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

by **İhsan Çalış*** and **Ayşen Yürüker**

Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University, TR–06100 Ankara

and **Heinz Rüegger**

Swiss Federal Institute of Technology Zurich (ETHZ), Laboratory of Inorganic Chemistry, CH–8092 Zürich

and **Anthony D. Wright** and **Otto Sticher**

Swiss Federal Institute of Technology Zurich (ETHZ), Department of Pharmacy, CH–8057 Zürich

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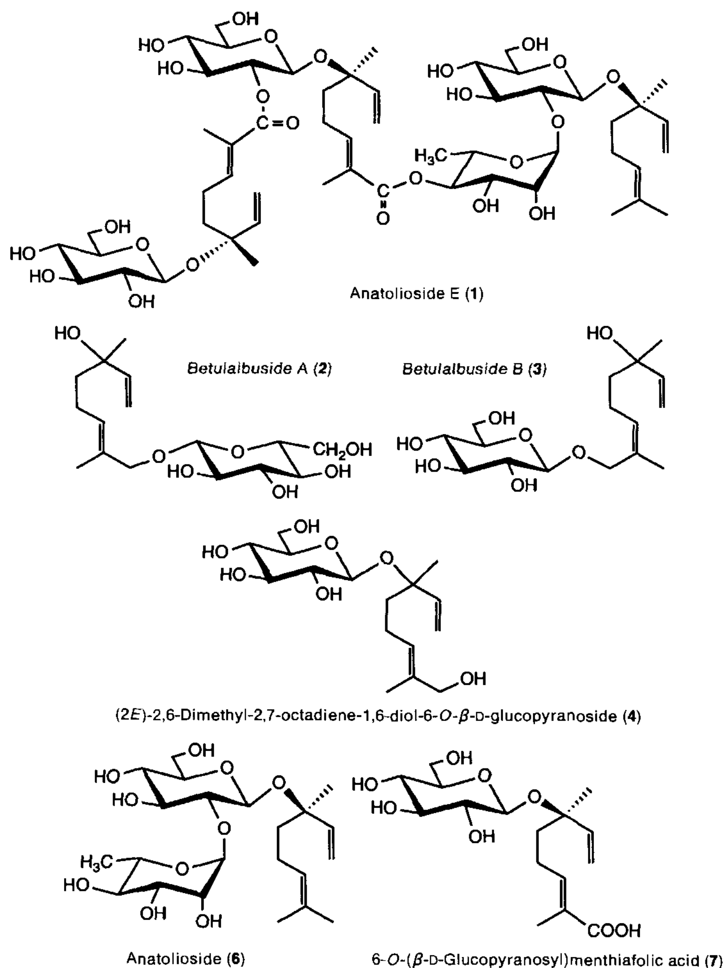
A new open-chain monoterpene glycoside, anatolioside E (**1**), was isolated from the leaves of *Viburnum orientale* in addition to three known acyclic monoterpene glycosides, betulalbusides A (**2**) and B (**3**), and 2(*E*)-2,6-dimethyl-2,7-octadien-1,6-diol-6-*O*-β-D-glucopyranoside (**4**). The 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-octadienoyl-(1′′′′′→2′′′′)-β-D-glucopyranosyl-(1′′′′→6′′′)-2(*E*), 6(*R*), 2,6-dimethyl-6-hydroxy-2,7-octadienoyl-(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 $C_{54}H_{86}O_{24}$ (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 ^{1}H-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-

[1]) This paper was presented at the poster session of the '40th Annual Congress on Medicinal Plant Research', Trieste, Italy, September 1–5, 1992; see [1].

[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 (2*E*)-6-hydroxy-2,6-dimethylocta-2,7-dienoic acid (= menthiafolic 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 menthiafolic acid [6], and this clearly indicated three sites of glycosidations.

