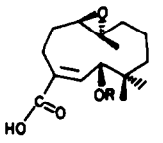
4 R = Benzoate

5 R = Vanillate



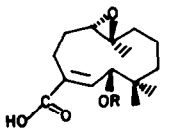
6 R = Angelate

7 R = Benzoate

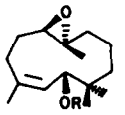


8 R = Angelate

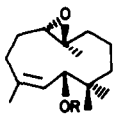
9 R = Benzoate



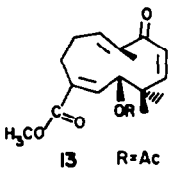
10 R = Benzoate



11 R = Ac



12 R = Ac



13 R = Ac

Table 3. NOEs with compounds 3, 4, 9 and 10

Irrad. of	3 NOE
Compound 3	
H-5	H-12, H-15
H-6	H-7, H-1, H-3α
H-7	H-6, H-9α
H-12	H-5
H-13	H-6, H-7
H-14	H-2β
Compound 4	
H-1	H-6, H-7α, H-3α, H-9α
H-5	H-12, H-15
H-6	H-1, H-3α, H-7α, H-13
H-14	H-2β
H-15	H-5
Compound 9	
H-5	H-12
H-6	H-1, H-3α, H-13
H-1 & 3α	H-6, H-2α
H-12 & 14	H-5
Compound 10	
H-1	H-7β, H-9β
H-5	H-12
H-6	H-3α, H-8α
H-12	H-5
H-13	H-6, H-8α
H-14	H-3α, H-8α, H-9α

Table 2. ^{13}C NMR spectral data for compounds 3, 4, 7 and 10 ($CDCl_3$, TMS)

C	3 (125.8 MHz)	4 (22.6 MHz)	7 (125.8 MHz)	10 (125.8 MHz)
1	126.9 *d*	124.4 *d*	123.9 *d*	60.8 *d*
2	30.2 *t*	25.3 *t*	26.0 *t*	26.2 *t*
3	31.5 *t*	25.6 *t*	27.7 *t*	25.1 *t*
4	148.3 *s*	143.0 *s*	136.1 *s*	136.0 *s*
5	138.5 *d*	143.0 *d*	138.3 *d*	138.2 *d*
6	128.5 *d*	72.8 *d*	73.2 *d*	76.7 *d*
7	83.6 *d*	35.8 *t*	35.6 *t*	37.3 *t*
8	30.2 *t*	23.8 *t*	23.7 *t*	19.8 *t*
9	40.9 *t*	35.8 *t*	35.9 *t*	38.3 *t*
10	135.5 *s*	136.8 *s*	136.9 *s*	60.6 *s*
11	37.7 *s*	37.8 *s*	37.8 *s*	37.7 *s*
12	26.0 *q*	24.3 *q*	24.3 *q*	24.5 *q*
13	26.0 *q*	22.9 *q*	22.8 *q*	22.9 *q*
14	17.0 *q*	19.4 *q*	19.2 *q*	16.6 *q*
15	114.7 *t*	218.1 *d*	173.4 *s*	171.7 *s*
1′	166.0 *s*	165.5 *s*	165.5 *s*	165.8 *s*
2′	122.9 *s*	130.2 *s*	130.2 *s*	130.0 *s*
3′	124.0 *d*	129.7 *d*	129.6 *d*	129.6 *d*
4′	111.8 *d*	128.5 *d*	128.3 *d*	128.5 *d*
5′	148.3 *s*	133.2 *d*	132.9 *d*	133.2 *d*
6′	150.0 *s*	128.5 *d*	128.3 *d*	128.5 *d*
7′	114.1 *d*	129.7 *d*	129.6 *d*	129.6 *d*
OCH_3	56.1 *q*			

–CH_2Cl_2–EtOH (7:4:1) and prep. TLC (1.5–2 mm thickness, silica gel developed with cyclohexane–EtOAc mixtures, 4:1, 7:3 or 3:2) was used for final purification of compounds.

