24. Anatoliosides: Five Novel Acyclic Monoterpene Glycosides from *Viburnum orientale*[1])

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Five new acyclic monoterpene glycosides **1–5** were isolated from the leaves of *Viburnum orientale* (Caprifoliaceae). Anatolioside (**1**) is a monoterpene diglycoside and its structure was elucidated as linalo-6-yl 2′-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside (arbitrary numbering of linalool moiety). Compounds **2–5** are all derivatives of **1**, containing additional monoterpene and sugar units, connected by ester and glycoside bonds. Their structures were established as linalo-6-yl *O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside (= anatolioside A; **2**), linalo-6-yl *O*-β-D-glucopyranosyl-(1⁗→6‴)-*O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside (= anatolioside B; **3**), linalo-6-yl *O*-β-D-*ribo*-hexopyranos-3-ulosyl-(1⁗→6‴)-*O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside (= anatolioside C; **4**) and linalo-6-yl *O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1⁗→2⁗)-*O*-β-D-glucopyranosyl-(1⁗→6‴)-*O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside (= *anatolioside D*; **5**). The structure determinations were based on spectroscopic and chemical methods (acid and alkaline hydrolysis, acetylation, and methylation).

1. Introduction. – *Viburnum* is a genus of mostly ornamental trees and shrubs of the family Caprifoliaceae. Some of them are used in traditional folk medicine. *V. opulus* L., a well known plant, is one of the three species growing in Turkey [1]. Its fruits are used as diuretic, laxative, and sedative in central Anatolia (Turkish crude drug name: gilaburu). *V. orientale* PALLAS is another species growing in northeastern Anatolia. For this species, there are no records for its uses among the people of this region, and no chemical investigations have been performed.

The H_2O-soluble part of the MeOH extract of the air-dried leaves of the plant was extracted with Et_2O, AcOEt, and then BuOH. From the AcOEt extract, we previously [2] obtained an ester iridoid glycoside, viborientoside. As a result of our continued work on the same plant, we now report the isolation and structure elucidation of five new acyclic monoterpene glycosides, anatolioside (**1**) and anatoliosides A–D (**2–5**) from the BuOH extract.

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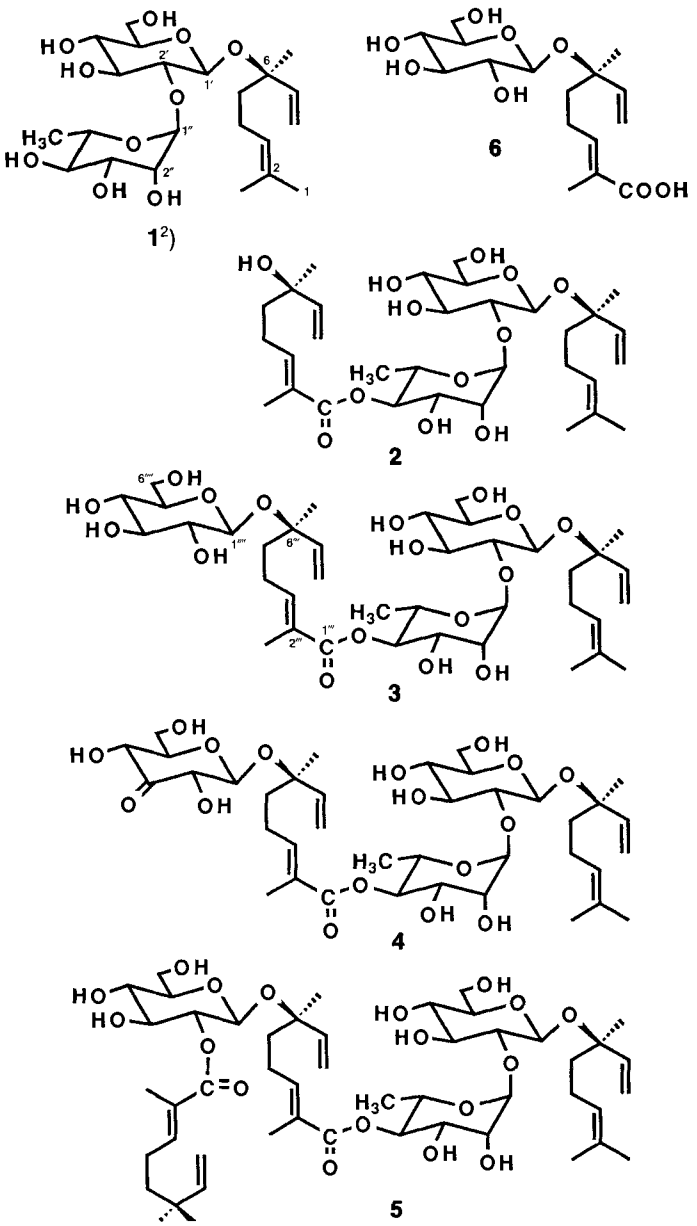

2. Results and Discussion. – Anatolioside (**1**) is obtained as colourless, amorphous compound of molecular formula $C_{22}H_{38}O_{10}$. The IR spectrum shows characteristic absorption bands at 3400 (OH groups) and 1640 cm^{-1} (C=C). The structure and the interglycosidic linkages of **1** are established by their ^1H- and ^{13}C-NMR data (*Tables 1* and *2*) as well as by C,H long-range correlation experiments HMBC performed with **2** (see

Table 1. *^{1}H-NMR Spectral Data of Anatolioside* (**1**), *Anatoliosides A–D* (**2–5**), *and Anatolioside-B Nonaacetate* (**3a**). For **1** and **3–5** at 300 MHz, for **2** at 400 MHz.

