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# FLAVONOID GLYCOSIDES FROM *ANTHYLLIS SERICEA*

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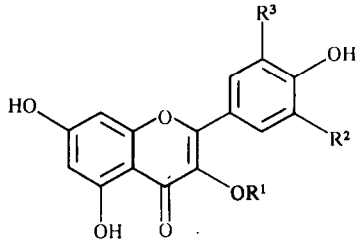
**Key Word Index**—*Anthyllis sericea*; Leguminosae; flavonol glycosides; isorhamnetin 3-*O*-(2-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside; $^1$H NMR; $^{13}$C NMR.

**Abstract**—A fraction of a methanolic extract of *Anthyllis sericea* yielded the known compounds quercetin 3-galactoside, kaempferol 3-galactoside, isorhamnetin 3-galactoside, syringetin 3-galactoside, vitexin, quercetin 3-robinobioside, isorhamnetin 3-robinobioside, kaempferol 3-*O*-(2-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside and the new flavonol diglycoside isorhamnetin 3-*O*-(2-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside.

## INTRODUCTION

*Anthyllis sericea* Lag., non Willd. (syn. *A. henoniana* Cosson ex Batt.) (Leguminosae) is a medium-sized shrub with woody branches and grey-greenish leaves, which is scattered in south and east Spain [1]. It was investigated 11 years ago [2] in our laboratory and was found to contain waxes, ursolic acid, sitosterol and several free acids. We are currently interested in the chemotaxonomy of the genus *Anthyllis*, which is known to contain appreciable amounts of flavonoid glycosides [3]. We now wish to report the isolation of eight flavonol *O*-glycosides **1**–**8** and a flavone *C*-glycoside (vitexin) from an extract of *A. sericea*. One of the flavonol glycosides was shown from its spectral and chemical properties to be isorhamnetin 3-*O*-(2-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside **8**, a new natural product.




**1** $R^1$ = βGal; $R^2$ = $R^3$ = H
**2** $R^1$ = βGal; $R^2$ = OH; $R^3$ = H
**3** $R^1$ = βGal; $R^2$ = OMe; $R^3$ = H
**4** $R^1$ = βGal; $R^2$ = $R^3$ = OMe
**5** $R^1$ = βGal (6→1α) Rha; $R^2$ = OH; $R^3$ = H
**6** $R^1$ = βGal (6→1α) Rha; $R^2$ = OMe; $R^3$ = H
**7** $R^1$ = βGal (2→1β) Glc; $R^2$ = $R^3$ = H
**8** $R^1$ = βGal (2→1β) Glc; $R^2$ = OMe; $R^3$ = H

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## RESULTS AND DISCUSSION

Compound **8** was a yellow amorphous powder with the expected chromatographic behaviour for a flavonol diglycoside [4] (see Experimental for $R_f$ values). The UV spectrum and its changes after addition of shift reagents [5] pointed to the presence of free hydroxyl groups at C-5, C-7 and C-4′. Acid hydrolysis yielded isorhamnetin, compared with an authentic sample, and the sugars glucose and galactose, identified by GC of their silylated derivatives. The negative ion FAB mass spectrum of **8** showed a $[M-H]^-$ peak at *m/z* 639, consistent (high resolution measurement) with a molecular formula $C_{28}H_{32}O_{17}$ for the glycoside. Other significant peaks were visible at *m/z* 477 $[M-\text{hexose}]^-$ and 315 $[M-2\times\text{hexose}]^-$. These findings supported a 3-glycosylated flavonol structure.

The 200 MHz $^1$H NMR spectrum (Table 1) evidenced the expected signals in the aromatic region: two doublets at δ6.13 and 6.37 ($J$ = 1.9 Hz) for H-6 and H-8, respectively; two doublets at δ6.90 ($J$ = 8.5 Hz) and 7.89 ($J$ = 2 Hz) for H-5′ and H-2′, respectively; and a double doublet at δ7.59 ($J$ = 8.5 and 2 Hz) for H-6′. The anomeric protons appeared as doublets at δ5.72 ($J$ = 7.5 Hz) and 4.58 ($J$ = 7.2 Hz), and the methoxyl singlet was located at δ3.85. The high field position of the second anomeric proton signal pointed to a sugar–sugar linkage, thus further supporting the proposed 3-diglycosylated isorhamnetin structure. The coupling constants for both anomeric signals are of the axial-axial type, as observed in β anomers of related glucopyranose and galactopyranose derivatives.

The resolution allowed for a 200 MHz $^1$H NMR spectrum was not good enough for ascertaining the site of sugar linkage, for the sugar non-anomeric protons gave an unresolved multiplet in the range 3–4 ppm. At 400 MHz, however (Table 2), a signal was visible as a double doublet at δ3.82 ($J$ = 7.7 and 9.4 Hz). This signal showed a marked cross peak in the H, H-COSY spectrum [6] with the doublet at δ5.68 from the anomeric proton H-1″ (that from the glycosyl residue bonded to the aromatic aglycone) and was thus assigned to H-2″.

