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Phytochemistry 64 (2003) 655–660
PHYTOCHEMISTRY
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Acylated flavonoid and phenylethanoid glycosides from *Marrubium velutinum*

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Received 8 January 2003; received in revised form 26 March 2003

Dedicated to the memory of Professor Jeffrey B. Harborne

Abstract

From the aerial parts of *Marrubium velutinum*, one acylated flavonoid glycoside, chrysoeriol 7-*O*-(3″,6″-di-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside, and two tetrasaccharidic phenylethanoid glycosides, velutinosides I-II, have been isolated together with ten known flavonoids and seven known phenylethanoid glycosides. The structures of the isolated compounds were established by means of NMR, MS, and UV spectral analyses.

Keywords: *Marrubium velutinum*; Lamiaceae; Acylated flavonoid glycosides; Tetrasaccharidic phenylethanoid glycosides; Velutinosides

1. Introduction

The genus *Marrubium* comprises around 30 species, indigenous in Europe, the Mediterranean area and Asia (Mabberley, 1997). Most of the species are annual or rhizomatous perennial herbs with a distinct indumentum of often very complex hairs, and verticillasters subtended by floral leaves. *Marrubium velutinum* Sibth. and Sm. (Lamiaceae) is an endemic herb of central and southern Greece with petiolate leaves and yellowish-tomentose corolla growing in dry rocky places in pastures (Baden, 1991). In this paper, we report on the isolation and identification of one new and 10 known flavonoids from this species, as well as two new and seven known phenylethanoid glycosides.

2. Results and discussion

From the methanolic extract of the aerial parts of *M. velutinum* 11 flavonoids (**1–11**) and nine phenylethanoid glycosides (**12–20**) were isolated.

Compound **1** was identified as chrysoeriol 7-*O*-(3″,6″-di-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside by 1D, 2D NMR and UV spectroscopic analyses and by MS spectrometry. ^{1}H NMR and ^{13}C NMR spectra (including DEPT 135) of **1** showed characteristic shift values and multiplicities of a 7-*O*-β-glucosylated chrysoeriol derivative (Markham et al., 1982). Besides the 15 carbon signals of the flavonoid nucleus, the ^{13}C NMR spectrum of **1** exhibited six carbon resonances of a sugar moiety, and 18 carbon signals indicating the presence of two acyl groups. An additional signal at δ 56.0 indicated a methoxylated flavonoid. Accordingly, the ^{1}H NMR spectrum showed 12 protons resonating as doublets at δ 7.59, 6.43, 7.49 and 6.33 (each 1H, each $J = 16.0$ Hz, H-7‴, H-8‴, H-7⁗ and H-8⁗, respectively), as well as at δ 7.57, 6.80, 7.37 and 6.68 (each 2H, $J = 8.5$ Hz, H-2‴/H-6‴, H-3‴/H-5‴, H-2⁗/H-6⁗ and H-3⁗/H-5⁗) indicating the presence of two *p*-coumaroyl moieties with *trans* geometry. This was confirmed by ^{13}C NMR spectral data (see Table 1) and all protons and carbons were assigned with the help of interpretation of ^{1}H–^{1}H COSY, HSQC and HMBC spectra. The linkage of the *trans* coumaroyl groups to the sugar was deduced from the downfield shifted signals of H-3″, and H-6a″, and H-6b″ (at δ 5.10, and 4.46 and 4.20, respectively). Additionally, the attachment of

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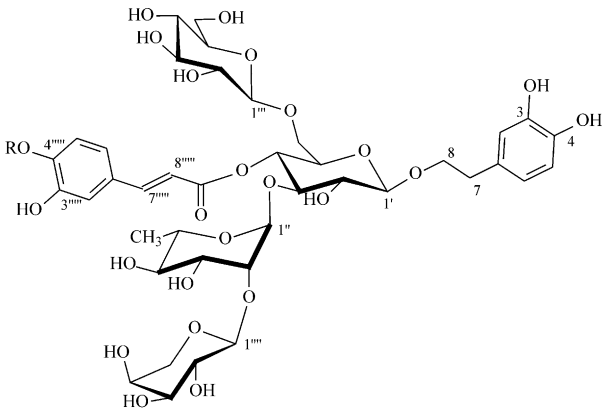
doi:10.1016/S0031-9422(03)00242-5