H-Atom[2])	**1** (CD_3OD)		**2** (CD_3OD)		**3** (CD_3OD)		**3a** ($CDCl_3$)[a])		**4** (CD_3OD)		**5** (CD_3OD)	
	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]
Me–C(2)	1.64 (*s*)		1.66 (*s*)		1.62 (*s*)		1.63 (*s*)		1.62 (*s*)		1.62 (*s*)	
H–C(3)	5.13 (br. *t*)	7.1	5.09 (br. *t*)	7	5.06[b])		4.98[b])		5.06[b])		5.06[b])	
CH_2(4)	2.05 (*m*)		2.13 (*m*)		2.08 (*m*)		1.98 (*m*)		2.08 (*m*)		2.2–2.0[b])	
CH_2(5)	1.66, 1.56[b])		1.81, 1.55 (*m*)		1.74, 1.56[b])		1.56[b])		1.74, 1.56[b])		1.74–1.54[b])	
H–C(7)	5.98 (*dd*)	18, 10.6	5.97 (*dd*)	17.4, 10.8	5.99 (*dd*)	17.7, 11	5.91 (*dd*)	17.6, 10.9	6.0 (*dd*)	17.7, 10.5	6.0 (*dd*)	18, 10.6
H_a–C(8)	5.26 (*dd*)	1.2, 10.6	5.13 (*dd*)	10.8, 1.5	5.25 (*dd*)	11, 1.2	5.24[b])		5.26 (br. *d*)	10.5	5.26 (br. *d*)	10.6
H_b–C(8)	5.25 (*dd*)	1.2, 18	5.30 (*dd*)	17.4, 1.5	5.31 (*dd*)	17.7, 1.2	5.32[b])		5.33 (br. *d*)	17.7	5.27 (*dd*)	18, 1.3
Me–C(2)	1.42 (*s*)		1.49 (*s*)		1.44 (*s*)		1.55 (*s*)		1.46 (*s*)		1.44 (*s*)	
Me–C(6)	1.7 (*s*)		1.72 (*s*)		1.68 (*s*)		1.37 (*s*)		1.68 (*s*)		1.67 (*s*)	
H–C(1′)	4.46 (*d*)	7.4	4.52 (*d*)	7.6	4.48 (*d*)	7.5	4.57 (*d*)	7.8	4.49 (*d*)	7.8	4.48 (*d*)	7.4
H–C(2′)	3.43 (*dd*)	7.4, 9.5	3.57–3.51[b])		3.47–3.52[b])		3.75 (*dd*)	7.8, 9.4	3.53–3.47[b])		3.54–3.49[b])	
H–C(3′)	3.47 (*t*)	9.0	3.57–3.51[b])		3.47–3.52[b])		5.26 (*t*)	9.3	3.53–3.47[b])		3.54–3.49[b])	
H–C(4′)	3.31 (*t*)	9.5	3.36 (*t*)	9.5	3.34 (*t*)	9.5	4.90 (*t*)	9.7	3.4–3.3[b])		3.36–3.29[b])	
H–C(5′)	3.19 (*m*)		3.25 (*m*)		3.22 (*m*)		3.64 (*m*)		3.23 (*m*)		3.22 (*m*)	
H_a–C(6′)	3.66 (*dd*)	11.9, 5.6	3.71 (*dd*)	11.9, 5.7	3.67[b])		4.21 (br. *d*)	12.2	3.67 (*dd*)	11.9, 5.5	3.67 (*dd*)	12, 5.4
H_b–C(6′)	3.84 (*dd*)	11.9, 2.4	3.88 (*dd*)	11.9, 2.4	3.85[b])		4.08 (*dd*)	12.2, 2.5	3.85 (*d*)	11.9, 2.4	3.84 (*dd*)	12, 2.4
H–C(1″)	5.34 (*d*)	1.7	5.52 (*d*)	1.2	5.48 (br. *s*)		5.03[b])	5.48 (br. *s*)		5.5 (br. *s*)		
H–C(2″)	3.95 (*dd*)	1.7, 3.4	4.0 (*dd*)	1.2, 3.4	3.97[b])		5.0[b])		3.96[b])		3.96[b])	
H–C(3″)	3.73 (*dd*)	3.4, 9.5	3.99 (*dd*)	3.4, 9.5	3.94 (*dd*)	3.4, 9.5	5.36 (*dd*)	3.3, 10	3.94[b])		3.94 (*dd*)	3.4, 9.5
H–C(4″)	3.47 (*t*)	9.5	5.08 (*t*)	9.5	5.04 (*t*)	9.5	5.13 (*t*)	10	5.04 (*t*)	9.6	5.03 (*t*)	9.7
H–C(5″)	4.13 (*dq*)	6.2, 9.5	4.48 (*dq*)	6.2, 10	4.46 (*dq*)	6.2, 10	4.37 (*dq*)	6.2, 10	4.39 (*m*)		4.43 (*m*)	
Me(6″)	1.26 (*d*)	6.2	1.16 (*d*)	6.2	1.12 (*d*)	6.2	1.17 (*d*)	6.2	1.12 (*d*)	6.2	1.12 (*d*)	6.2

Table 1 (cont.)