Table 1. *^{1}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 (*s*, J = 0.9)	1.48 (*s*)
H–C(3)	5.04 (*dt*, J = 6.7, 1.4)	4.90 (br. *t*, 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 (*dd*, J = 11.0, 17.7)	5.84 (*dd*, J = 10.9, 17.6)
H_a–C(8)	5.24–5.29[b])	5.25 (*dd*, J = 10.9, 0.7)
H_b–C(8)	5.33 (*dd*, J = 17.7, 1.2)	5.17 (br. *d*, J = 17.6)
Me–C(2)	1.67 (*d*, J = 1.0)	1.55 (*s*)
Me–C(6)	1.41 (*s*)	1.30 (*s*)
H–C(1′)	4.49 (*d*, J = 7.5)	4.51 (*d*, J = 7.5)
H–C(2′)	3.32 (*dd*, J = 7.5, 9.8)	3.68 (*dd*, J = 7.5, 9.8)
H–C(3′)	3.49 (*t*, J = 9.8)	5.19 (*t*, J = 9.8)
H–C(4′)	3.42 (*dd*, J = 9.0, 9.8)	4.84 (*dd*, J = 9.0, 9.8)
H–C(5′)	3.19–3.34[b])	3.56–3.62[b])
H_a–C(6′)	3.70 (*dd*, J = 12.0, 4.7)	4.14 (*dd*, J = 12.0, 5.7)
H_b–C(6′)	3.88 (*dd*, J = 12.0, 2.4)	4.02 (*dd*, J = 12.0, 2.3)
H–C(1″)	5.48 (br. *s*)	4.98 (*d*, J = 1.6)
H–C(2″)	3.96[b])	4.96[b])
H–C(3″)	3.95 (*dd*, J = 3.4, 9.8)	5.29 (*dd*, J = 3.4, 10.0)
H–C(4″)	5.03 (*t*, J = 9.8)	5.06 (*t*, J = 10.0)
H–C(5″)	4.43 (*dq*, J = 6.2, 9.8)	4.30 (*dq*, J = 6.2, 10.0)
H–C(6″)	1.12 (*d*, J = 6.2)	1.10 (*d*, J = 6.2)
H–C(3‴)	6.89 (*dt*, J = 7.5, 1.5)	6.55 (*dt*, 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 (*dd*, J = 11.0, 17.7)	5.55 (*dd*, J = 11.0, 17.6)
H_a–C(8‴)	5.24–5.29[b])	5.23 (*dd*, J = 11.0, 0.7)
H_b–C(8‴)	5.30 (*dd*, J = 17.7, 1.1)	5.17 (br. *d*, J = 17.6)
Me–C(2‴)	1.84 (*d*, J = 1.3)	1.67 (br. *s*)
Me–C(6‴)	1.45 (*s*)	1.29 (*s*)
H–C(1⁗)	4.59 (*d*, J = 8.0)	4.52 (*d*, J = 8.0)
H–C(2⁗)	4.85 (*dd*, J = 8.0, 9.5)	5.01 (*dd*, J = 8.0, 9.5)
H–C(3⁗)	3.52 (*t*, J = 9.5)	5.13 (*t*, J = 9.5)
H–C(4⁗)	3.57 (*dd*, J = 9.0, 9.5)	4.94 (*dd*, J = 9.0, 9.5)
H–C(5⁗)	3.19–3.34[b])	3.56–3.62[b])
H_a–C(6⁗)	3.68 (*dd*, J = 12.0, 5.9)	4.13 (*dd*, J = 12.0, 5.9)
H_b–C(6⁗)	3.86 (*dd*, J = 12.0, 2.5)	4.015 (*dd*, J = 12.0, 2.3)
H–C(3′′′′′)	6.75 (*dt*, J = 7.5, 1.5)	6.61 (*dt*, J = 7.3, 1.2)
H–C(4′′′′′)	2.00–2.40[b])	2.1 (*m*)
H–C(5′′′′′)	1.50–1.80[b])	1.40–1.63[b])
H–C(7′′′′′)	5.75 (*dd*, J = 17.9, 10.8)	5.64 (*dd*, J = 17.6, 11.0)
H_a–C(8′′′′′)	5.24–5.29[b])	5.15 (*dd*, J = 11.0, 0.7)
H_b–C(8′′′′′)	5.27 (*dd*, J = 17.9, 1.1)	5.11 (br. *d*, J = 17.6)
Me–C(2′′′′′)	1.89 (*d*, J = 1.3)	1.71 (br. *s*)
Me–C(6′′′′′)	1.44 (*s*)	1.26 (*s*)

[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 (*d*, *J* = 7.8)	4.52 (*d*, *J* = 8.0)
H−C(2″″″)	3.23 (*dd*, *J* = 7.8, 9.2)	4.94 (*dd*, *J* = 8.0, 9.7)
H−C(3″″″)	3.37 (*t*, *J* = 9.2)	5.18 (*t*, *J* = 9.7)
H−C(4″″″)	3.33 (*t*, *J* = 9.2)	4.94 (*t*, *J* = 9.7)
H−C(5″″″)	3.19–3.34[b])	3.56–3.62[b])
H_a−C(6″″″)	3.67 (*dd*, *J* = 12.0, 5.9)	4.13 (*dd*, *J* = 12.0, 5.9)
H_b−C(6″″″)	3.85 (*dd*, *J* = 12.0, 2.4)	3.98 (*dd*, *J* = 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. *^{13}C-NMR Data* (125.8 MHz) *of Anatolioside E* (**1**) (CD_3OD) *and Anatolioside E Dodecaacetate* (**5**) ($CDCl_3$)