Table 1
^{1}H NMR (DMSO-d_6, 500 MHz, J in Hz) and ^{13}C NMR (75.5 MHz at 295 K) data of compound **1**

Position	δ_H	δ_C
2		146.6
3	6.91 *s*[a]	103.3
4		182.7
5		161.2
6	6.51 *br s*	99.5
7		162.5
8	6.86 *br s*	95.0
9		156.9
10		105.5
$-OCH_3$	3.88 *s*	56.0
1′		122.3
2′	7.56 *d* (J = 2.0)[a]	110.3
3′		148.1
4′		164.3
5′	6.91 *d* (J = 8.5)[a]	115.8
6′	7.58 *dd* (J = 2.0, 8.5)[a]	120.6
1″	5.36 *d* (J = 8.0)	99.2
2″	3.57 *br t* (J = 8.5)	71.1
3″	5.10 *dd* (J = 9.0, 9.5)	76.9
4″	3.53 *dd* (J = 9.5, 10.0)	68.1
5″	4.02 *m*	73.6
6″	4.46 *d* (J = 11.5), 4.20 *dd* (J = 6.5, 11.5)	63.1
1‴		125.2
2‴ and 6‴	7.57 *d* (J = 8.5)	130.3
3‴ and 5‴	6.80 *d* (J = 8.5)	115.9
4‴		159.9
7‴	7.59 *d* (J = 16.0)	144.7
8‴	6.43 *d* (J = 16.0)	114.7
9‴		166.2
1⁗		124.9
2⁗ and 6⁗	7.37 *d* (J = 8.5)[a]	130.2
3⁗ and 5⁗	6.68 *d* (J = 8.5)	115.7
4⁗		159.9
7⁗	7.49 *d* (J = 16.0)[a]	145.1
8⁗	6.33 *d* (J = 16.0)	110.3
9⁗		166.5

[a] Overlapping signals.

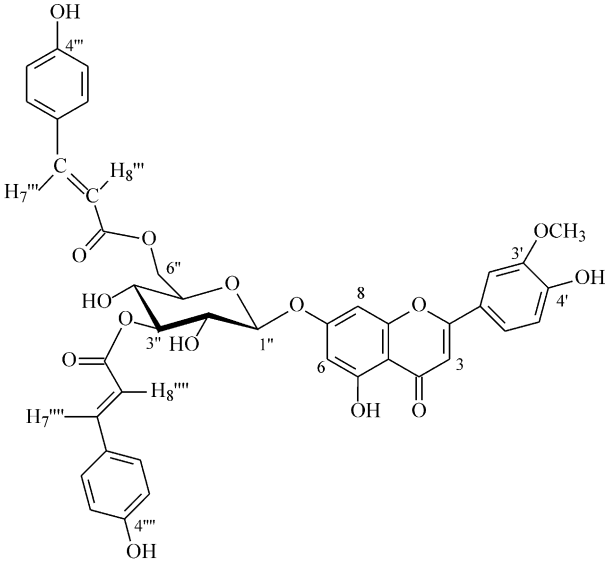
the acyl groups to glucose was confirmed by HMBC crosspeaks between C-9‴/H-3″ and C-9‴/H_2-6″. It was also proved by the HMBC spectrum, that the β-glucopyranosyl moiety is attached to C-7, showing correlations between the anomeric proton H-1″ (δ 5.36, J = 8.0 Hz, *d*) and C-7 (δ 162.5). Accordingly, the ROESY exhibited crosspeaks between H-1″, H-8, and H-6. The position of the methoxyl group was assigned to C-3′ on the basis of HMBC correlations between C-3′ and the protons of the methoxyl group. This was confirmed by ROE correlations between the methoxyl group and H-2′. UV and MS data (see Section 3) corroborated the results obtained from the NMR spectra (see Table 1).