H-Atom[2])	**1** (CD_3OD)		**2** (CD_3OD)		**3** (CD_3OD)		**3a** ($CDCl_3$)[a])		**4** (CD_3OD)		**5** (CD_3OD)	
	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]	δ [ppm]	J [Hz]
H–C(3‴)			6.87 (*dt*)	1.5, 7.5	6.83 (*dt*)	1.4, 6.1	6.42 (*dt*)	1.2, 6.2	6.83 (br. *t*)		6.89 (br. *t*)	7.4
CH_2(4‴)			2.31 (*m*)		2.34 (*m*)		2.2 (*m*)		2.37 (*m*)		2.38–2.2[b])	
CH_2(5‴)			1.65 (*m*)		1.69 (*m*)		1.6 (*m*)		1.7–1.65[b])		1.7–1.5[b])	
H–C(7‴)			6.04 (*dd*)	17.7, 11	5.98 (*dd*)	17.7, 11	5.69 (*dd*)	17.7, 10.9	5.96 (*dd*)	17.8, 10.5	5.96 (*dd*)	18, 11.7
H_a–C(8‴)			5.34 (*dd*)	17.7, 1.1	5.31 (*dd*)	17.7, 1.1	5.28[b])		5.29 (br. *d*)	10.5	5.27 (*dd*)	18, 1.3
H_b–C(8‴)			5.32 (*dd*)	11, 1.1	5.32 (*dd*)	11, 1.1	5.22[b])		5.3 (br. *d*)	17.8	5.3 (br. *d*)	11.7
Me–C(2‴)			1.91 (*d*)	1.3	1.87 (br. *s*)		1.76 (*s*)		1.88 (*s*)		1.84 (*s*)	
Me–C(6‴)			1.34 (*s*)		1.43 (*s*)		1.34 (*s*)		1.44 (*s*)		1.41 (*s*)	
H–C(1⁗)					4.4 (*d*)	7.8	4.57 (*d*)	7.8	4.49 (*d*)	7.8	4.59 (*d*)	8
H–C(2⁗)					3.21 (*dd*)	7.8, 9	4.99 (*dd*)	7.8, 9.5	4.14 (*dd*)	7.8, 1.5	4.85 (*dd*)	8, 9.5
H–C(3⁗)					3.36[b])		5.19 (*t*)	9.4	–		3.57 (*t*)	9
H–C(4⁗)					3.34 (*t*)	9.7	5.02 (*t*)	9.8	4.25 (*dd*)	10.1, 1.5	3.42 (*t*)	9
H–C(5⁗)					3.22 (*m*)		3.64 (*m*)		3.29[b])		3.3 (*m*)	
H_a–C(6⁗)					3.67[b])		4.19 (br. *d*)	12.2	3.8 (*dd*)	12.2, 4.8	3.7 (*dd*)	12, 5.7
H_b–C(6⁗)					3.85[b])		4.04 (*dd*)	12.2, 2.4	3.92 (*dd*)	12.2, 1.5	3.86 (*dd*)	12, 2.4
H–C(3⁗′)											6.75 (*dt*)	1.5, 7.5
CH_2(4⁗′)											2.38–2.0[b])	
CH_2(5⁗′)											1.7–1.5[b])	
H–C(7⁗′)											5.79 (*dd*)	18, 10.8
H_a–C(8⁗′)											5.11 (*dd*)	10.8,1.6
H_b–C(8⁗′)											5.27 (*dd*)	18, 1.3
Me–C(2⁗′)											1.9 (*s*)	
Me–C(6⁗′)											1.32 (*s*)	

[a]) Additional Ac signals: 2.13, 2.06 (2×), 2.04, 2.03, 2.01, 2.0 (2×), 1.93 (aliph. ×9).

[b]) Signal patterns are unclear due to overlapping.

Table 2. *^{13}C-NMR Spectral Data of Anatolioside* (**1**), *Anatoliosides A–D* (**2–5**), *and Anatolioside-B Nonaacetate* (**3a**). For **1** and **3–5** at 75.5 MHz, for **2** at 100 MHz.