Fervanol benzoate (**1**). Gum (21 mg); IR ν_{max}^{NaCl} cm^{-1}: 3070, 2970, 2940, 2875, 1720, 1602, 1585, 1450, 1270, 1215, 1040, 880, 830, 710, 688, 675. EIMS (probe, 70 eV) *m/z* (rel. int.): 324 $[M]^+$ (1.2), 202 [M—benzoic acid]$^+$ (12.1), 187 (5.6), 159 (9.4), 122 [benzoic acid]$^+$ (60), 105 [benzoate]$^+$ (100).

Fervanol p-hydroxybenzoate (**2**). Gum (34 mg); IR ν_{max}^{NaCl} cm^{-1}: 3360, 2970, 2940, 2870, 1680, 1610, 1595, 1512, 1450, 1365, 1280, 1220, 1160, 1100, 880, 850, 830, 770, 700. EIMS (probe, 70 eV) *m/z* (rel. int.): 340 $[M]^+$ (0.8), 202 [M – *p*-hydroxybenzoic acid]$^+$ (9.4), 187 (4.9), 159 (8.8), 138 [*p*-hydroxybenzoic acid]$^+$ (40), 121 [*p*-hydroxybenzoate]$^+$ (100).

Fervanol vanillate (**3**). Gum (9 mg); IR ν_{max}^{NaCl} cm^{-1}: 3400, 3080, 2975, 2938, 2870, 1710, 1610(sh), 1600, 1515, 1460, 1450, 1428, 1283, 1220, 1105, 1030, 880, 830, 785, 762, 725. EIMS (probe, 70 eV) *m/z* (rel. int.): 370 $[M]^+$ (4), 202 [M – vanillic acid]$^+$ (13.9), 187 (11.6), 168 [vanillic acid]$^+$ (18), 159 (15.8), 151 [vanillate]$^+$ (100).

Kurubasch aldehyde benzoate (**4**). Gum (45 mg); IR ν_{max}^{NaCl} cm^{-1}: 3060, 2970, 2930, 2865, 2710, 1720, 1695, 1602, 1586, 1490, 1450, 1318, 1270, 1110, 1098, 1028, 950, 935, 800, 710, 688, 672. EIMS (probe, 70 eV) *m/z* (rel. int.): 340 $[M]^+$ (6.9), 218 [M – benzoic acid]$^+$ (14.8), 203 (13.6), 189 (8.6), 175 (10), 122 [benzoic acid]$^+$ (16.6), 105 [benzoate]$^+$ (100).

Oxidation of **4**. Kurubasch aldehyde benzoate (**4**) (10 mg) was dissolved in Et_2O (3 ml), chromic acid soln (0.3 ml) [20] was added dropwise and the soln stirred at room temp. for 1 hr. The Et_2O layer was separated and washed with $NaHCO_3$ soln (1%), dried over anhyd. Na_2SO_4 and evapd *in vacuo* to yield 7 mg gum. Spectral properties of the product were found to be identical with **7**.

Kurubasch aldehyde vanillate (**5**). Gum (11 mg); IR ν_{max}^{NaCl} cm^{-1}: 3400, 3080, 2970, 2940, 2870, 2715, 1710(sh), 1692, 1610(sh), 1600, 1512, 1460, 1430, 1388, 1370, 1280, 1215, 1100, 1032, 958, 878, 785, 762, 725. EIMS (probe, 70 eV) *m/z* (rel. int.): 386 $[M]^+$ (3.3), 218 [M – vanillic acid]$^+$ (5.9), 203 (2.3), 189 (3.1), 175 (4), 168 [vanillic acid]$^+$ (15.9), 151 [vanillate]$^+$ (100).

Kurubaschic acid angelate (**6**). Gum (25 mg); IR ν_{max}^{NaCl} cm^{-1}: 3100(sh), 2970, 2940, 2880, 2670, 2520(sh), 1715(sh), 1695, 1640, 1510, 1458, 1385, 1368, 1355, 1270, 1230, 1150, 1040, 960, 938, 845, 795. EIMS (probe, 70 eV) *m/z* (rel. int.): 334 $[M]^+$ (1.1), 234 [M – angelic acid]$^+$ (13), 219 (15.9), 206 (10.1), 191 (13.2), 149 (67.8), 105 (97), 100 [angelic acid]$^+$ (68.6), 83 [angelate]$^+$ (100).