	1	**5**[a])		**1**	**5**[a])
Me−C(2)	18.3 (*q*)	16.7 (*q*)	C(1″″)	98.5 (*d*)	95.2 (*d*)
C(2)	132.7 (*s*)	130.6 (*s*)	C(2″″)	75.7 (*d*)	70.4 (*d*)
C(3)	125.9 (*d*)	123.0 (*d*)	C(3″″)	76.4 (*d*)	71.9 (*d*)
C(4)	24.0 (*t*)	21.6 (*t*)	C(4″″)	72.2 (*d*)	67.8 (*d*)
C(5)	43.3 (*t*)	40.4 (*t*)	C(5″″)	78.1 (*d*)	70.3 (*d*)
C(6)	82.0 (*s*)	80.5 (*s*)	C(6″″)	63.0 (*t*)	61.4 (*t*)
C(7)	144.8 (*d*)	140.9 (*d*)			
C(8)	116.4 (*t*)	115.9 (*t*)	C(1″″′)	168.8 (*s*)	164.9 (*s*)
Me−C(2)	22.9 (*q*)	24.7 (*q*)	C(2″″′)	129.1 (*s*)	126.1 (*s*)
Me−C(6)	26.4 (*q*)	20.7 (*q*)	C(3″″′)	143.4 (*d*)	142.1 (*d*)
C(1′)	98.9 (*d*)	95.8 (*d*)	C(4″″′)	24.8 (*t*)	22.0 (*t*)
C(2′)	80.3 (*d*)	73.7 (*d*)	C(5″″′)	41.6 (*t*)	39.5 (*t*)
C(3′)	77.2 (*d*)	74.1 (*d*)	C(6″″′)	81.1 (*s*)	79.1 (*s*)
C(4′)	72.1 (*d*)	68.2 (*d*)	C(7″″′)	145.0 (*d*)	140.0 (*d*)
C(5′)	77.9 (*d*)	70.6 (*d*)	C(8″″′)	116.9 (*t*)	115.4 (*t*)
C(6′)	63.0 (*t*)	61.5 (*t*)	Me−C(2″″′)	13.1 (*q*)	11.3 (*q*)
			Me−C(6″″′)	23.9 (*q*)	21.9 (*q*)
C(1″)	101.4 (*d*)	96.1 (*d*)	C(1″″″)	98.0 (*d*)	95.3 (*d*)
C(2″)	72.5 (*d*)	67.7 (*d*)	C(2″″″)	75.5 (*d*)	70.6 (*d*)
C(3″)	70.7 (*d*)	67.2 (*d*)	C(3″″″)	78.6 (*d*)	71.9 (*d*)
C(4″)	76.6 (*d*)	70.2 (*d*)	C(4″″″)	72.0 (*d*)	69.4 (*d*)
C(5″)	67.6 (*d*)	65.9 (*d*)	C(5″″″)	77.9 (*d*)	70.2 (*d*)
C(6″)	18.3 (*q*)	16.3 (*q*)	C(6″″″)	63.1 (*t*)	61.3 (*t*)
C(1‴)	169.5 (*s*)	166.0 (*s*)			
C(2‴)	129.0 (*s*)	126.1 (*s*)			
C(3‴)	144.3 (*d*)	142.3 (*d*)			
C(4‴)	24.4 (*t*)	22.0 (*t*)			
C(5‴)	42.5 (*t*)	39.6 (*t*)			
C(6‴)	81.3 (*s*)	79.2 (*s*)			
C(7‴)	144.4 (*d*)	140.2 (*d*)			
C(8‴)	116.4 (*t*)	115.5 (*t*)			
Me−C(2‴)	13.0 (*q*)	11.2 (*q*)			
Me−C(6‴)	24.3 (*q*)	21.9 (*q*)			

[a]) Additional signals: 169.6–168.0 ($COCH_3$); 19.9–19.6 ($COCH_3$).

Acetylation of **1** yielded the dodecaacetate **5**, as judged from the ^{1}H-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 H–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 + Na]$^+$), calc. for $C_{78}H_{110}O_{36}$) 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 anatolioside (**6**) and 6-*O*-(*β*-D-glucopyranosyl)menthiafolic acid (**7**). These results suggested **1** to be 6″‴″-*O*-(*β*-D-glucopyranosyl)anatolioside D. Final structural proof came from the ^{1}H-detected ^{13}C,^{1}H 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*.