C-Atom[2])	**1** (CD_3OD)	**2** (CD_3OD)	**3** (CD_3OD)	**3a**[a])	**4** (CD_3OD)	**5** (CD_3OD)
Me–C(2)	18.0 (*q*)	17.9 (*q*)	17.9 (*q*)	(17.3)	17.9 (*q*)	18.0 (*q*)
C(2)	132.2 (*s*)	132.4 (*s*)	132.4 (*s*)	(131.6)	132.4 (*s*)	132.4 (*s*)
C(3)	125.6 (*d*)	125.5 (*d*)	125.5 (*d*)	(123.9)	125.5 (*d*)	125.5 (*d*)
C(4)	23.7 (*t*)	23.7 (*t*)	23.7 (*t*)	(22.6)	23.7 (*t*)	23.7 (*t*)
C(5)	42.8 (*t*)	43.0 (*t*)	43.0 (*t*)	(41.4)	43.0 (*t*)	43.0 (*t*)
C(6)	81.8 (*s*)	81.7 (*s*)	81.7 (*s*)	(80.1)	81.7 (*s*)	81.7 (*s*)
C(7)	144.6 (*d*)	144.7 (*d*)	144.7 (*d*)	(143.1)	144.7 (*d*)	144.7 (*d*)
C(8)	115.9 (*t*)	115.9 (*t*)	116.1 (*t*)	(116.6)	116.0 (*t*)	116.0 (*t*)
Me–C(2)	22.5 (*q*)	22.6 (*q*)	22.5 (*q*)	(21.7)	22.5 (*q*)	22.6 (*q*)
Me–C(6)	25.8 (*q*)	25.9 (*q*)	26.0 (*q*)	(25.6)	26.0 (*q*)	26.0 (*q*)
C(1′)	98.8 (*d*)	98.2 (*d*)	98.2 (*d*)	(96.8)	98.2 (*d*)	98.2 (*d*)
C(2′)	79.8 (*d*)	80.1 (*d*)	80.0 (*d*)	(75.1)	80.0 (*d*)	80.0 (*d*)
C(3′)	78.2 (*d*)	77.0 (*d*)	76.9 (*d*)	(71.3)	76.9 (*d*)	76.9 (*d*)
C(4′)	72.0 (*d*)	72.0 (*d*)	71.9 (*d*)	(70.3)	72.0 (*d*)	71.8 (*d*)
C(5′)	77.6 (*d*)	77.6 (*d*)	77.6 (*d*)	(72.9)	77.6 (*d*)	77.6 (*d*)
C(6′)	62.8 (*t*)	62.8 (*t*)	62.8 (*t*)	(62.5)	62.6 (*t*)	62.8 (*t*)
C(1″)	101.9 (*d*)	101.1 (*d*)	101.1 (*d*)	(97.1)	101.2 (*d*)	101.1 (*d*)
C(2″)	72.3 (*d*)	72.2 (*d*)	72.2 (*d*)	(68.2)	72.2 (*d*)	72.2 (*d*)
C(3″)	72.1 (*d*)	70.5 (*d*)	70.4 (*d*)	(68.7)	70.5 (*d*)	70.4 (*d*)
C(4″)	74.0 (*d*)	76.1 (*d*)	76.0 (*d*)	(71.2)	76.0 (*d*)	76.3 (*d*)
C(5″)	69.8 (*d*)	67.4 (*d*)	67.4 (*d*)	(66.9)	67.4 (*d*)	67.3 (*d*)
C(6″)	17.8 (*q*)	17.9 (*q*)	17.9 (*q*)	(17.6)	17.9 (*q*)	18.0 (*q*)
C(1‴)		169.3 (*s*)	169.3 (*s*)	(166.9)	169.3 (*s*)	169.2 (*s*)
C(2‴)		128.7 (*s*)	128.7 (*s*)	(127.2)	128.7 (*s*)	128.7 (*s*)
C(3‴)		144.2 (*d*)	144.1 (*d*)	(141.1)	143.6 (*d*)	144.0 (*d*)
C(4‴)		24.6 (*t*)	24.5 (*t*)	(23.0)	24.4 (*t*)	24.1 (*t*)
C(5‴)		41.9 (*t*)	41.3 (*t*)	(40.4)	41.3 (*t*)	41.9 (*t*)
C(6‴)		73.5 (*s*)	80.9 (*s*)	(81.5)	81.5 (*s*)	80.8 (*s*)
C(7‴)		145.9 (*d*)	144.4 (*d*)	(142.0)	144.2 (*d*)	144.4 (*d*)
C(8‴)		112.5 (*t*)	116.1 (*t*)	(116.4)	116.4 (*t*)	116.6 (*t*)
Me–C(2‴)		12.6 (*q*)	12.7 (*q*)	(12.2)	12.7 (*q*)	12.8 (*q*)
Me–C(6‴)		27.9 (*q*)	23.7 (*q*)	(23.1)	23.6 (*q*)	24.0 (*q*)
C(1⁗)			99.6 (*d*)	(96.1)	101.0 (*d*)	97.7 (*d*)
C(2⁗)			75.2 (*d*)	(71.5)	78.4 (*d*)	75.4 (*d*)
C(3⁗)			78.3 (*d*)	(74.7)	207.4 (*s*)	76.1 (*d*)
C(4⁗)			71.1 (*d*)	(71.4)	73.8 (*d*)	71.9 (*d*)
C(5⁗)			77.6 (*d*)	(69.2)	77.9 (*d*)	77.9 (*d*)
C(6⁗)			62.7 (*t*)	(62.3)	62.8 (*t*)	62.8 (*t*)
C(1⁗′)						168.4 (*s*)
C(2⁗′)						128.8 (*s*)
C(3⁗′)						143.1 (*d*)
C(4⁗′)						24.6 (*t*)
C(5⁗′)						42.2 (*t*)
C(6⁗′)						73.5 (*s*)
C(7⁗′)						145.9 (*d*)
C(8⁗′)						112.5 (*t*)
Me–C(2⁗′)						12.6 (*q*)
Me–C(6⁗′)						27.9 (*q*)

[a]) Additional signals: 170.5–168.9 (Me*C*O), 20.8–20.6 (*Me*CO).

below), and with **3a** (see below, *Fig.*). Additional confirmation gives the alkaline hydrolysis of compounds **2**–**5** which each yield **1**. These results indicate **1** to be linalo-6-yl 2′-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside[2]) for which we propose the trivial name anatolioside.