		R
19	velutinoside **I**	H
20	velutinoside **II**	CH_3

Compound **19** was obtained as an amorphous yellowish powder. Its MALDI-HRMS exhibited a pseudomolecular ion $[M+Na]^+$ at m/z 941.2905, compatible with the molecular formula $C_{40}H_{54}O_{24}$. In agreement, 40 carbon signals were observed in the ^{13}C NMR spectrum. The IR spectrum showed absorption bands typical of hydroxyl (3380 cm^{-1}), α,β-unsaturated ester (1690, 1630 cm^{-1}) and aromatic rings (1630, 1600, and 1520 cm^{-1}). The ^{1}H NMR spectrum of **19** exhibited proton signals characteristic of an *E*-caffeoyl group (three aromatic protons resonating at δ 7.06–6.96 as an ABX system and two *trans* olefinic protons as an AB system at δ 7.60, 6.28 J = 15.9 Hz) and a 3,4-dihydroxyphenylethanol moiety (three aromatic protons at δ 6.71, 6.68 and 6.58 as an ABX system, a double doublet at δ 2.80 due to a β-methylene and two non-equivalent protons at δ 4.05 and 3.73 of the side chain of the aglycone moiety). Additionally, four signals assignable to anomeric protons indicated the presence of four sugar moieties in **19**: a doublet at δ 4.39 (J = 8.0 Hz, H-1′ of inner β-glucose), a broad singlet at δ 5.49 (H-1″ of α-rhamnose) and two doublets, partially overlapped, at δ 4.30 and 4.31 (J = 6.9 Hz, H-1⁗ of α-arabinose and J = 8.0 Hz, H-1‴ of outer β-glucose, respectively). These findings matched those in the HMQC/^{13}C NMR spectra, where four corresponding anomeric carbons resonated at δ 104.7, 102.5, 105.2, and 108.0, respectively. Furthermore, DEPT experiments clearly showed the presence of five methylene groups, two resonating at δ 37.1 and 72.9, belonging to C-7 and C-8 of the phenylethanoid moiety and three methylenes at δ 69.8, 63.1 and 67.8 corresponding to C-6′ of inner β-glucose, C-6‴ of outer β-glucose and C-5⁗ of α-arabinose, respectively. The downfield shift of C-6′, which is similar to that of e.g. echinacoside (**14**), and forsythoside B (**15**), indicated that this position is a glycosylation site. This

finding was further confirmed by HMBC experiments, where a crosspeak between H-1‴ and C-6′ was observed. The carbon resonances assigned to the outer β-glucose unit showed no unusual chemical shifts, suggesting its terminal position. A further site of connectivity was proved to be C-2″ of rhamnose, on the basis of ^{1}H and ^{13}C NMR spectra, as well as HMBC connectivities: H-2″ and C-2″ of rhamnose were highly deshielded compared to acteoside (**12**, δ 5.49 vs 5.19, and δ 83.4 vs 72.4), whereas ^{1}H and ^{13}C NMR spectroscopic data showed a close relation to the stucture of stachysoside A (**17**), which contains the same sugar subunits (Ara$^{1\rightarrow2}$ Rha$^{1\rightarrow3}$ Glu) (Nishimura et al., 1991) and was also isolated from this plant. The site of attachment of arabinose was further confirmed by crosspeaks between H-1⁗/C-2″ and H-2″/C-1⁗ in the HMBC spectrum. In the spectrum, same crosspeaks between H-1″/C-3′ and H-3′/C-1″ confirmed the usual linkage between glucose and rhamnose (Rha $^{1\rightarrow3}$ Glu), as can be observed for example in acteoside (**12**). The acylation site is on position C-4′ of glucose and this was evident from the strong deshielding of H-4′ (δ 5.01). The complete assignment of all proton and carbon resonances was achieved after careful analysis of ^{1}H-^{1}H COSY, HMQC, HMBC, ^{1}H–^{1}H TOCSY and HMQC-TOCSY experiments. Some significant HMBC correlations are shown in Fig. 1.