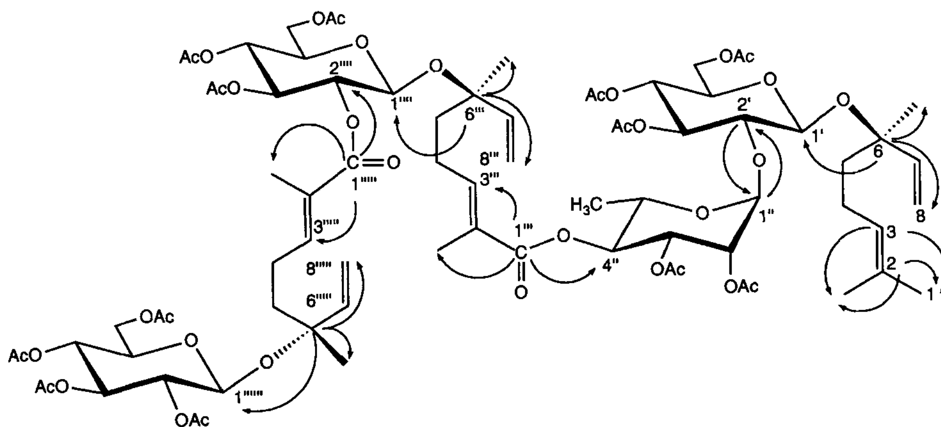


Figure. *Schematic representation of diagnostic heteronuclear multiple bond correlations found for anatolioside E dodecaacetate* (**5**). Arrows point from carbon-to-proton resonances, whose shift values are given in *Tables 2* and *1*, respectively.

Compound **1** was thus established as 6-*O*-[*β*-D-glucopyranosyl-(1″‴″→6″‴′)-(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl-(1″″→2″″)-*β*-D-glucopyranosyl-(1″″→6‴)-(2*E*,6*R*)-6-hydroxy-2,6-dimethylocta-2,7-dienoyl-(1‴→4″)-α-L-rhamnopyranosyl-(1″→2′)-*β*-D-glucopyranosyl]linalool, for which the trivial name *anatolioside E*, is proposed.

The ^{1}H-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-^{1}H,^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H- 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 ^{1}H- 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.

The authors thank Mrs. *C. Oertel* for optical-rotation and *R. Häfliger* for FAB-MS measurements.

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 $CHCl_3/MeOH/H_2O$ (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. $[\alpha]_D^{20} = -49.9$ (*c* = 0.40, MeOH). UV: 217.5. IR: 3360, 2950, 2900, 1690, 1630, 1260 and 1060. ^{1}H-NMR (500.13 MHz, CD_3OD): see *Table 1*. ^{13}C-NMR (125.8 MHz, CD_3OD): see *Table 2*. FAB-MS: 1141 (61, $[M + Na]^+$); calc. for $C_{54}H_{86}O_{24}$, 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 C_6H_6/Me_2CO 9:1 gave a dodecaacetate, **5**. ^{1}H-NMR (500.13 MHz, $CDCl_3$): see *Table 1*. ^{13}C-NMR (125.8 MHz, $CDCl_3$): see *Table 2*. FAB-MS: 1645 (3, $[M + Na]^+$), 1469 (3, $[M - \text{linalool}]^+$), 1181 (11, $[M - \text{glucosyl} - \text{linalool} - (Ac)_3]^+$), 785 (35,

[glucopyranosyl – menthiafolioyl – glucopyranosyl – $(Ac)_7]^+$), 497 (6, [glucopyranosyl – menthiafolioyl – $(Ac)_4]^+$), 331 (6, [tetraacetyl] – glucoseoxonium$]^+$).

Alkaline Hydrolysis of Anatolioside 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 anatolioside and 6-*O*-(*β*-D-glucopyranosyl)menthiafolic acid, respectively, according to TLC comparison with authentic samples [3].

Betulalbuside A (**2**). ^{1}H-NMR (500.13 MHz, CD_3OD): 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′)). ^{13}C-NMR (125.8 MHz, CD_3OD): 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′)).

Betulalbuside B (**3**). ^{1}H-NMR (300.13 MHz, CD_3OD): 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′)). ^{13}C-NMR (75.5 MHz, CD_3OD): 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′)).

*(2*E*)-2,6-Dimethylocta-2,7-dien-1,6-diol-6-*O*-β-*D*-glucopyranoside* (**4**). ^{1}H-NMR (500.13 MHz, CD_3OD): 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′)). ^{13}C-NMR (125.8 MHz, CD_3OD): 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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