Table 1. $^1$H NMR spectra of compounds **4–8***

| Compound | Aromatic protons | | | | | | Anomeric protons† | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | H-6 | H-8 | H-2′ | H-3′ | H-5′ | H-6′ | H-1″ | H-1‴ | OMe | $Me_{rha}$ |
| **4** | 6.06 *d* (1.8) | 6.31 *d* (1.8) | 7.50 *s* | | | 7.50 *s* | 5.49 *d* (7.6) | | 3.83 *s* | |
| **5** | 6.15 *d* (1.9) | 6.35 *d* (1.9) | 7.51 *d* (2.2) | | 6.80 *d* (8.5) | 7.63 *dd* (8.5; 2.2) | 5.29 *d* (7.6) | 4.41 *br s* | | 1.06 *d* (6.1) |
| **6** | 6.18 *d* (2.0) | 6.41 *d* (2.0) | 8.00 *d* (2.0) | | 6.90 *d* (8.5) | 7.50 *dd* (8.5; 2.0) | 5.44 *d* (7.5) | 4.42 *br s* | 3.85 *s* | 1.05 *d* (6.1) |
| **7** | 6.13 *d* (1.9) | 6.36 *d* (1.9) | 8.06 *d* (8.9) | 6.87 *d* (8.9) | 6.87 *d* (8.9) | 8.06 *d* (8.9) | 5.70 *d* (7.5) | 4.58 *d* (7.2) | | |
| **8** | 6.13 *d* (1.9) | 6.37 *d* (1.9) | 7.89 *d* (2.0) | | 6.90 *d* (8.5) | 7.59 *dd* (8.5; 2.0) | 5.72 *d* (7.5) | 4.58 *d* (7.2) | 3.85 *s* | |

*At 200.13 MHz in DMSO-$d_6$ (30°); $\delta$ values are followed by multiplicity and below, in parentheses, coupling constants in Hz. Only aromatic, anomeric and methoxyl signals are given, sugar non anomeric protons showing consistently a broad absorption in the range $\delta$3.00–4.00. The 5-OH originates a broad singlet at $\delta$12.5–12.7 in all compounds.

†″Indicates the galactose residue and ‴ indicates the other sugar moiety (glucose or rhamnose).

Table 2. $^1$H NMR of **8** at 400 MHz (sugar part)*

| H | $\delta$(ppm) | (*J* Hz) |
|---|---|---|
| 1″ | 5.68 *d* | (7.7) |
| 2″ | 3.82 *dd* | (9.4; 7.7) |
| 3″ | 3.64 *dd* | (9.4; 3.4) |
| 4″ | 3.70 *dd* | (3.4; < 1) |
| 5″ | 3.29–3.44 *m* | |
| $6''_{A+B}$ | | |
| 1‴ | 4.58 *d* | (7.8) |
| 2‴ | 3.05 *dd* | (8.8; 7.8) |
| 3‴ | 3.05–3.18 *m* | |
| 4‴ | | |
| 5‴ | | |
| $6'''_{A+B}$ | 3.51–3.36 *m* | |

*At 25° in DMSO-$d_6$/$D_2O$.

The rather low field position of this signal strongly suggested the second glycosyl residue being linked to O-2″. Furthermore, a careful analysis of the H,H-COSY spectrum enabled the identification of most of the protons of the first hexose moiety. The small value of the vicinal coupling constants $J_{3'',4''}$ and $J_{4'',5''}$ (axial–equatorial type) indicated that this sugar was galactose (axial 4-OH group) [7], thus identifying **8** as isorhamnetin 3-*O*-(2-*O*-*β*-D-glucopyranosyl)-*β*-D-galactopyranoside.

Additional confirmation of this structural assignment was sought by NMR examination of the peracetylated derivative. While the sugar region in the $^1$H NMR spectrum of underivatized glycosides may be quite complex, the spectra of the corresponding peracetates are often well resolved in this zone and display resonances spread over 2 ppm. The signals of the hydrogens contiguous to free secondary OH groups undergo very marked downfield shifts after acetylation and appear usually in the range 5.0–5.5 ppm. In the case of substituted (i.e. glycosylated) secondary OH groups and for all primary OH groups, the corresponding signals remain below 4.5 ppm [8]. The $^1$H NMR spectrum of peracetylated **8** showed a doublet ($J$ = 7.7 Hz) at $\delta$5.84 for the anomeric proton H-1″, a complex multiplet (5 H) for the CHOAc protons in the range 5.0–5.4 ppm, and another multiplet (11 H) in the range 3.7–4.2 ppm for the CHOR (R ≠ Ac), $CH_2OR$, $CH_2$ OAc and OMe protons. Although these multiplets could not be further analysed at 200 MHz, a distinct cross peak was visible in the H,H-COSY spectrum between the anomeric doublet at $\delta$5.84 (H-1″) and the high-field multiplet at $\delta$3.7–4.2. This fact implied that H-2″ belonged to the CHOR type (R ≠ Ac) or, in other words, that the 2″-OH group was glycosylated [8, 9], as proposed before.