The ^{1}H-NMR spectrum of **1** contains signals belonging to a monoterpene: *i*) 3 olefinic protons for a monosubstituted double bond appear at δ 5.25, 5.26, and 5.98 (*ABX* pattern, J_{AB} = 1.2, J_{AX} = 10.6 (*cis*-coupling), and J_{BX} = 18 Hz (*trans*-coupling)); *ii*) an olefinic proton resonating at δ 5.13 shows couplings to $CH_2(4^2)$ (δ 2.05 (*m*)), which in turn are further coupled to $CH_2(5^2)$ (δ 1.66–1.56 (*m*)); *iii*) additionally, 3 signals are observed at δ 1.70, 1.64, and 1.42 for tertiary Me groups. These ^{1}H-NMR results, as well as the ^{13}C-NMR data, attributed to the monoterpene moiety of **1** are in good accordance with those reported for the linalool moiety in linalo-6-yl β-D-glucopyranoside[2]) and linalo-6-yl 6′-*O*-(β-L-fucopyranosyl)-β-D-glucopyranoside[2]) [3]. The remaining signals in both the ^{1}H- and the ^{13}C-NMR spectra of **1** are consistent with the presence of the sugars glucose and rhamnose, *e.g.* the anomeric protons of β-D-glucose and α-L-rhamnose are observed at δ 4.46 (*d*, *J* = 7.4 Hz) and 5.34 (*d*, *J* = 1.7 Hz), respectively. The signals attributed to $C(6^2)$ of the linalool and C(2′) of the glucose moiety appear at δ 81.8 and 79.8, respectively, with a *ca.* +9 and +6 ppm downfield shift when compared to linalool (72.7 ppm) [4] and glucose (74.0 ppm) respectively; these shifts are due to the α-effect of glycosidation, clearly indicating the sites of glycosidation.

Anatolioside A (**2**), obtained as a colourless, amorphous powder of molecular formula $C_{32}H_{52}O_{12}$, shows characteristic IR absorptions for OH groups (3400 cm^{-1}) and an α,β-unsaturated ester (1690 and 1640 cm^{-1}), the latter function also being indicated by the UV spectrum (λ_{max} 218 nm). Comparison of the ^{1}H- and ^{13}C-NMR data of **2** with those of **1** clearly indicate **2** to be a monoterpene derivative of **1**. The complete assignments of the ^{1}H- and ^{13}C-NMR signals are based on homo- and heteronuclear correlation experiments (*Tables 1* and *2*). The additional monoterpene moiety is identified as (2*E*)-6-hydroxy-2,6-dimethyl-octa-2,7-dienoic acid (= menthiafolic acid) [5] by its ^{1}H- and ^{13}C-NMR data. The configuration at C(6‴) of menthiafolic acid is (*R*) based on the *Klyne* rule [6], the molecular rotation difference between anatolioside A (**2**) and anatolioside (**1**), Δ [*M*] = −106.8, being comparable with that of (−)-(*R*)-linalool ([*M*] = −20) [7]. This monoterpene fragment is connected to C(4″) of rhamnose based on evidence from the HMBC spectrum. Consequently, the monoterpene glycoside **2** is linalo-6-yl *O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside[2]), for which we propose the trival name anatolioside A.

Anatolioside B (**3**) is obtained as a colourless, amorphous compound with the molecular formula $C_{38}H_{62}O_{17}$. The UV and IR spectra show similar absorption bands as for **2** (UV: 217 nm; IR: 3400, 1690, 1640 cm^{-1}), as does the ^{1}H-NMR spectrum (*Table 1*). The results indicate **3** to be 6‴-*O*-(β-D-glucopyranosyl)anatolioside A.

The main difference between the ^{1}H-NMR data of **2** and **3** is the appearance of additional signals, which are attributed to a second glucose moiety, *e.g.* its anomeric proton appears at δ 4.4 (*d*, *J* = 7.8 Hz). The ^{13}C-NMR data of **3** (*Table 2*) indicate this second glucose moiety to be attached to the tertiary OH group of menthiafolic acid. Comparison of the δ (C) values of **3** and **2** allow the signal at δ 80.9 (*s*) to be assigned to C(6‴), the downfield shift of +7.4 ppm indicating glycosidation at this location. All other signals are in good accordance with those of **2**.

Hydrolysis of **3** under alkaline conditions produces **1** and **6**. The ^{1}H-NMR spectrum of **6** (see *Exper. Part*) is consistent with its structure. On methylation with diazomethane,

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[2]) For convenience, the linalool moiety in **1**–**5** is numbered arbitrarily, starting with one of the geminal Me groups; the systematic name of this moiety is (3*R*)-3,7-dimethylocta-1,6-dien-3-yl or (1*R*)-1-ethenyl-1,5-dimethylhex-4-en-1-yl.

6 affords an ester, clearly indicating the site of glycosylation to be the tertiary OH group of the menthiafolic acid. Compound **6** is thus 6-*O*-(*β*-D-glucopyranosyl)menthiafolic acid. Acetylation of **3** yields the nonaacetate **3a** which confirms the structure of monoterpene glycoside **3** to be linalo-6-yl *O*-*β*-D-glucopyranosyl-(1''''→6''')-*O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1'''→4'')-*O*-α-L-rhamnopyranosyl)-(1''→2')-*β*-D-glucopyranoside, for which we propose the trivial name anatolioside B.