1

The ^{1}H and ^{13}C NMR spectroscopic data of compound **20** showed that its structure is closely related to that of compound **19**, with the exception of a singlet at δ 3.89 (3H, *s*) due to a methoxyl group. ROESY crosspeaks between OCH_3/H-2⁗ revealed that the site of attachment of this additional methoxyl group is on C-3 of the acyl chain, therefore a feruloyl moiety is linked to C-4′ of the inner glucose.

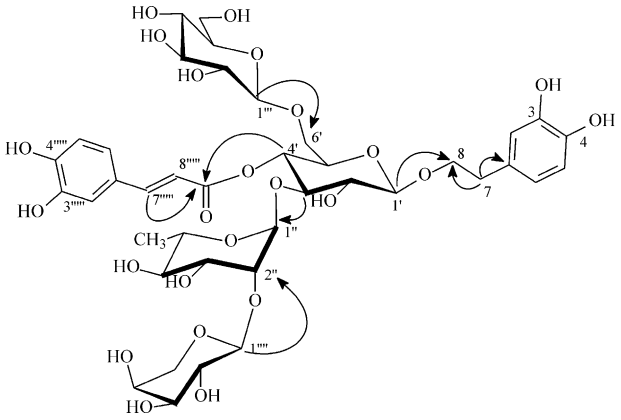


Fig. 1. Selected HMBC correlations for velutinoside I (**19**).

As far as we know, the described flavonoid (**1**) and the phenylethanoid glycosides named velutinosides I (**19**) and II (**20**) are reported here for the first time.

On the basis of ^{1}H and ^{13}C NMR, UV and MS data compounds **2-11** and **12-18** were identified as apigenin 7-*O*-(3″,6″-di-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside (**2**) (Rao et al., 1982), apigenin 7-*O*-(3′-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside (**3**) (El-Ansari et al., 1995), isorhamnetin 3-*O*-(6″-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside (**4**) (Zadorozhny et al., 1986), quercetin 3-*O*-(6″-acetyl)-β-D-glucopyranoside (**5**) (Wagner et al., 1971), isoquercitrin (**6**) (Pakudina et al., 1970), kaempferol-3-*O*-β-D-rutinoside (**7**) (Vermes et al., 1976), isorhamnetin 3-*O*-β-D-rutinoside (**8**) (Hörhammer et al., 1966), chrysoeriol (**9**) (Brieskorn and Riedel, 1977), isorhamnetin 3-*O*-β-D-glucopyranoside (**10**) (Rahman and Ilyas, 1962) and isorhamnetin 7-*O*-(6″-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside (**11**) (Kubo and Yokokawa, 1992), acteoside (**12**) (Birkofer et al., 1968), leucosceptoside A (**13**) (Miyase et al., 1982), echinacoside (**14**) (Stoll et al., 1950), forsythoside B (**15**) (Endo et al., 1982), alyssonoside (**16**) (Çalis et al., 1992), stachysoside A (**17**) (Nishimura et al., 1991) and 2-(3-hydroxy-4-methoxyphenyl)ethyl-*O*-[α-L-rhamnopyranosyl-(1→3)]-*O*-[β-D-glucopyranosyl-(1→6)]-4-*O*-*E*-feruloyl-β-D-glucopyranoside (**18**) (Warashina et al., 1992).

Tetrasaccharidic phenylethanoid glycosides are a rare group of plant secondary metabolites and only four compounds, namely magnoloside C (Hasegawa et al., 1988), ballotetroside (Seidel et al., 1997, Sahpaz et al., 2002a), trichosanthoside B (Çalis et al., 1999), and marruboside (Sahpaz et al., 2002b) have been isolated before. Two of these compounds, marruboside and ballotetroside, were isolated from *M. vulgare* (Sahpaz et al., 2002a, b).

In the present study, in addition to acylated flavone glucosides, flavonol derivatives have also been isolated from *M. velutinum*. The majority of the flavonoids occurring in the Lamiaceae family are flavones, while flavonols are found only in a few instances (Tomás-Barberán et al.,

1988). The taxa included in the subfamily Lamioideae (tribe Stachydeae) are normally rich in 7-*O*-glycosides of apigenin, luteolin and chrysoeriol (Tomás-Barberán et al., 1988). Earlier flavonoid surveys of *Marrubium* sp. (Saleh et al., 1981; Savona et al., 1984; Nawwar et al., 1989; Tomás-Barberán, 1992; Hatam et al., 1995; Nagy et al., 1996), revealed a nearly complete dominance of flavones and the presence of only one flavonol (kaempferol), isolated from *M. peregrinum* (Nagy et al., 1996). Therefore the isolation of flavonol glucosides from *M. velutinum* appears as a characteristic feature of this plant.