The $^{13}$C NMR of **8** (Table 3) proved completely consistent with this structure and was very similar to that of the corresponding, recently described quercetin 3-glucogalactoside [10]. The characteristic signal at $\delta$79.81 was assigned to C-2″ and is at a somewhat higher field than the C-2″ peak in the structurally similar kaempferol 3-sophoroside (2-glucosylglucoside) [11], a further support of a galactose (not a glucose) being bonded to the aglycone. The signals have been assigned with recourse to comparison with model compounds [11–15].

The other compounds were identified by a combination of spectral properties and hydrolysis results (**4–7**) or by direct comparison with authentic samples (**1–3** and vitexin). Compounds **4–7** are not common flavonoids. Prior to this work, syringetin 3-galactoside **4** was reported only in *Phylidrum lanuginosum* (Phylidraceae) [16] and in some *Chondropetalum* spp. (Restionaceae) [17]. Isorhamnetin 3-robinobioside **6** was described unequivocally only six years ago [18], although several isorhamnetin 3-rhamnogalactosides had been reported earlier [19]. We conclude that our product is the robinobioside from a careful examination of the $^{13}$C NMR spectrum (Table 3) [13–15, 18, 20]. An NMR analysis of the mother liquors of the crystallizations of **6** revealed the presence of small amounts of kaempferol 3-robinobioside [21], the separation of which was not attempted. Lastly,

Table 3. $^{13}C$ NMR spectra of compounds **6–8***

| C | Aromatic region | | | Carbon number | Sugar region† | | |
|---|---|---|---|---|---|---|---|
| | **6** | **7** | **8** | | **6** | **7** | **8** |
| 2 | 156.51[a] | 156.39[a] | 156.33[a] | 1″ | 101.91 | 98.59 | 98.59 |
| 3 | 133.05 | 132.72 | 132.86 | 2″ | 71.16[b] | 79.72 | 79.81 |
| 4 | 177.21 | 177.11 | 177.33 | 3″ | 72.97 | 73.25 | 73.32 |
| 5 | 161.17 | 161.12 | 161.20 | 4″ | 67.99[c] | 67.65 | 67.71 |
| 6 | 99.01 | 99.02 | 98.88 | 5″ | 73.56 | 75.77 | 75.86 |
| 7 | 165.25 | 164.50 | 164.87 | 6″ | 65.20 | 60.02 | 60.07 |
| 8 | 93.89 | 93.86 | 93.78 | 1‴ | 100.06 | 103.48 | 103.68 |
| 9 | 156.22[a] | 155.42[a] | 155.67[a] | 2‴ | 70.63[b] | 74.18 | 74.24 |
| 10 | 103.62 | 103.24 | 103.58 | 3‴ | 70.43[b] | 76.78[b] | 76.83[b] |
| 1′ | 121.05 | 121.10 | 121.13 | 4‴ | 71.90[b] | 69.82 | 69.83 |
| 2′ | 113.45 | 130.87 | 113.22 | 5‴ | 68.29[c] | 76.54[b] | 76.59[b] |
| 3′ | 147.00 | 115.20 | 147.08 | 6‴ | 17.89 | 60.84 | 60.86 |
| 4′ | 149.48 | 160.10 | 149.53 | | | | |
| 5′ | 115.17 | 115.20 | 115.28 | | | | |
| 6′ | 121.95 | 130.87 | 122.48 | | | | |
| OMe | 55.92 | | 55.99 | | | | |

*At 50.32 MHz in DMSO-$d_6$ (30°). The signals with the same superscript ([a, b, c]) may be interchanged within the corresponding spectrum.

†″Indicates the galactose residue and ‴ indicates the other sugar moiety (glucose or rhamnose).

quercetin 3-robinobioside **5** was first reported in *Crataegus pinnatifida* (Rosaceae), although a quercetin 3-rhamnogalactoside (sugar linkage not specified) had been found before in *Lasthenia* ssp. (Compositae) [19]. Very recently, it has been found again in *Strychnos variabilis* (Loganiaceae), together with kaempferol 3-robinobioside [21].

