

**187. Anatolioside E:
A New Acyclic Monoterpene Glycoside from *Viburnum orientale*¹⁾²⁾**

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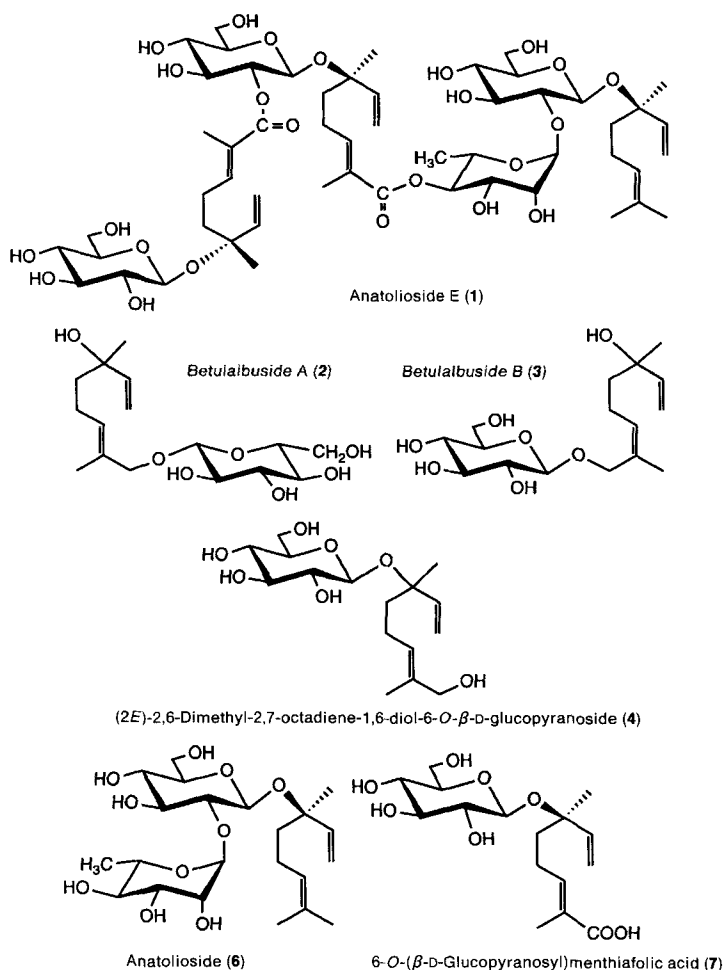
A new open-chain monoterpene glycoside, anatolioside E (**1**), was isolated from the leaves of *Viburnum orientale* in addition to three known acyclic monoterpene glycosides, betulalbusides A (**2**) and B (**3**), and 2(*E*)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -D-glucopyranoside (**4**). The structure of anatolioside E (**1**) was elucidated on the basis of chemical and spectral data as 6-*O*-[β -D-glucopyranosyl-(1^{'''}→6^{'''})-2-(*E*), 6(*R*), 2,6-dimethyl-6-hydroxy-2,7-octadienyl-(1^{'''}→2^{'''})- β -D-glucopyranosyl-(1^{'''}→6^{'''})-2(*E*), 6(*R*), 2,6-dimethyl-6-hydroxy-2,7-octadienyl-(1^{'''}→4^{'''})- α -L-rhamnopyranosyl-(1^{''}→2^{''})- β -D-glucopyranosyl]linalool.

1. Introduction. – In the course of investigations into the chemical constituents of *Viburnum orientale* PALLAS (Caprifoliaceae), the isolation and identification of an ester iridoid glycoside, viborientoside [2], as well as of five acyclic monoterpene glycosides, anatolioside and anatoliosides A–D, have been reported [3]. As a result of a continuing investigation into the same plant, it is now possible to report the isolation and structure elucidation of a new acyclic monoterpene glycoside, anatolioside E (**1**), as well as of betulalbusides A (**2**) [4] [5] and B (**3**) [4], and 2(*E*)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -D-glucopyranoside (**4**).