Kurubaschic acid benzoate (**7**). Gum (230 mg); IR ν_{max}^{NaCl} cm^{-1}: 3100(sh), 3065, 2970, 2940, 2875, 2660, 2520(sh), 1720, 1692, 1640, 1602, 1585, 1512, 1450, 1388, 1370, 1320, 1270, 1210, 1108, 1070, 1026, 1002, 952, 938, 880, 796, 710, 688, 675. EIMS (probe, 70 eV) *m/z* (rel. int.): 356 $[M]^+$ (0.14), 234 [M – benzoic acid]$^+$ (32), 219 (33.9), 206 (5.7), 191 (24.7), 149 (38.5), 122 [benzoic acid]$^+$ (82.4), 105 [benzoate]$^+$ (100). CIMS (methane, probe, 70 eV) *m/z* (rel. int.): 355 $[M-1]^+$ (5.9), 339 $[M+1-H_2O]^+$ (6.4), 251 [M – 1 – benzoate + H]$^+$ (9.8), 235 [M + 1 – benzoic acid]$^+$ (100), 233 [M – 1 – benzoic acid]$^+$ (62.5), 217 (43.2), 205 (20.3), 189 (48), 123 [benzoic acid + H]$^+$ (59.8), 105 [benzoate]$^+$ (51.5).

1β,10α-Epoxykurubaschic acid angelate (**8**). Gum (12 mg); IR ν_{max}^{NaCl} cm^{-1}: 3200(sh), 2975, 2930, 2870, 2660, 2520(sh), 1715, 1695, 1645, 1510, 1453, 1385, 1270, 1260, 1230, 1150, 1040, 962, 862, 780, 710. EIMS (probe, 70 eV) *m/z* (rel. int.): 350 $[M]^+$ (0.1), 250 [M – angelic acid]$^+$ (4.4), 235 (2.7), 232 (4.2), 205 (5.2), 191 (6), 189 (6.6), 165 (12.9), 151 (17.7), 149 (17.6), 121 (19.3), 105 (28.9), 100 [angelic acid]$^+$ (18.4), 83 [angelate]$^+$ (100).

1β,10α-Epoxykurubaschic acid benzoate (**9**). Gum (14 mg); IR ν_{max}^{NaCl} cm^{-1}: 3200(sh), 3060, 2970, 2940, 2875, 2660, 2520(sh), 1720, 1693, 1642, 1602, 1585, 1490, 1450, 1385, 1370, 1320, 1270, 1110, 1070, 1025, 955, 770, 710, 685, 677. EIMS (probe, 70 eV) *m/z* (rel. int.): 372 $[M]^+$ (0.12), 250 [M – benzoic acid]$^+$ (2.5), 235 (2.1), 232 (3.9), 205 (2), 191 (3.7), 189 (4.3), 165 (6.6), 151 (5.1), 122 [benzoic acid]$^+$ (82.2), 105 [benzoate]$^+$ (100). CIMS (methane, probe, 70 eV) *m/z* (rel. int.): 373 $[M+1]^+$ (1.1), 371 $[M-1]^+$ (1.3), 251 [M + 1 – benzoic acid]$^+$ (20.6), 233 [M + 1 – benzoic acid – H_2O]$^+$ (100), 223 (6.7), 215 (16.2), 205 (39.3), 193 (8.7), 187 (19.8), 177 (11.4), 123 [benzoic acid + H]$^+$ (18.2), 105 [benzoate]$^+$ (25.2).

1α,10β-Epoxykurubaschic acid benzoate (**10**). Gum (8.5 mg); IR ν_{max}^{NaCl} cm^{-1}: 3200(sh), 3070, 2970, 2940, 2870, 2660, 2530(sh), 1720, 1695, 1645, 1602, 1588, 1490(sh), 1465, 1450, 1388, 1370, 1270, 1178, 1110, 1070, 1050, 1028, 960, 865, 775, 710, 688, 678. EIMS (probe, 70 eV) *m/z* (rel. int.): 272 $[M]^+$ (0.3), 250 [M – benzoic acid]$^+$ (1.8), 235 (1.4), 191 (3.1), 189 (3.9), 165 (6.4), 151 (3.7) 122 [benzoic acid]$^+$ (56), 105 [benzoate]$^+$ (100).

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