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IRIDOID GLUCOSIDES FROM *VIBURNUM RHYTIDOPHYLLUM*

LAMBERTO TOMASSINI, DEJAN BRKIC,* SEBASTIANO FODDAI and MARCELLO NICOLETTI

Dipartimento di Biologia Vegetale, Università degli Studi 'La Sapienza', P. le A. Moro 5, I-00185, Rome, Italy;
* Institute for Medicinal Plant Research 'Dr Josif Pancic', Tadeusa Koscuska 1, 11000 Belgrade, Yugoslavia

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Key Word Index—*Viburnum rhytidophyllum*; Caprifoliaceae; iridoid glucosides; 7,10,2′-triacetylpatrinoside; 7-*p*-coumarylpatrinoside; 10-acetylpatrinoside.

Abstract—Three new *Valeriana*-type iridoid glucosides, 7,10,2′-triacetylpatrinoside; 7-*p*-coumarylpatrinoside and 10-acetylpatrinoside, have been isolated, together with decapetaloside, from the stem bark of *Viburnum rhytidophyllum*. The structures have been elucidated mainly by spectroscopic means. Copyright © 1997 Elsevier Science Ltd

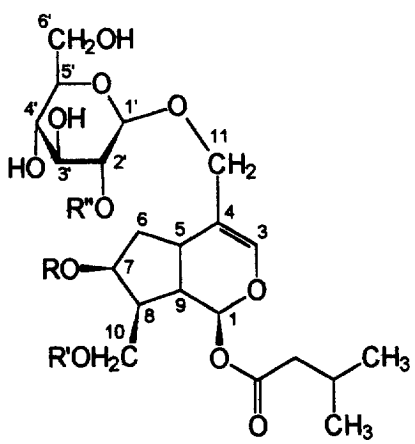
INTRODUCTION

A number of iridoid glycosides characterized, for the most part, by a sugar moiety at C-11 and an isovaleroyl group at C-1 (*Valeriana*-type iridoids) have been isolated from various *Viburnum* species [1–3]. The present study reports on the isolation and chemical characterization of four iridoid glucosides, three of them of novel structure, from *Viburnum rhytidophyllum* Hemsl., an evergreen shrub of oriental origin, introduced in Yugoslavia as a decorative species [4].

RESULTS AND DISCUSSION

After a preliminary fractionation of the alcoholic extract (see Experimental), two glycoside containing fractions were obtained. CC separation of the EtOAc fraction afforded pure **1** and **2**, while **3** and **4** were obtained as pure compounds by CC from the *n*-BuOH fraction. Among the four isolated compounds, **1–3** proved to be new compounds.

Compounds **1–3**, as evident from the ^1H and ^{13}C NMR data and in accordance with *Valeriana*-type iridoid glucosides, contained a β-D-glucopyransyl moiety bound to C-11 and an esterifying isovaleryl group at C-1. In particular, the base structure of patrinoside [1] was indicated for all three products, with small spectroscopic differences directly related to the acylation effects. The ^1H NMR of compound **1** ($C_{27}H_{40}O_{14}$) showed, besides the presence of three acetyl groups (δ 2.02*s*, 2.04*s* and 2.09*s*), a significant low field shift of the signals for H-7, H-2′ and H-10 (δ 5.26, 4.70 and 4.22, respectively) clearly due to a triple acetylation. All of the data, confirmed by the ^{13}C



1 R= R'= R"= Ac

2 R= *p*-coumaryl; R'= R"= H

3 R= R"= H; R'= Ac

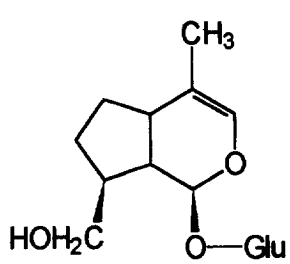


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Table 1. ^{13}C NMR spectral data of compounds **1**–**3** (CD_3OD)*