2. Results and Discussion. – Compound **1** was obtained as a colourless, amorphous optically active powder of molecular formula C₅₄H₈₆O₂₄ (FAB-MS: 1141 ([*M* + Na]⁺). The IR spectrum showed absorptions characteristic of OH (3500 cm⁻¹) and α,β -unsaturated-ester (1690 and 1630 cm⁻¹) functions, the latter being also supported by the UV spectrum (λ_{max} 217.5 nm). The ¹H-NMR spectrum of **1** exhibited resonances for *i*) three vinyl groups in the form of *ABX* systems, *ii*) three additional olefinic protons, *iii*) seven tertiary Me groups, and *iv*) four sugar moieties (Table 1). The signals arising from the anomeric protons of the sugars were assigned to one rhamnose (5.48, br. *s*) and three glucose units (4.49, 4.59, 4.41; each *d*, *J* = 7.5, 8.0, 7.8 Hz, respectively). Two-dimen-

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²⁾ Dedicated to Prof. Dr. Mekin Tanker on the occasion of his 40th academic year.



sional homo- and heteronuclear correlations led to the identification of the remaining carbohydrate resonances. From these, the signals observed at 5.03 (*t*, $J = 9.8$ Hz) and 4.85 (*dd*, $J = 8.0, 9.6$ Hz) were attributed to H-C(4'') of rhamnose and H-C(2''') of one of the glucose units, respectively, indicating two sites of acylation.

The ^{13}C -NMR spectrum of **1** (Table 2) contained 54 C-signals arising from three monoterpene and four sugar units. The chemical-shift values attributed to the monoterpene units were in good accordance with the data given for linalool [4] and (2E)-6-hydroxy-2,6-dimethylocta-2,7-dienoic acid (= menthialfolic acid) [6]. The number of carbonyl C-signals (168.8 and 169.5) was consistent with the presence of two monoterpene acid residues. The C(6) resonances of these monoterpene units were observed at 82.0, 81.3, and 81.1 ppm; each being *ca.* 9 ppm down-field when compared to the equivalent resonances in linalool [4] and menthialfolic acid [6], and this clearly indicated three sites of glycosidations.

Table 1. $^1\text{H-NMR}$ Data (500.13 MHz) of Anatolioside E (1) (CD_3OD) and Anatolioside E Dodecaacetate (5) (CDCl_3 ; δ in ppm, J in Hz)

