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POLIUMOSIDE, A CAFFEIC GLYCOSIDE ESTER FROM *TEUCRIUM BELION*

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Key Word Index—*Teucrium belion*; Lamiaceae; caffeic glycoside ester; poliumoside; high-resolution ^{1}H NMR and ^{13}C NMR.

Abstract—A new caffeic glycoside ester, poliumoside, has been isolated from the aerial parts of *Teucrium belion.* Its structure, [β-(3′,4′-dihydroxyphenyl)-ethyl]-(3,6-*O*-α-L-dirhamnopyranosyl)-(4-*O*-caffeoyl)-β-D-glucopyranoside, was established mainly by high-resolution ^{1}H NMR and ^{13}C NMR spectroscopy.

INTRODUCTION

While studying the chemotaxonomy of the *Polium* section of the genus *Teucrium* [1], we found a caffeic acid derivative, typical of this section, and present in all 15 species investigated. This compound is a glycoside ester of caffeic acid, called poliumoside, and was isolated from *Teucrium belion* Schreb. It was also found in six of ten *Verbascum* species (i.e. *V. thapsus* L., *V. phlomoides* L., *V. sinuatum* L., *V. blattaria* L., *V. boerhavii* L. and *V. chaixii* Vill.) [2].

Herein we describe the structure determined by high-resolution ^{1}H NMR and ^{13}C NMR analysis with selective decoupling techniques and by comparison with verbascoside [3] and echinacoside [4].

RESULTS AND DISCUSSION

The new glycoside ester is closely related to forsythoside A [5] and to echinacoside [4], the only difference being in the nature of the sugars and their linkages, since all these molecules have in common caffeic acid and 3,4-dihydroxyphenylethanol units.

Here we found the disaccharide moiety: Rha′ (1 → 3) Glc described for the verbascoside, linked by the C-1 Glc to dihydroxy-β-phenylethanol. Caffeic acid is linked to C-4 of the same glucose moiety as in all the other glycoside esters cited. The new feature is a second molecule of rhamnose linked to the glucose moiety in the 6-position. We have verified this by mild acid hydrolysis of the molecule which immediately gives verbascoside [6].

Tables 1 and 2 give the chemical shift values of the protons and carbons of the different parts of the molecule. The proton shift values in the ^{1}H NMR spectrum are very close to those attributed to verbascoside. So the chemical shifts of the anomeric protons of Glc and of Rha′, that of H-4Glc, α to the ester function and that of H-3Glc, α to Rha′ are essentially the same. The methyl of Rha″ (deshielded in comparison with that of Rha′) corroborates well with our observations on methyl-α-rhamnopyranose and rutinose [7]. All the proton values attributed to Rha″ are equally comparable to those of Rha in rutinose (Rha (1 → 6) Glc) and slightly different from Rha (1 → 3) Glc.

In the ^{13}C NMR spectrum (Table 2), we found the values of verbascoside carbons, the values of the second rhamnose unit being identified without much difficulty. On the other hand, we observed in the uncoupled spectrum that the carbon intensities of Rha″ are incon-

Table 1. ^{1}H NMR peaks (ppm) of poliumoside in DMSO-d_6 + CF_3CO_2H (two drops)

	H	δ	
Caffeic acid	2	7.09	(*s*)
	5	6.82	(*d*, 8)
	6	7.00	(*d*, 8)
	7	7.52	(*d*, 16)
	8	6.24	(*d*, 16)
Aglycone	2′	6.69	(*d*, 2.5)
	5′	6.54	(*d*, 8)
	6′	6.68	(*d*, 8)
	7′	2.75	(*m*, 10)
	8′	3.70	(*m*)
		3.89	(*m*)
Glucose	1	4.41	(*d*, 8)
	2	3.28	(*dd*, 8–8.5)
	3	3.77	(*dd*, 8.5–9.5)
	4	4.81	(*t*, 9.5)
	5	3.69	(*m*)
	6	3.58–3.39	(*m*, 10.5)
Rhamnose′	1′	5.10	(*d*, 1)
	2′	3.75	(*dd*, 1, 3)
	3′	3.35	(*dd*, 3, 9.5)
	4′	3.17	(*t*, 9.5)
	5′	3.42	(*m*)
	6′	1.02	(*d*, 6)
Rhamnose″	1″	4.55	(*d*, 1)
	2″	3.66	(*dd*, 1, 3)
	3″	3.48	(*dd*, 3, 9.5)
	4″	3.20	(*t*, 9.5)
	5″	3.43	(*m*)
	6″	1.10	(*d*, 6)

Splitting patterns and *J* values (Hz) are given in parentheses.

Table 2. ^{13}C NMR peaks (ppm) of poliumoside in DMSO-d_6 + CF_3CO_2H (two drops)

Aglycone							
C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	C-8′
129.99	116.27	144.88	143.45	115.47	119.48	35.05	70.25

Caffeic acid								
C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
125.52	114.72	145.48	148.39	113.41	121.32	145.59	115.73	165.51

Glycoside moiety					
Glc		Rha′		Rha″	
C		C		C	
1	102.37	1′	101.14	1″	100.48
2	74.36	2′	70.42*	2″	70.61
3	78.88	3′	70.25	3″	70.47*
4	68.99	4′	71.71	4″	71.88
5	72.91	5′	68.65	5″	68.35
6	65.94	6′	18.07	6″	17.69

*Uncertainty concerning relative assignments.

testably higher (for each carbon) than those of Rha′ (*ca* 30%), the glucose intensities being about the same as those of Rha′. The intensity differences, in relation to the NOE effects and relaxation times (not measured in this work), correspond well with the freedom of the Rha″ unit and with the binding (1 → 6) in which it is involved. This observation could help in distinguishing between the resonances of different sugar units. This was specially mentioned in the polysaccharide-branched *Klebsiella* type K^{23} and other oligosaccharides [8–11].