The molecular weight of nonaacetate **3a** is 1169 (FAB-MS: 1191 ($[M + Na]^+$), calc. for $C_{56}H_{80}O_{26}$). The ^{1}H-NMR spectrum of **3a** (*Table 1*) reveals the presence of 9 Ac signals belonging to the sugar moieties. The sugar protons are assigned on the basis of a 2D homonuclear correlation spectrum and the ^{13}C-NMR signals from a C,H heteronuclear correlation. The ^{1}H-COSY of **3a** confirms in particular the site of attachment of rhamnose to glucose as no downfield shift is observed for H–C(2') (δ 3.75 (*dd*, J = 7.8 and 9.4 Hz)) of glucose upon acetylation. The linkages of sugar and monoterpene units result from a HMBC experiment (*Fig.*), where correlations between *H*–C(1') of the bridging glucose (δ 4.57) and C(6) of linalool (δ 80.1), *H*–C(4'') of rhamnose (δ 5.13) and C(1''') of menthiafolic acid (δ 166.9), and *H*–C(1'''') of the terminal glucose (δ 4.57) and C(6''') of menthiafolic acid (δ 81.5) are indicated.

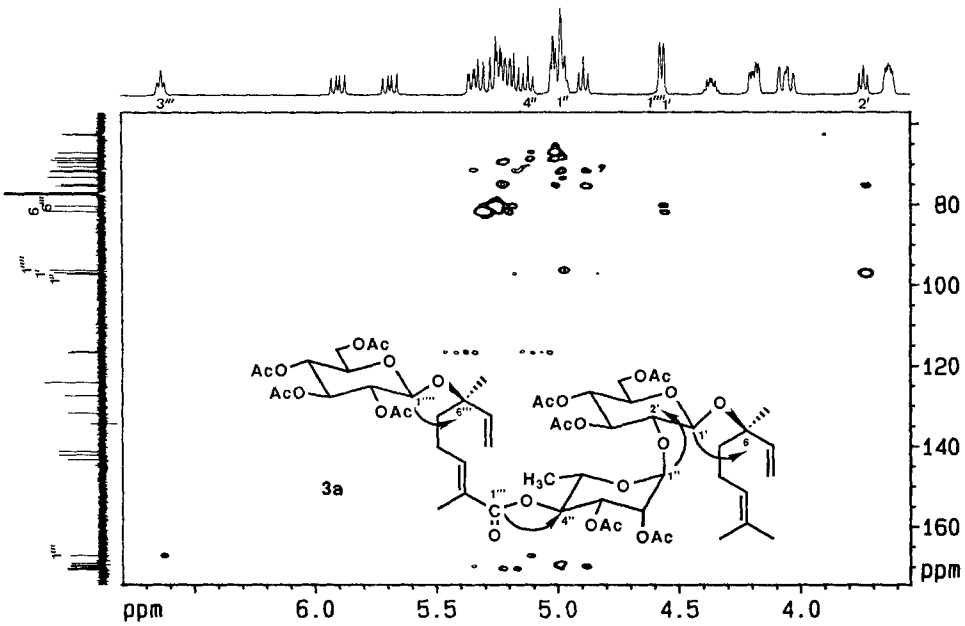

Figure. *Heteronuclear multiple-bond correlation* (HMBC) *experiment of anatolioside B nonaacetate* (**3a**). At 500 MHz; J = 10 Hz; in $CDCl_3$.

Anatolioside C (**4**) is obtained as a colourless amorphous compound with the molecular formula $C_{38}H_{60}O_{17}$. Comparison of all spectroscopic data (IR, UV, MS, and ^{1}H- and ^{13}C-NMR) of **4** with those of **3** reveals that the two molecules are virtually identical except in the region of the terminal sugar moiety. In **3** this unit is glucose, while in **4** it is *β*-D-*ribo*-hexos-3-ulose [8–10]. Alkaline hydrolysis of **4** yields anatolioside (**1**) supporting the terminal position of *β*-D-*ribo*-hexos-3-ulose. This deduction is further supported by the ^{13}C-NMR chemical shift of C(6''') of **4** (δ 81.5 (*s*)), as in anatolioside B (**3**; *Table 2*). Compound **4** is thus linalo-6-yl *O*-*β*-D-*ribo*-hexopyranos-3-ulosyl-(1''''→6''')-*O*-[(2*E*,6*R*)-

6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside[2]) (= anatolioside C).

Anatolioside D (**5**) is obtained as a colourless amorphous compound with the molecular formula $C_{48}H_{76}O_{19}$. The UV (λ_{max} 218 nm) and IR spectra (3400, 1700, 1690, and 1640 cm^{-1}) are similar to those of **4**. The structure of **5** is established by further spectral data to be linalo-6-yl *O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1⁗→2‴)-*O*-β-D-glucopyranosyl-(1‴→6″)-*O*-[(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl]-(1‴→4″)-*O*-α-L-rhamnopyranosyl-(1″→2′)-β-D-glucopyranoside[2]) (= anatolioside D).