C	1	2	3
1	92.7	92.7	93.4
3	140.6	140.3	140.1
4	116.2	115.6	116.4
5	34.1	33.7	34.1
6	38.1	37.9	40.8
7	75.7	76.0	72.4
8	43.4	47.5	46.4
9	44.0	43.5	43.3
10	63.8	61.5	64.8
11	69.2	69.4	69.6
Glucose unit			
1′	100.7	103.1	103.3
2′	75.3	74.9	75.1
3′	76.1	77.7	77.9
4′	71.7	71.5	71.7
5′	78.1	77.9	78.1
6′	62.6	62.6	62.2
Acetyl group			
CH_3	20.7, 20.9 21.1		20.8
COO-	171.6, 172.0 172.5		172.9
p-Coumaryl group			
1″		127.2	
2″, 6″		131.0	
3″, 5″		116.6	
4″		161.1	
α		115.1	
β		146.4	
COO-		168.7	

* All the compounds had additional signals arising from the isovaleryl group at *ca* 173.0, 43.5, 26.0 and 22.5.

NMR spectrum, allowed us to assign to **1** the structure of 7,10,2′-triacetylpatrinoside.

In the ^1H NMR spectrum of compound **2** ($C_{30}H_{40}O_{13}$), in which in comparison to the patrinoside spectrum only the H-7 resonance was shifted to lower field (δ 5.39), the typical signals of a *trans*-*p*-coumaryl were observed, together with the absence of acetyl groups. A comparable low field shift of C-7 in the ^{13}C NMR spectrum (Table 1), confirmed for **2** the structure of 7-*p*-coumarylpatrinoside.

Finally, the ^1H spectrum of compound **3** ($C_{23}H_{36}O_{12}$), corresponded to that of patrinoside, except for an acetyl group linked to position 10 (acylation shift of H_2-10 to δ 4.21). Thus compound **3** was assigned the structure of 10-acetylpatrinoside.

The stereochemical assignments in compounds **1**, **2** and **3**, for the chiral centres at C-7 and C-8, also consistent with the configuration of patrinoside, were confirmed by NOE-difference NMR experiments, whereas unambiguous confirmation of the acylation sites assignment was obtained by ^1H–^{13}C COLOC experiments.

The fourth compound **4** was identified as decapetaloside, an iridoid glucoside already isolated from other *Viburnum* species, by comparing its NMR spectra with those reported in the literature [1, 2].

EXPERIMENTAL

^1H NMR: 500 MHz (the CHD_2OD peak is assigned to δ 3.30); ^{13}C NMR: 125 MHz (the CD_3OD peak is assigned to 49.0 ppm).

Extraction and isolation. Fresh plant material (150 g of stem bark) was collected in the Botanical Garden of Belgrade and exhaustively extracted with MeOH. The extract was concd to dryness. The residue was diluted with H_2O and re-extracted with EtOAc followed by *n*-BuOH. The EtOAc extract, on CC on silica gel with MeOH-$CHCl_3$ (1:9), afforded pure **1** (10 mg) and **2** (9 mg), while the *n*-BuOH extract, on CC on silica gel with MeOH-$CHCl_3$ (1:4), gave pure **3** (18 mg) and **4** (24 mg).

7,10,2′-*Triacetylpatrinoside* (**1**). Powder, $[\alpha]_D^{20} = -19.5$ (MeOH; *c* 0.5); ^1H NMR (CD_3OD): δ 0.96 (6H, *d*, $J = 6.6$ Hz, $\underline{Me_2}CHCH_2$–), 1.96 (1H, *ddd*, $J = 5.1$, 7.3, 13.0 Hz, H-6a), 2.02 (3H, *s*, Ac), 2.04 (3H, *s*, Ac), 2.07 (1H, *ddd*, $J = 3.4$, 7.3, 13.0 Hz, H-6b), 2.09 (3H, *s*, Ac), 2.16 (1H, *m*, $Me_2\underline{CH}CH_2$–), 2.25 (1H, *m*, H-8), 2.25 (2H, *d*, $J = 7.8$ Hz, $Me_2CH\underline{CH_2}$–), 2.34 (1H, *dt*, $J = 1.3$ and 5.2 Hz, H-9), 2.90 (1H, *m*, H-5), 3.31 (1H, *m*, H-5′), 3.32 (1H, *t*, $J = 9.0$ Hz, H-4′), 3.51 (1H, *t*, $J = 9.0$, H-3′), 3.68 (1H, *dd*, $J = 5.3$ and 12.0 Hz, H-6′a), 3.84 (1H, *dd*, $J = 2.0$ and 12.0 Hz, H-6′b), 4.08 (1H, *d*, $J = 11.6$ Hz, H-11a), 4.22 (2H, *bs*, H_2-10), 4.24 (1H, *d*, $J = 11.6$ Hz, H-11b), 4.46 (1H, *d*, $J = 7.8$ Hz, H-1′), 4.70 (1H, *dd*, $J = 7.8$ and 9.0 Hz, H-2′), 5.26 (1H, *m*, H-7), 5.96 (1H, *d*, $J = 5.2$ Hz, H-1), 6.37 (1H, *bs*, H-3).