	1	5 ^{a)}
Me-C(2)	1.61 (<i>s</i> , $J = 0.9$)	1.48 (<i>s</i>)
H-C(3)	5.04 (<i>dt</i> , $J = 6.7, 1.4$)	4.90 (<i>br. t</i> , $J = 7.0$)
H-C(4)	2.00–2.40 ^{b)}	1.90 ^{b)}
H-C(5)	1.50–1.80 ^{b)}	1.40–1.63 ^{b)}
H-C(7)	6.00 (<i>dd</i> , $J = 11.0, 17.7$)	5.84 (<i>dd</i> , $J = 10.9, 17.6$)
H _a -C(8)	5.24–5.29 ^{b)}	5.25 (<i>dd</i> , $J = 10.9, 0.7$)
H _b -C(8)	5.33 (<i>dd</i> , $J = 17.7, 1.2$)	5.17 (<i>br. d</i> , $J = 17.6$)
Me-C(2)	1.67 (<i>d</i> , $J = 1.0$)	1.55 (<i>s</i>)
Me-C(6)	1.41 (<i>s</i>)	1.30 (<i>s</i>)
H-C(1')	4.49 (<i>d</i> , $J = 7.5$)	4.51 (<i>d</i> , $J = 7.5$)
H-C(2')	3.32 (<i>dd</i> , $J = 7.5, 9.8$)	3.68 (<i>dd</i> , $J = 7.5, 9.8$)
H-C(3')	3.49 (<i>t</i> , $J = 9.8$)	5.19 (<i>t</i> , $J = 9.8$)
H-C(4')	3.42 (<i>dd</i> , $J = 9.0, 9.8$)	4.84 (<i>dd</i> , $J = 9.0, 9.8$)
H-C(5')	3.19–3.34 ^{b)}	3.56–3.62 ^{b)}
H _a -C(6')	3.70 (<i>dd</i> , $J = 12.0, 4.7$)	4.14 (<i>dd</i> , $J = 12.0, 5.7$)
H _b -C(6')	3.88 (<i>dd</i> , $J = 12.0, 2.4$)	4.02 (<i>dd</i> , $J = 12.0, 2.3$)
H-C(1'')	5.48 (<i>br. s</i>)	4.98 (<i>d</i> , $J = 1.6$)
H-C(2'')	3.96 ^{b)}	4.96 ^{b)}
H-C(3'')	3.95 (<i>dd</i> , $J = 3.4, 9.8$)	5.29 (<i>dd</i> , $J = 3.4, 10.0$)
H-C(4'')	5.03 (<i>t</i> , $J = 9.8$)	5.06 (<i>t</i> , $J = 10.0$)
H-C(5'')	4.43 (<i>dq</i> , $J = 6.2, 9.8$)	4.30 (<i>dq</i> , $J = 6.2, 10.0$)
H-C(6'')	1.12 (<i>d</i> , $J = 6.2$)	1.10 (<i>d</i> , $J = 6.2$)
H-C(3''')	6.89 (<i>dt</i> , $J = 7.5, 1.5$)	6.55 (<i>dt</i> , $J = 7.3, 1.3$)
H-C(4''')	2.00–2.40 ^{b)}	1.90–2.00 ^{b)}
H-C(5''')	1.50–1.80 ^{b)}	1.40–1.63 ^{b)}
H-C(7''')	5.99 (<i>dd</i> , $J = 11.0, 17.7$)	5.55 (<i>dd</i> , $J = 11.0, 17.6$)
H _a -C(8''')	5.24–5.29 ^{b)}	5.23 (<i>dd</i> , $J = 11.0, 0.7$)
H _b -C(8''')	5.30 (<i>dd</i> , $J = 17.7, 1.1$)	5.17 (<i>br. d</i> , $J = 17.6$)
Me-C(2''')	1.84 (<i>d</i> , $J = 1.3$)	1.67 (<i>br. s</i>)
Me-C(6''')	1.45 (<i>s</i>)	1.29 (<i>s</i>)
H-C(1''')	4.59 (<i>d</i> , $J = 8.0$)	4.52 (<i>d</i> , $J = 8.0$)
H-C(2''')	4.85 (<i>dd</i> , $J = 8.0, 9.5$)	5.01 (<i>dd</i> , $J = 8.0, 9.5$)
H-C(3''')	3.52 (<i>t</i> , $J = 9.5$)	5.13 (<i>t</i> , $J = 9.5$)
H-C(4''')	3.57 (<i>dd</i> , $J = 9.0, 9.5$)	4.94 (<i>dd</i> , $J = 9.0, 9.5$)
H-C(5''')	3.19–3.34 ^{b)}	3.56–3.62 ^{b)}
H _a -C(6''')	3.68 (<i>dd</i> , $J = 12.0, 5.9$)	4.13 (<i>dd</i> , $J = 12.0, 5.9$)
H _b -C(6''')	3.86 (<i>dd</i> , $J = 12.0, 2.5$)	4.015 (<i>dd</i> , $J = 12.0, 2.3$)
H-C(3''''')	6.75 (<i>dt</i> , $J = 7.5, 1.5$)	6.61 (<i>dt</i> , $J = 7.3, 1.2$)
H-C(4''''')	2.00–2.40 ^{b)}	2.1 (<i>m</i>)
H-C(5''''')	1.50–1.80 ^{b)}	1.40–1.63 ^{b)}
H-C(7''''')	5.75 (<i>dd</i> , $J = 17.9, 10.8$)	5.64 (<i>dd</i> , $J = 17.6, 11.0$)
H _a -C(8''''')	5.24–5.29 ^{b)}	5.15 (<i>dd</i> , $J = 11.0, 0.7$)
H _b -C(8''''')	5.27 (<i>dd</i> , $J = 17.9, 1.1$)	5.11 (<i>br. d</i> , $J = 17.6$)
Me-C(2''''')	1.89 (<i>d</i> , $J = 1.3$)	1.71 (<i>br. s</i>)
Me-C(6''''')	1.44 (<i>s</i>)	1.26 (<i>s</i>)

^{a)} Additional Ac signals: 1.87, 1.88, 1.93, 1.94, 1.947, 1.953, 1.98, 1.986, 1.998 (each 3 H), 2.00 (6 H), 2.06 (3 H).^{b)} Signal pattern unclear due to overlapping.

Table 1 (cont.)