The ^{1}H-NMR spectrum of **5** (*Table 1*) shows resonances belonging to 3 vinyl groups, additional olefinic protons, seven tertiary Me groups, and 3 sugar moieties. The signals arising from the anomeric sugar protons are assigned to 1 rhamnose (δ 5.5 (br. *s*, H–C(1″)) and 2 glucose molecules (δ 4.48 (*d*, J = 7.4 Hz, H–C(1′)) and 4.59 (*d*, J = 8 Hz, H–C(1⁗)). Comparison with the corresponding data of **1**–**4** reveals that **5** contains an extra menthiafolic acid unit, which is attached *via* an ester linkage to C(2‴) of the second glucose moiety (H–C(2‴) at δ 4.85 (*dd*, J = 8 and 9.5 Hz)). The other menthiafolic acid is attached *via* an ester link to C(4″) (H–C(4″) at δ 5.03 (*t*, J = 9.7Hz)) of the rhamnose moiety, as found in anatoliosides A (**2**), B (**3**), and C (**4**). Downfield shifts for C(6) of linalool (δ 81.7 (*s*)), C(2′) of glucose (δ 80.0 (*d*)), and C(6‴) of menthiafolic acid (δ 80.8 (*s*)) in the ^{13}C-NMR spectrum of **5** further confirm the proposed sites of glycosidation, as does the alkaline hydrolysis of **5**, which yields anatolioside (**1**), **6** and menthiafolic acid.

Experimental Part

General. MPLC: *Sepralyte C18*, 40 μm (*Analytichem*); *Labomatic* column (1.8 × 35.2 cm); *LEWA-M5* pump; *Rheodyne* injector; *LKB 17000 Minirac* fraction collector; flow rate 4–5 ml/min. CC: Silica gel *60* (70–230 mesh, *Merck*). TLC: Silica gel F_{254} (*Merck*; for glycosides) and cellulose F_{254} (*Merck*; for sugars) plates; detection of monoterpene glycosides by spraying with 1% vanillin/H_2SO_4 and of sugars by aniline phthalate reagent followed by heating at 100° for 5–10 min. UV Spectra (λ_{max} [nm]): *Shimadzu-UV-160A* spectrophotometer; spectroscopic-grade MeOH (*Merck*). IR Spectra (cm^{-1}); *Perkin-Elmer-257* instrument; KBr pellets. Optical rotations: *Perkin-Elmer-141 polarimeter*. ^{1}H- and ^{13}C-NMR Spectra (δ [ppm], J [Hz]): at 300, 400, and 500 MHz (^{1}H) and at 75.5 and 100 MHz (^{13}C) in FT mode using *Bruker AMX300*, *AMX400*, and *AMX500* instruments. FAB-MS (*m/z* (%)): *ZAB2-SEQ*; in 3-nitrobenzyl alcohol (NOBA).

Extraction and Purification. Viburnum orientale PALLAS was collected from Turkey, N.E. Anatolia, Rize, Pazar, July 1989. A voucher specimen was deposited in the Herbarium of Pharmacognosy Dept., Faculty of Pharmacy, Hacettepe University (HUEF-89-045). The air-dried leaves (500 g) were extracted with MeOH (2 × 2 l) at *ca.* 40°. The H_2O-soluble part of the MeOH extract was successively extracted with Et_2O, AcOEt, and BuOH (Et_2O extract, 23.4 g; AcOEt extract, 27.7 g; BuOH extract, 44.4 g). The BuOH extract (15 g) was chromatographed over silica gel (220 g) with $CHCl_3$/MeOH/H_2O 80:20:2, 70:30:3, and 60:40:4 to give 10 main fractions *A*–*J* (*A*, 290 mg; *B*, 580 mg; *C*, 375 mg; *D*, 840 mg; *E*, 780 mg; *F*, 460 mg; *G*, 660 mg; *H*, 455 mg; *I*, 470 mg; *J*, 3.5 g).

Isolation of Anatoliosides **1**–**5**. *Fr. B* (580 mg) was subjected to MPLC (H_2O/MeOH stepwise gradient (30, 40, 50, 60, and 70% MeOH)): pure *anatolioside A* (**2**, 135 mg). *Fr. D* (840 mg) was first subjected to MPLC (same conditions as for **2**) to give 6 main fractions *D1*–*D6*. *Fr. D4* (80 mg), *D5* (63 mg), and *D6* (92 mg) were further chromatographed separately over silica gel ($CHCl_3$/MeOH 4:1 for *Fr. D4*, $CHCl_3$/MeOH/H_2O 40:10:1 for *Fr. D5* and *D6*). *Fr. D4* afforded *anatolioside* (**1**, 38 mg), while *Fr. D5* and *D6* yielded *anatolioside C* (**4**, 34 mg) and *anatolioside D* (**5**, 70 mg), respectively. *Fr. F* (460 mg) and *G* (660 mg) were subjected separately to MPLC (H_2O/MeOH stepwise gradient (20–65% MeOH): pure *anatolioside B* (**3**; total: 385 mg).

Anatolioside (**1**). Amorphous, colourless powder. $[\alpha]_D^{20} = -31.4$ (c = 0.29, MeOH). UV (MeOH): 203. IR (KBr): 3400 (br., OH), 1640 (C=C). ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*. ^{13}C-NMR (75.5 MHz, CD_3OD): *Table 2*. FAB-MS: 485 (82, $[M + Na]^+$), 947 (2, $[2M + Na]^+$), 963 (1, $[2M + K]^+$).