3. Experimental

3.1. General

^{1}H, ^{13}C and 2D NMR spectra were recorded in CD_3OD, CD_3OD/D_2O and DMSO-d_6 on Bruker AMX 300 (75.5 MHz for ^{13}C NMR), Bruker DRX 400 and Bruker DRX 500 instruments (399.95 and 500.1 MHz for ^{1}H NMR and 2D NMR, respectively) at 295 K. Chemical shifts are given in ppm (δ) and the spectra were referenced against undeuterated solvent. UV spectra were recorded on a Shimadzu UV-160A spectrophotometer, according to Mabry et al. (1970). HR-MALDI mass spectra were measured on an Ionspec Ultima FTMS spectrometer using 2,5-dihydroxybenzoic acid (DHB) as matrix. The $[\alpha]_D$ values were obtained in MeOH at 20 °C on a Perkin-Elmer 341 Polarimeter. FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 Spectrometer.

Vacuum liquid chromatography (VLC): silica gel 60H (Merck, Art. 7736); MPLC: Büchi 668, RP-silica gel 60 (Merck, Art. 10167), HPLC: Sykam S1021 solvent delivery system. UV/Vis detector S3200, Column: Kromasil C_{18}. Column chromatography (CC): silica gel 60 (Merck, Art. 9385), gradient elution with the solvents mixtures indicated in each case; Sephadex LH-20 (Pharmacia). TLC: Merck silica gel 60 F_{254} (Art. 5554); Merck cellulose (Art. 5552). Detection: UV-light, spray reagent [vanillin–H_2SO_4 on silica gel; Neu's reagent on cellulose (Neu, 1957)].

3.2. Plant material

Aerial parts of *M. velutinum* Sibth. and Sm. were collected from Kellaria—Parnassos mountain (Sterea Hellas) in July 1998. Voucher specimen has been kept in the Herbarium of Patras University (UPA) under the number Skaltsa and Lazari 114.