	1	5 ^{a)}
H–C(1''''')	4.41 (<i>d</i> , <i>J</i> = 7.8)	4.52 (<i>d</i> , <i>J</i> = 8.0)
H–C(2''''')	3.23 (<i>dd</i> , <i>J</i> = 7.8, 9.2)	4.94 (<i>dd</i> , <i>J</i> = 8.0, 9.7)
H–C(3''''')	3.37 (<i>t</i> , <i>J</i> = 9.2)	5.18 (<i>t</i> , <i>J</i> = 9.7)
H–C(4''''')	3.33 (<i>t</i> , <i>J</i> = 9.2)	4.94 (<i>t</i> , <i>J</i> = 9.7)
H–C(5''''')	3.19–3.34 ^{b)}	3.56–3.62 ^{b)}
H _a –C(6''''')	3.67 (<i>dd</i> , <i>J</i> = 12.0, 5.9)	4.13 (<i>dd</i> , <i>J</i> = 12.0, 5.9)
H _b –C(6''''')	3.85 (<i>dd</i> , <i>J</i> = 12.0, 2.4)	3.98 (<i>dd</i> , <i>J</i> = 12.0, 2.3)

^{a)} Additional Ac signals: 1.87, 1.88, 1.93, 1.94, 1.947, 1.953, 1.98, 1.986, 1.998 (each 3 H), 2.00 (6 H), 2.06 (3 H).

^{b)} Signal pattern unclear due to overlapping.

Table 2. ¹³C-NMR Data (125.8 MHz) of Anatosioid E (1) (CD₃OD) and Anatosioid E Dodecaacetate (5) (CDCl₃)

	1	5 ^{a)}		1	5 ^{a)}
Me–C(2)	18.3 (<i>q</i>)	16.7 (<i>q</i>)	C(1''''')	98.5 (<i>d</i>)	95.2 (<i>d</i>)
C(2)	132.7 (<i>s</i>)	130.6 (<i>s</i>)	C(2''''')	75.7 (<i>d</i>)	70.4 (<i>d</i>)
C(3)	125.9 (<i>d</i>)	123.0 (<i>d</i>)	C(3''''')	76.4 (<i>d</i>)	71.9 (<i>d</i>)
C(4)	24.0 (<i>t</i>)	21.6 (<i>t</i>)	C(4''''')	72.2 (<i>d</i>)	67.8 (<i>d</i>)
C(5)	43.3 (<i>t</i>)	40.4 (<i>t</i>)	C(5''''')	78.1 (<i>d</i>)	70.3 (<i>d</i>)
C(6)	82.0 (<i>s</i>)	80.5 (<i>s</i>)	C(6''''')	63.0 (<i>t</i>)	61.4 (<i>t</i>)
C(7)	144.8 (<i>d</i>)	140.9 (<i>d</i>)			
C(8)	116.4 (<i>t</i>)	115.9 (<i>t</i>)	C(1''''')	168.8 (<i>s</i>)	164.9 (<i>s</i>)
Me–C(2)	22.9 (<i>q</i>)	24.7 (<i>q</i>)	C(2''''')	129.1 (<i>s</i>)	126.1 (<i>s</i>)
Me–C(6)	26.4 (<i>q</i>)	20.7 (<i>q</i>)	C(3''''')	143.4 (<i>d</i>)	142.1 (<i>d</i>)
			C(4''''')	24.8 (<i>t</i>)	22.0 (<i>t</i>)
C(1')	98.9 (<i>d</i>)	95.8 (<i>d</i>)	C(5''''')	41.6 (<i>t</i>)	39.5 (<i>t</i>)
C(2')	80.3 (<i>d</i>)	73.7 (<i>d</i>)	C(6''''')	81.1 (<i>s</i>)	79.1 (<i>s</i>)
C(3')	77.2 (<i>d</i>)	74.1 (<i>d</i>)	C(7''''')	145.0 (<i>d</i>)	140.0 (<i>d</i>)
C(4')	72.1 (<i>d</i>)	68.2 (<i>d</i>)	C(8''''')	116.9 (<i>t</i>)	115.4 (<i>t</i>)
C(5')	77.9 (<i>d</i>)	70.6 (<i>d</i>)	Me–C(2''''')	13.1 (<i>q</i>)	11.3 (<i>q</i>)
C(6')	63.0 (<i>t</i>)	61.5 (<i>t</i>)	Me–C(6''''')	23.9 (<i>q</i>)	21.9 (<i>q</i>)
C(1'')	101.4 (<i>d</i>)	96.1 (<i>d</i>)	C(1''''')	98.0 (<i>d</i>)	95.3 (<i>d</i>)
C(2'')	72.5 (<i>d</i>)	67.7 (<i>d</i>)	C(2''''')	75.5 (<i>d</i>)	70.6 (<i>d</i>)
C(3'')	70.7 (<i>d</i>)	67.2 (<i>d</i>)	C(3''''')	78.6 (<i>d</i>)	71.9 (<i>d</i>)
C(4'')	76.6 (<i>d</i>)	70.2 (<i>d</i>)	C(4''''')	72.0 (<i>d</i>)	69.4 (<i>d</i>)
C(5'')	67.6 (<i>d</i>)	65.9 (<i>d</i>)	C(5''''')	77.9 (<i>d</i>)	70.2 (<i>d</i>)
C(6'')	18.3 (<i>q</i>)	16.3 (<i>q</i>)	C(6''''')	63.1 (<i>t</i>)	61.3 (<i>t</i>)
C(1''')	169.5 (<i>s</i>)	166.0 (<i>s</i>)			
C(2''')	129.0 (<i>s</i>)	126.1 (<i>s</i>)			
C(3''')	144.3 (<i>d</i>)	142.3 (<i>d</i>)			
C(4''')	24.4 (<i>t</i>)	22.0 (<i>t</i>)			
C(5''')	42.5 (<i>t</i>)	39.6 (<i>t</i>)			
C(6''')	81.3 (<i>s</i>)	79.2 (<i>s</i>)			
C(7''')	144.4 (<i>d</i>)	140.2 (<i>d</i>)			
C(8''')	116.4 (<i>t</i>)	115.5 (<i>t</i>)			
Me–C(2''')	13.0 (<i>q</i>)	11.2 (<i>q</i>)			
Me–C(6''')	24.3 (<i>q</i>)	21.9 (<i>q</i>)			