7-*p*-*Coumarylpatrinoside* (**2**). Powder, $[\alpha]_D^{20} = -36.9$ (MeOH; *c* 0.5); UV λ_{max} nm (log ε): 310 (4.1), 298 (sh. 3.8), 226 (2.9); ^1H NMR (CD_3OD): δ 0.95 (6H, *d*, $J = 6.6$ Hz, $\underline{Me_2}CHCH_2$–), 2.05–2.20 (3H, *m*, H_2-6 and $Me_2\underline{CH}CH_2$–), 2.24 (2H, *d*, $J = 7.8$ Hz, $Me_2CH\underline{CH_2}$–), 2.26 (1H, *m*, H-8), 2.28 (1H, *dd*, $J = 4.5$ and 8.2 Hz, H-9), 3.07 (1H, *m*, H-5), 3.20 (1H, *dd*, $J = 7.8$ and 9.0 Hz, H-2′), 3.27 (1H, *m*, H-5′), 3.34 (1H, *t*, $J = 9.0$ Hz, H-4′), 3.40 (1H, *t*, $J = 9.0$, H-3′), 3.67 (2H, *m*, H-10a and H-6′a), 3.70 (1H, *dd*, $J = 7.9$ and 11.3 Hz, H-10b), 3.86 (1H, *dd*, $J = 2.0$ and 12.0 Hz, H-6′b), 4.09 (1H, *d*, $J = 11.6$ Hz, H-11a), 4.28 (1H, *d*, $J = 11.6$ Hz, H-11b), 4.30 (1H, *d*, $J = 7.8$ Hz, H-1′), 5.39 (1H, *m*, H-7), 6.06 (1H, *d*, $J = 4.5$ Hz, H-1), 6.33 (1H, *d*, $J = 16.3$ Hz, H-α), 6.41 (1H, *bs*, H-3), 6.81 (2H, *d*, $J = 8.5$ Hz, H-3″ and H-5″), 7.47 (2H, *d*, $J = 8.5$ Hz, H-2″ and H-6″), 7.61 (1H, *d*, $J = 16.3$ Hz, H-β).

10-*Acetylpatrinoside* (**3**). Powder, $[\alpha]_D^{20} = -51.6$ (MeOH; *c* 0.8); ^1H NMR (CD_3OD): δ 0.97 (6H, *d*,

J = 6.6 Hz, $\underline{Me_2}CHCH_{2\_}$), 1.83 (1H, *ddd*, J = 4.7, 8.1 and 13.0 Hz, H-6a), 1.98–2.05 (2H, *m*, H-6b and $Me_2\underline{CH}CH_{2\_}$), 2.04 (3H, *s*, Ac), 2.15 (3H, *m*, H-6b, H-8 and H-9), 2.21 (2H, *d*, J = 7.8 Hz, $Me_2CH\underline{CH_{2\_}}$), 3.03 (1H, *m*, H-5), 3.20 (1H, *dd*, J = 7.7 and 9.0 Hz, H-2′), 3.24–3.33 (3H, *m*, H-5′, H-4′ and H-3′), 3.66 (1H, *dd*, J = 5.3 and 11.6 Hz, H-6′a), 3.86 (1H, *dd*, J = 2.0 and 11.6 Hz, H-6′b), 4.09 (1H, *d*, J = 11.3 Hz, H-11a), 4.21–4.30 (5H, *m*, H_2-10, H-11b, H-7 and H-1′), 5.89 (1H, *d*, J = 5.2 Hz, H-1), 6.38 (1H, *bs*, H-3).

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