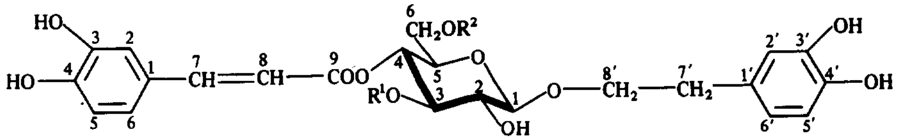
In the case of poliumoside, the C-4 and C-5 chemical shifts, very similar in the two rhamnoses, are thus clearly identified by their intensity difference. The Rha″ influence on the C-4 Glc and C-3 Glc, as well as on the carbons of the caffeic acid, is weak. Thus, we also found the same differences in the chemical shift values of the two rhamnoses whether they were linked in 3- or in 6-positions (particularly anomeric C and methyl C-6) [7]. As expected, Rha″ (1 → 6) Glc binding gives a deshielding effect of $\Delta\delta$ 5.2 ppm on C-6 Glc and a shielding effect of $\Delta\delta$ 1.7 ppm on C-5 Glc.

Therefore poliumoside is [β-(3′,4′-dihydroxyphenyl)-ethyl]-(3,6-*O*-α-L-dirhamnopyranosyl)-(4-*O*-caffeoyl)-β-D-glucopyranoside. Poliumoside is probably very close to magnolidine [12] in which the glucose moiety is substituted in positions 3 and 6 by two rhamnoses, the position of caffeic acid being unknown.

EXPERIMENTAL

NMR spectra were measured at 360 MHz for ^1H NMR and 90.53 MHz for ^{13}C NMR (Bruker WM 360 WB). Chemical shifts are given on the δ (ppm) scale with TMS as internal standard. Column chromatography (460 × 25 mm) was carried out with polyamide MN-S-6. TLC was conducted on cellulose plates with EtOAc–MeOH–H_2O–Me_2CO–$CHCl_3$ (60:11:11:5:1.5), using 2-aminoethyl diphenylborinate reagent for detection.

Isolation of poliumoside. The dried and finely powdered herbs



	R^1	R^2
Verbascoside	Rha	H
Forsythoside A	H	Rha
Echinacoside	Rha	Glc
Poliumoside	Rha′	Rha″

of *Teucrium belion* (aerial parts) were extracted with EtOH–H_2O (7:3) (3 ×) at room temp. The extracts were combined and the EtOH was eliminated by concn. The aq. soln was then extracted with EtOAc to give a pale-beige powder. 200 mg of this residue was passed through a polyamide column (40 g) and elution with H_2O–MeOH (13:7) yielded 30 mg pure poliumoside, R_f 0.32, $[\alpha]_D^{22}$ −80° (MeOH).

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(−)-MASSONIRESINOL, A LIGNAN FROM *PINUS MASSONIANA**

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Key Word Index—*Pinus massoniana*; Pinaceae; needles; lignan; massoniresinol; olivil.

Abstract—A new lignan, named (−)-massoniresinol, has been isolated from *Pinus massoniana* needles. Its structure has been proved to be (2*R*,3*S*,4*R*)-3,4-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-4-(4-hydroxy-3-methoxybenzyl)-3-tetrahydrofuranmethanol by ^{1}H NMR, ^{13}C NMR, mass and CD spectroscopy.

INTRODUCTION

We recently isolated and identified seven flavonoids, including three, to our knowledge, new natural compounds, 6-*C*-methylaromadendrin 7-*O*-*β*-D-glucopyranoside, taxifolin 3′-*O*-*β*-D-(6″-phenylacetyl)-glucopyranoside and eriodictyol 3′-*O*-*β*-D-glucoside, from *Pinus massoniana* L. needles [1]. This paper describes the isolation and structural elucidation of a new lignan, named (−)-massoniresinol, from the same needles. The other hydrophilic phenolic compounds of the acetone and aqueous acetone extracts, mainly dilignol glycosides, will be reported elsewhere.

RESULTS AND DISCUSSION

(−)-Massoniresinol (**1**), $C_{20}H_{24}O_8$, $[M]^+$ 392, $[\alpha]_D^{25}$ −31.4°, was isolated from the ethyl acetate fraction of the needles of *P. massoniana*, as described previously [1]. The compound gave a yellow-green colour with diazotized sulphanilic acid spray reagent on silica gel HF_{254} plates similar to that given by (+)-lariciresinol and (−)-olivil. The ^{1}H NMR spectrum of **1** showed the presence of seven protons apart from six aromatic protons and two aryl methoxyl groups. These protons were comprised of an oxymonobenzylic proton (*s*, δ5.01), and the protons of a benzylic methylene group (*s*, δ2.93) and two methylene groups, attached to oxygen atoms (*m*, δ3.6–4.0). On acetylation with acetic anhydride and pyridine at room temperature overnight, a triacetate (**2**), $[M]^+$ 518, $[\alpha]_D^{25}$ −13.2°, was obtained. The ^{1}H NMR spectrum of **2** showed one aliphatic and two aromatic acetoxyl groups. The seven proton signals mentioned above appeared as a singlet for one proton at δ5.07 and three double-doublets of an AB pattern for three methylene groups. The downfield shift of one of the methylene groups to δ4.28 and 4.45 on acetylation of compound **1** indicated the presence of a

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*Part 11 in the series "The Constituents of Conifer Needles". For Part 10 see ref. [1].

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