^{a)} Additional signals: 169.6–168.0 (COCH₃); 19.9–19.6 (COCH₃).

Acetylation of **1** yielded the dodecaacetate **5**, as judged from the ^1H -NMR spectrum, which contained resonances for twelve AcO Me groups (Table 1). This experiment also clarified the fourth glycosidation site to be on a glucose unit, as no down-field shift upon acetylation for $\text{H}-\text{C}(2')$ (3.68 (*dd*, $J = 7.5, 9.8$ Hz)) was observed. These results also confirmed that four sugar and three monoterpene units are attached to each other *via* four glycosidic and two ester linkages, indicating a linear sequence. The FAB-MS of **5** confirmed the molecular weight to be 1622 (1645 ($[M + \text{Na}]^+$), calc. for $\text{C}_{78}\text{H}_{110}\text{O}_{36}$) and the fragment-ion peak at m/z 331 indicated a glucose unit to be the terminal sugar. Alkaline hydrolysis of **1** yielded **6** and **7** which were identified [3] as anatosioid (6) and 6-*O*-(β -D-glucopyranosyl)menthiafolic acid (7). These results suggested **1** to be 6''''-*O*-(β -D-glucopyranosyl)anatosioid D. Final structural proof came from the ^1H -detected ^{13}C , ^1H long-range correlation (HMBC) performed for **5**. All of the relevant interfragment connectivities were clearly established from the results of this experiment and are summarized in the Figure.

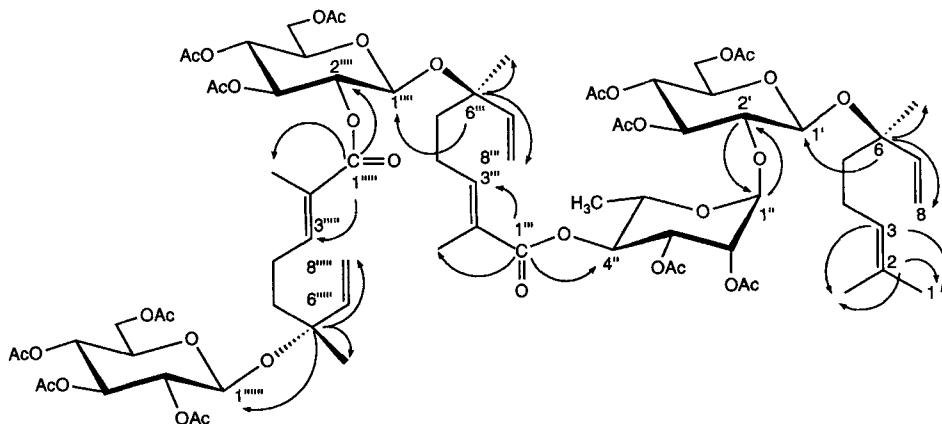


Figure. Schematic representation of diagnostic heteronuclear multiple bond correlations found for anatosioid *E* dodecaacetate (**5**). Arrows point from carbon-to-proton resonances, whose shift values are given in Tables 2 and 1, respectively.