Anatolioside A (**2**). Amorphous, colourless powder. $[\alpha]_D^{20} = -40.1$ (c = 0.39, MeOH). UV (MeOH): 218. IR (KBr): 3400 (br., OH), 1690 (α,β-unsat. ester), 1640 (C=C). ^{1}H-NMR (400 MHz, CD_3OD): *Table 1*. ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*. FAB-MS: 651 (100, $[M + Na]^+$).

Anatolioside B (**3**). Amorphous, colourless powder. $[\alpha]_D^{20} = -50.3$ ($c = 0.39$, MeOH). UV (MeOH): 217. IR (KBr): 3400 (br., OH), 1690 (α,β-unsat. ester), 1640 (C=C). ^{1}H-NMR (400 MHz, CD_3OD): *Table 1.* ^{13}C-NMR (75.5 MHz, CD_3OD): *Table 2.* FAB-MS: 813 (93, $[M + Na]^+$).

Acetylation of **3** (75 mg) with Ac_2O (1 ml), pyridine (1 ml), and 4-(dimethylamino)pyridine (20 mg) at r.t. overnight followed by CC (silica gel, benzene/acetone 9:1) gave nonaacetate **3a**. ^{1}H-NMR (300 MHz, $CDCl_3$): *Table 1.* ^{13}C-NMR (75.5 MHz, $CDCl_3$): *Table 2.* FAB-MS: 1191 (5, $[M + Na]^+$), 727 (100), 655 (4, $[M$ – linalool – 331$]^+$), 519 (5.4, [pentaacetyl-rhamnopyranosyl-glucoseoxonium]$^+$), 497 (4, [6-*O*-(tetraacetylglucopyranosyl)menthiafolioyl]$^+$), 331 (14, [tetraacetyl-glucoseoxonium]$^+$), 170 (4), 169 (34.5), 153 (26, [linalool]$^+$).

Acid Hydrolysis of **3**. Compound **3** (20 mg) in 5% HCl soln. was heated at 100° for 2 h, cooled, and filtered. The filtrate was neutralized passing it through *Dowex* (Cl^- form) and evaporated. The residue was examined for sugars by paper chromatography (descending mode; BuOH/AcOH/H_2O 4:1:5) and TLC (AcOEt/pyridine/AcOH/H_2O 36:36:7:21).

Alkaline Hydrolysis of **3**. Compound **3** (65 mg) was heated in 5% aq. KOH soln. (5 ml) at 80° for 2 h. After neutralization with 5% aq. HCl soln. and evaporation, the residue was chromatographed (silica gel (30 g), $CHCl_3$/MeOH/H_2O 80:20:2, 70:30:3, and 60:40:4): **1** (20 mg) and **6**.

Compound **1** was identified by comparison (^{1}H-NMR, FAB-MS, TLC) with an authentic sample.

6-O-(β-D-Glucopyranosyl)menthiafolic Acid (= *(2E,6R)-6-(β-D-Glucopyranosyloxy)-2,6-dimethylocta-2,7-dienoic Acid*; **6**): ^{1}H-NMR (300 MHz, CD_3OD): menthiafolic acid: 5.99 (*dd*, $J = 17.2, 11.1$, H–C(7)); 5.58 (br. *t*, $J = 6.2$, H–C(3)); 5.22 (br. *d*, $J = 11.1$, H_b–C(8)); 5.21 (br. *d*, $J = 17.2$, H_a–C(8)); 2.26 (*m*, 2 H–C(4)); 1.61–1.21 (*m*, 2 H–C(5)); 1.35 (*s*, Me–C(2)); 1.29 (*s*, Me–C(6)); glucose: 4.37 (*d*, $J = 7.6$, H–C(1′)); 3.83 (br. *d*, $J = 12$, H_b–C(6′)); 3.67 (*dd*, $J = 12, 4.9$, H_a–C(6′)); 3.46–3.18 (*m*, H–C(2′), H–C(3′), H–C(4′), H–C(5′)).

Alkaline Hydrolysis of **2**, **4**, *and* **5**. Compound **2**, **4**, or **5** (each 5 mg) was refluxed in 5% aq. KOH soln. (1 ml) at 80° for 1 h. Then the soln. was neutralized and evaporated. The residue was dissolved in MeOH and compared by TLC. Anatolioside (**1**) was found in each hydrolysate.

Anatolioside C (**4**). Amorphous, colourless powder. $[\alpha]_D^{20} = -49.4$ ($c = 0.37$, MeOH). UV (MeOH): 217. IR (KBr): 3400 (br., OH), 1700, 1690 (α, β-unsat. ester), 1640 (C=C). ^{1}H-NMR (300 MHz, CD_3OD): *Table 1.* ^{13}C-NMR (75.5 MHz, CD_3OD): *Table 2.* FAB-MS: 811 (65, $[M + Na]^+$), 1599.6 (67, $[2M + Na]^+$).

Anatolioside D (**5**). Amorphous, colourless powder. $[\alpha]_D^{20} = = -45.0$ ($c = 0.40$, MeOH). UV (MeOH): 218. IR (KBr): 3400 (br., OH), 1700, 1690 (α,β-unsat. ester), 1640 (C=C). ^{1}H-NMR (300 MHz, CD_3OD): *Table 1.* ^{13}C-NMR (75.5 MHz, CD_3OD): *Table 2.* FAB-MS: 979 (100, $[M + Na]^+$).

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