3.3. Extraction and isolation

The air-dried powdered aerial parts of *M. velutinum* (0.63 kg) were successively extracted at room temperature with petroleum ether, ether, EtOAc and MeOH (2 × 2 l of each solvent, 48 h). The dried MeOH extract (77.0 g) was subjected to VLC over silica gel (10 × 8 cm) with CH_2Cl_2–MeOH mixtures of increasing polarity to yield eight fractions (A–H) of 500 ml. Fraction E (13.4 g; eluted with CH_2Cl_2–MeOH 5:5–4:6) was further applied to VLC over silica gel using CH_2Cl_2–MeOH and yielded four fractions (A_1–D_1). Further purification of fraction B_1 (0.77 g) by CC over silica gel with mixtures of CH_2Cl_2–MeOH–H_2O (98:2:0.2–30:7:0.7) afforded 12 fractions (A_2–L_2), which were further purified by CC over Sephadex LH-20 (MeOH), as follows: fraction C_2 (9.8 mg) yielded compound **9** (1.0 mg); fraction E_2 (25.0 mg) compound **1** (4.4 mg); fraction F_2 (64.5 mg) compound **2** (3.7 mg); fraction G_2 (50.2 mg) compound **5** (2.3 mg) and a mixture of **3** and **11** (4.5 mg), which was further purified by TLC on silica gel (CH_2Cl_2–MeOH–H_2O 85:15:1.5) and yielded compound **3**; fraction I_2 (213.8 mg) compound **4** (19.8 mg). Fraction C_1 (6.49 g) was applied to VLC over silica gel using mixtures of CH_2Cl_2–MeOH (9:1–3:7) and afforded six fractions (A_3–F_3). Fraction D_3 (2.31 g) was applied to CC on silica gel with mixtures of CH_2Cl_2–MeOH–H_2O (97:3:0.3–30:7:0.7) and to Sephadex LH-20 (MeOH) and yielded compounds **4** (47.4 mg), **6** (5.0 mg), **7** (19.9 mg), **8** (2.2 mg) and **10** (13.7 mg). Purification of fraction H_2 (55.3 mg) by RP-18 HPLC (MeOH–aq. MeOH 59:41) allowed the isolation of **11** (5.6 mg; R_t 34.0 min). Further purification of fraction D_2 by CC on silica gel and Sephadex LH-20, as well as RP-HPLC (MeOH–H_2O 1:1) afforded compounds (**12**) (11.8 mg), (**13**) (14.8 mg), (**16**) (3.9 mg) and (**18**) (6.5 mg; R_t 10.1 min). Fraction D_1 was fractionated by CC over Sephadex LH-20 and yielded seven fractions (A_3–G_3). Fraction D_3 was subjected to RP-MPLC (RP-18 silica gel) and yielded compounds (**14**) (27.3 mg), (**15**) (11.0 mg) and a mixture of (**14**), (**15**) and (**17**). This mixture was further subjected to RP-HPLC (MeOH–aq. AcOH 5% 4:6) to afford pure compound (**17**) (11.3 mg; R_t 11.3 min). Fraction F was subjected to VLC over silica gel with CH_2Cl_2–MeOH mixtures of increasing polarity to yield 10 fractions (A_4–J_4). Fraction C_8 (632 mg; eluted with DCM-MeOH 1:1) was subjected to RP-VLC and afforded 5 fractions (A_5–E_5). Fraction D_5 was subjected to RP-HPLC (MeOH–aq. AcOH 5% 3:7) to yield compounds (**19**) (7.8 mg; R_t 11.0 min) and (**20**) (2.3 mg; R_t 14.5 min).

3.3.1. Chrysoeriol 7-O-(3″,6″- di-O-E- p-coumaroyl)-β-D-glucopyranoside (1)

Amorphous yellow powder (4.4 mg); UV λ_{max} (MeOH): 271, 316, 345^{sh} (nm); $[\alpha]_D^{20}$ −13.2° (MeOH, *c* 0.05). MALDI-HRMS (pos.) *m*/*z*: 777.1815 (requires for 777.1785); ^{1}H and ^{13}C NMR spectral data see Table 1.

3.3.2. Velutinoside I (19)

Amorphous yellow powder (7.8 mg); UV λ_{max} (MeOH): 285, 334 (nm); $[\alpha]_D^{20}$ −6.1° (MeOH, *c* 0.21). MALDI-HRMS (pos.) *m*/*z*: 941.2905 (requires for 941.2886); ^{1}H and ^{13}C NMR spectral data see Table 2.

3.3.3. Velutinoside II (20)

Amorphous yellow powder (2.3 mg); UV λ_{max} (MeOH): 295, 328 (nm); $[\alpha]_D^{20}$ −6.6° (MeOH, *c* 0.05). MALDI-HRMS *m*/*z*: 955.2995 (requires for 955.3042); ^{1}H NMR (400 MHz, CD_3OD) *δ*: aglycone: 6.74 (1H, *d*, *J* = 2.0, H-2), 6.71 (1H, *d*, *J* = 8.2, H-5), 6.60 (1H, *dd*, *J* = 2.0, 8.2, H-6), 2.81 (1H, *dd*, *J* = 7.5, 7.8, H-7), 4.04 and 3.76[a] (1H, *m*, H-8); inner glucose: 4.43 (1H, *d*, *J* = 7.8, H-1′), 3.41 (1H, *dd J* = 7.8, 8.9, H-2′), 3.83–3.78[a] (1H, H-3′), 5.03 (1H, H-4′), 3.83–3.78[a] (1H, H-5′), 3.94 and 3.69–3.63[a] (1H, H-6′); rhamnose: 5.48 (1H, *d*, *J* = 1.4, H-1″), 3.98 (1H, *brs*, H-2″), 3.69–3.63[a] (1H, H-3″), 3.36–3.27[a] (1H, H-4″), 3.54[a] (1H, H-5″), 1.05 (1H, *d*, *J* = 6.2, H-6″); outer glucose: 4.31 (1H, *d*, *J* = 7.5, H-1‴), 3.22 (1H, *dd*, *J* = 7.5, 8.9, H-2‴), 3.36–3.27[a] (1H, H-3‴), 3.36–3.27[a] (1H, H-4‴), 3.36–3.27[a] (1H, H-5‴), 3.83–3.78[a] and 3.69–3.63[a] (1H, H-6‴); arabinose: 4.33 (1H, *d*, *J* = 6.5, H-1⁗), 3.69–3.63[a] (1H, H-2⁗), 3.54–3.51* (1H, H-3⁗), 3.83–3.78* (1H, H-4⁗), 3.83–3.78 and 3.54–3.51* (1H, H-5⁗); acyl group: 7.21 (1H, *d*, *J* = 1.9, H-2⁗′), 6.83 (1H, *d*, *J* = 8.2, H-5⁗′), 7.11 (1H, *dd*, *J* = 1.9, 8.2, H-6⁗′), 7.68 (1H, *d J* = 16.0, H-7⁗′), 6.38 (1H, *d J* = 16.0, H-8⁗′), OCH_3 3.89 (*s*, 3H).