Compound **1** was thus established as 6-*O*-[β -D-glucopyranosyl-(1'''''' $\rightarrow$ 6''''')-(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienyl-(1'''' $\rightarrow$ 2''')- β -D-glucopyranosyl-(1'''' $\rightarrow$ 6''')-(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienyl-(1'' $\rightarrow$ 4'')- α -L-rhamnopyranosyl-(1'' $\rightarrow$ 2')- β -D-glucopyranosyl]linalool, for which the trivial name *anatosioid E*, is proposed.

The ^1H -NMR spectrum of **3** showed the presence of a Me group (1.29), an allylic Me group (1.81 (*d*, $J = 1.2$ Hz)), an olefinic proton (5.44 (br. *t*, $J = 7.0$ Hz)), three olefinic protons of a terminal vinyl group (5.06, 5.23, and 5.95 ($J_{AB} = 1.6$, $J_{AX} = 10.8$, $J_{BX} = 17.4$ Hz)), and an anomeric proton of a β -D-glucose moiety (4.26 (*d*, $J = 7.8$ Hz)). The assignment of all proton resonances was based on a 2D- ^1H , ^1H homonuclear COSY experiment. These results suggested **3** to be a monoterpene glucoside, whose proposed structure was confirmed from ^{13}C -NMR spectral data which exhibited sixteen resonances, including six signals of β -D-glucose moiety, two Me, two CH_2 ^{13}C signals, four olefinic ^{13}C signals, and two O-bearing ^{13}C signals of the terpene moiety. These spectral

data were identical with those of 1-hydroxylinalool 1-*O*- β -D-glucopyranoside (= betulalbuside B), which had been previously isolated from *Betula alba* and *Chaenomeles japonica* [4].

Although compounds **2** and **4** were only obtained as a mixture, 2D-NMR experiments made it possible to determine unambiguously their structures. The intensity of ^1H and ^{13}C resonances were consistent with the presence of **2** and **4** in a molar ratio of *ca.* 3:1. The ^{13}C and ^1H resonances for both compounds were assigned by means of 2D homo- and heteronuclear correlation experiments, indicating the presence of closely related structures similar to **3**. The ^1H resonances and related ^{13}C signals attributed to **2** differed from **3** for the chemical-shift values of the CH_2OH group (2 H–C(1): 4.02, 4.19 ($J_{AB} = 11.4$ Hz); 75.9 (t)) and of the Me group attached to C(2) (Me–C(2): (1.67 (d , $J = 1.2$ Hz); 14.1 (q)). These shift differences can be explained by the conformation of the glycosylated primary OH group attached to C(1). The derived ^1H - and ^{13}C -NMR data of **2** were in good accordance with those of 9-hydroxylinalool 9-*O*- β -D-glucopyranoside (= betulalbuside A) [4].

The ^1H - and ^{13}C -NMR resonances of **4** (see *Exper. Part*) were also similar to those of **2** and **3** with some important exceptions. The CH_2OH protons were observed at 3.89 ppm as a 2-H br. *singlet*, and showed correlation with the ^{13}C signal at 69.0, assigned to C(1). The signal attributed to C(6) of the monoterpene moiety appeared at 81.4 ppm, with *ca.* + 7.3 ppm downfield shift when compared to that of **2**. This shift is due to the α -effect of glycosidation, indicating the site of attachment of glucose to the monoterpene unit. These results suggested a similar structure of that of **2** differing only in the site of glycosidation. The NMR spectral data obtained for **4** showed similarity with the data given for 9-hydroxylinalool 6-*O*- β -D-glucoside isolated from *Pluchea indica* [7]. Thus, the structure of **4** was established as (2*E*)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*- β -D-glucopyranoside.

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Experimental Part

General. See [3].

Plant Material. *Viburnum orientale* PALLAS was collected from N.E. Anatolia, Rize, Pazar, July 1989. A voucher specimen has been deposited in the Herbarium at the Pharmacognosy Department, Faculty of Pharmacy, Hacettepe University (HUEF 89–045).

Extraction and Isolation of Glycosides. The air-dried leaves (500 g) were extracted with MeOH at *ca.* 40°. The H_2O -soluble part of the MeOH extract was partitioned successively 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 $\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ (80:20:2, 70:30:3, and 60:40:4), and the fractions were combined into ten 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). Fr. H and I were subjected separately to MPLC (*Sepralyte* 40 μm , MeOH/ H_2O gradient, 40–65% MeOH) to give **1** (200 mg). Another part of the BuOH extract (14 g) was chromatographed over polyamide eluting with H_2O and with increasing amount of MeOH in H_2O to give six fractions, 1–6. Fr. 1 (3.9 g) was further applied to a series of chromatographic methods to yield **3** (7.5 mg) and a mixture **2/4** (6.5 mg).

Anatolioside E (1). White amorphous powder. $[\alpha]_{\text{D}}^{20} = -49.9$ ($c = 0.40$, MeOH). UV: 217.5. IR: 3360, 2950, 2900, 1690, 1630, 1260 and 1060. ^1H -NMR (500.13 MHz, CDCl_3): see Table 1. ^{13}C -NMR (125.8 MHz, CD_3OD): see Table 2. FAB-MS: 1141 (61, $[M + \text{Na}]^+$); calc. for $\text{C}_{54}\text{H}_{86}\text{O}_{24}$, 1622.

Acetylation of Anatolioside E (1). Treatment of **1** (30 mg) with Ac_2O (1 ml), pyridine (1 ml), and 4-dimethylaminopyridine (10 mg) at r.t. overnight followed by column chromatography over silica gel using $\text{C}_6\text{H}_6/\text{Me}_2\text{CO}$ 9:1 gave a dodecaacetate, **5**. ^1H -NMR (500.13 MHz, CDCl_3): see Table 1. ^{13}C -NMR (125.8 MHz, CDCl_3): see Table 2. FAB-MS: 1645 (3, $[M + \text{Na}]^+$), 1469 (3, $[M - \text{linalool}]^+$), 1181 (11, $[M - \text{glucosyl} - \text{linalool} - (\text{Ac})_3]^+$), 785 (35,

[glucopyranosyl – menthialfolioid – glucopyranosyl – (Ac)₇]⁺), 497 (6, [glucopyranosyl – menthialfolioid – (Ac)₄]⁺), 331 (6, [tetraacetyl] – glucoseoxonium)⁺).

Alkaline Hydrolysis of Anatoside E (1). Compound **1** (5 mg) was heated in aq. 5% KOH (1 ml) at 80° for 2 h. After neutralization with aq. 5% HCl, the soln. was evaporated to dryness. Residues were controlled by TLC, and the compounds **6** and **7** were found in the hydrolysate. These were identified as anatoside and 6-*O*-(β-D-glucopyranosyl)menthialfolic acid, respectively, according to TLC comparison with authentic samples [3].

Benulalbuside A (2). ¹H-NMR (500.13 MHz, CD₃OD): 4.02, 4.19 (*AB*, *J*_{AB} = 11.4, H_a–C(1), H_b–C(1), resp.); 5.46 (*dt*, *J* = 1.3, 7.3, H–C(3)); 2.09 (*m*, 2 H–C(4)); 1.53 (*m*, 2 H–C(5)); 5.90 (*dd*, *J* = 17.4, 10.8, H–C(7)); 5.19 (*dd*, *J* = 17.4, 1.6, H_a–C(8)); 5.03 (*dd*, *J* = 10.8, 1.6, H_b–C(8)); 1.67 (*d*, *J* = 1.2, Me–C(2)); 1.24 (*s*, Me–C(6)); 4.23 (*d*, *J* = 7.8, H–C(1′)); 3.18 (*dd*, *J* = 7.8, 9.3, H–C(2′)); 3.32 (*t*, *J* = 9, H–C(3′)); 3.26 (*t*, *J* = 8.7, H–C(4′)); 3.18 (*m*, H–C(5′)); 3.65 (*dd*, *J* = 11.9, 5.4, H_a–C(6′)); 3.85 (*dd*, *J* = 11.9, 2.4, H_b–C(6′)). ¹³C-NMR (125.8 MHz, CD₃OD): 75.9 (*t*, C(1)); 132.9 (*s*, C(2)); 130.1 (*d*, C(3)); 23.5 (*t*, C(4)); 42.9 (*t*, C(5)); 73.8 (*s*, C(6)); 146.2 (*d*, C(7)); 112.1 (*t*, C(8)); 14.1 (*q*, Me–C(2)); 27.7 (*q*, Me–C(6)); 102.6 (*d*, C(1′)); 75.1 (*d*, C(2′)); 78.2 (*d*, C(3′)); 71.7 (*d*, C(4′)); 77.9 (*d*, C(5′)); 62.9 (*t*, C(6′)).