Table 2
^{1}H NMR (400 MHz, CD_3OD, *J* in Hz) and ^{13}C NMR (75.5 MHz, at 295 K) data of compound **19**

Position	δ_H	δ_C
Aglycone		
1		131.9
2	6.71 *d* (*J* = 1.6)	117.6
3		147.3
4		146.6
5	6.68 *d* (*J* = 8.0)	116.8
6	6.58 *dd* (*J* = 1.6, 8.0)	121.8
7	2.80 *dd* (*J* = 7.0, 7.3)	37.1
8	4.05 *m* and 3.73 *m*	72.9
Inner glucose		
1′	4.39 *d* (*J* = 8.0)	104.7
2′	3.38 *dd* (*J* = 8.0, 9.2)	76.4
3′	3.76 *t* (*J* = 9.2)	82.9
4′	5.01 *t* (*J* = 9.6)	70.9[a]
5′	3.77[a]	75.2
6′	3.95[a] and 3.64[a]	69.8
Rhamnose		
1″	5.49 *brs*	102.5
2″	3.94 *brs*	83.4
3″	3.64[a]	72.4
4″	3.30[a]	74.6
5″	3.53[a]	70.9[a]
6″	1.05 *d* (*J* = 6.4)	18.9
Outer glucose		
1‴	4.31 *d* (*J* = 8.0)	105.2
2‴	3.20 *dd* (*J* = 8.0, 8.9)	75.6
3‴	3.35[a]	78.3
4‴	3.29[a]	71.9
5‴	3.29[a]	78.4
6‴	3.83 *dd* (*J* = 12.1, 2.9) and 3.66[a]	63.1
Arabinose		
1⁗	4.30 *d* (*J* = 6.9)	108.0
2⁗	3.60 *dd* (*J* = 6.9, 10.2)	73.3
3⁗	3.50[a]	74.8
4⁗	3.77[a]	70.3
5⁗	3.86 *dd* (*J* = 2.6, 12.4) and 3.53[a]	67.8
Acyl group		
1⁗′		128.1
2⁗′	7.06 *d* (*J* = 1.9)	115.7
3⁗′		148.2
4⁗′		150.3
5⁗′	6.79 *d* (*J* = 8.3)	117.0
6⁗′	6.96 *dd* (*J* = 1.9, 8.3)	123.7
7⁗′	7.60 *d* (*J* = 15.9)	148.7
8⁗′	6.28 *d* (*J* = 15.9)	115.1
9⁗′		168.9

[a] Signal pattern unclear due to overlapping.

Acknowledgements

The authors are grateful to Dr. Theophanis Constantinidis (Institute of Systematic Botany, Agricultural University of Athens) for the identification of the plant material and Dres. O. Zerbe and K. Winkelmann (Institute of Pharmaceutical Sciences, ETH Zurich) for recording the 500 MHz NMR spectra.

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