Benulalbuside B (3). ¹H-NMR (300.13 MHz, CD₃OD): 4.24, 4.37 (*AB*, *J*_{AB} = 11.4, H_a–C(1), H_b–C(1), resp.); 5.44 (*dt*, *J* = 1.3, 7.0, H–C(3)); 2.15 (*m*, 2 H–C(4)); 1.56 (*m*, 2 H–C(5)); 5.95 (*dd*, *J* = 17.4, 10.8, H–C(7)); 5.06 (*dd*, *J* = 17.4, 1.6, H_a–C(8)); 5.23 (*dd*, *J* = 10.8, 1.6, H_b–C(8)); 1.81 (*d*, *J* = 1.2, Me–C(2)); 1.29 (*s*, Me–C(6)); 4.26 (*d*, *J* = 7.8, H–C(1′)); 3.22 (*dd*, *J* = 7.8, 9.3, H–C(2′)); 3.38 (*t*, *J* = 9, H–C(3′)); 3.34 (*t*, *J* = 8.7, H–C(4′)); 3.26 (*m*, H–C(5′)); 3.73 (*dd*, *J* = 11.9, 5.4, H_a–C(6′)); 3.92 (*dd*, *J* = 11.9, 2.4, H_b–C(6′)). ¹³C-NMR (75.5 MHz, CD₃OD): 67.8 (*t*, C(1)); 132.7 (*s*, C(2)); 131.4 (*d*, C(3)); 23.5 (*t*, C(4)); 43.6 (*t*, C(5)); 73.8 (*s*, C(6)); 146.3 (*d*, C(7)); 112.1 (*t*, C(8)); 21.9 (*q*, Me–C(2)); 27.6 (*q*, Me–C(6)); 102.5 (*d*, C(1′)); 75.1 (*d*, C(2′)); 78.2 (*d*, C(3′)); 71.7 (*d*, C(4′)); 77.9 (*d*, C(5′)); 62.8 (*t*, C(6′)).

(2E)-2,6-Dimethylocta-2,7-dien-1,6-diol-6-*O*-β-D-glucopyranoside (4). ¹H-NMR (500.13 MHz, CD₃OD): 3.89 (*br. s*, H_a–C(1), H_b–C(1)); 5.38 (*dt*, *J* = 1.3, 7.3, H–C(3)); 2.10 (*m*, 2 H–C(4)); 1.62 (*m*, 2 H–C(5)); 5.93 (*dd*, *J* = 17.4, 10.8, H–C(7)); 5.23 (*dd*, *J* = 17.4, 1.6, H_a–C(8)); 5.21 (*dd*, *J* = 10.8, 1.6, H_b–C(8)); 1.63 (*d*, *J* = 1.2, Me–C(2)); 1.38 (*s*, Me–C(6)); 4.34 (*d*, *J* = 7.8, H–C(1′)); 3.18 (*dd*, *J* = 7.8, 9.3, H–C(2′)); 3.32 (*t*, *J* = 9, H–C(3′)); 3.26 (*t*, *J* = 8.7, H–C(4′)); 3.15 (*m*, H–C(5′)); 3.62 (*dd*, *J* = 11.9, 5.4, H_a–C(6′)); 3.80 (*dd*, *J* = 11.9, 2.4, H_b–C(6′)). ¹³C-NMR (125.8 MHz, CD₃OD): 69.0 (*t*, C(1)); 135.9 (*s*, C(2)); 126.9 (*d*, C(3)); 23.3 (*t*, C(4)); 42.3 (*t*, C(5)); 81.4 (*s*, C(6)); 144.5 (*d*, C(7)); 115.8 (*t*, C(8)); 13.7 (*q*, Me–C(2)); 31.1 (*q*, Me–C(6)); 99.6 (*d*, C(1′)); 75.2 (*d*, C(2′)); 78.3 (*d*, C(3′)); 71.7 (*d*, C(4′)); 77.6 (*d*, C(5′)); 62.8 (*t*, C(6′)).

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