The sugar moiety of **7** and **8** corresponds to the unusual disaccharide 2-*O*-(β-D-glucopyranosyl)-β-D-galactopyranose. Up to now, only two flavonoid glycosides with this sugar residue had been reported: the above-mentioned quercetin 3-*O*-(2-glucosylgalactoside) from *Coryllus avellana* (Betulaceae) [10] and the corresponding kaempferol derivative **7**, in *Lilium candidum* (Liliaceae) [22].

## EXPERIMENTAL

The solvent signals were used in NMR as reference (δ2.49 for $^1H$ and δ39.5 for $^{13}C$). COSY spectra were measured with Bruker standard software. Negative ion FAB mass spectra were run on a Kratos MS 50 S mass spectrometer, equipped with a Kratos FAB source.

*Plant material. A. sericea* was collected in May 1986 in La Cañada (Valencia, Spain). A voucher specimen is deposited in the herbarium of the Department of Botany at the Faculty of Biology in Valencia.

*Extraction and chromatography.* Aerial parts of the plant (1.8 kg) were air-dried at room temp., finely ground and extracted successively at room temp. with 80% aq MeOH (12 l, 30 days) and 50% aq MeOH (10 l, 10 days). The combined extracts were concd *in vacuo* to a vol. of 2 l, and extracted successively with $Et_2O$, EtOAc and *n*BuOH (10, 5 and 5 l, respectively). The ethereal extract did not contain flavonoids (inspection by TLC) and was discarded. Only the results of the EtOAc extract are reported here.

The solid residue after the evapn of the EtOAc (12.6 g) was placed on the top of a polyamide column (80 × 6 cm, MN SC6) and eluted with $H_2O$ containing an increasing percentage of MeOH (100 ml fractions). After inspection by TLC (silica gel, elution with EtOAc–MeCOEt–$HCO_2H$–$H_2O$ 5/3/1/1), four main flavonoid-containing fractions (A-1 to A-4) were collected. Fraction A-1 (4.5 g) was rechromatographed on polyamide with $H_2O$–MeOH mixtures (25 ml fractions were collected). The flavonoid-containing fractions (*ca* 100 mg) were shown to be by $^1H$ NMR a *ca* 1:1 mixture of **7** and **8**. A partial separation took place by a very lengthy Sephadex LH-20 column (100 × 2 cm, elution with water), which yielded **7** (20 mg) and **8** (20 mg), as well as mixed fractions.

Fraction A-2 weighed 2.5 g. An aliquot of it (200 mg) was rechromatographed on Sephadex LH-20 (elution with 80% aq MeOH). This yielded **6** (70 mg), contaminated with a small percentage (*ca* 10%) of kaempferol 3-robinobioside, which remained in the mother liquor of the crystallization (see text).

Fraction A-3 (4 g) was rechromatographed on polyamide and eluted with toluene containing increasing amounts of MeOH. The flavonoid-containing fractions were combined and rechromatographed on Sephadex LH-20 (elution with 80% aq MeOH). This gave a mixture of **5** and vitexin, free of other non-flavonoid impurities. The final separation was performed by paper chromatography (MN 216, elution with 15% HOAc). The main bands were cut off and stirred with MeOH, and the extracted material was percolated through Sephadex LH-20 (80% aq MeOH). This yielded **5** (4 mg) and vitexin (2 mg).

Fraction A-4 (1.5 g) was chromatographed on Sephadex LH-20 and eluted with 80% aq MeOH. This yielded two main flavonoid-containing fractions (inspection by TLC). One of the fractions was rechromatographed first on polyamide (toluene–MeOH mixtures) and then on Sephadex LH-20 (80% aq MeOH), affording the separation of **4** (3 mg). The other fraction was rechromatographed in the same way, yielding **2** (40 mg) and a *ca* 2:1 mixture of **3** and **1** (48 mg). Since these compounds could be compared with authentic samples, no further separation was attempted.

*Isorhamnetin 3-O-(2-O-β-D-glucopyranosyl)-β-D-galactopyranoside.* Amorphous yellow powder. $R_f$ values: silica gel, elution with $CHCl_3$–MeOH–$H_2O$ (14/6/1) 0.28 (0.93 relative to

rutin); silica gel, elution with EtOAc–MeCOEt–$HCO_2H$–$H_2O$ (5/3/1/1) 0.30 (0.67 relative to rutin); polyamide, elution with $CHCl_3$–MeOH–MeCOEt–acetylacetone (20/10/1/1) 0.52 (4.33 relative to rutin); cellulose, elution with water, 0.58 (1.57 relative to rutin); paper chromatography, elution with 15% HOAc, 0.85 (1.18 relative to rutin); paper chromatography, elution with TBA, 0.66 (1.06 relative to rutin). UV $\lambda_{max}$ nm: MeOH, 255, 266 sh, 300 sh, 356; (+NaOMe), 271, 329, 412; (+$AlCl_3$), 267, 301, 360 sh, 403; (+$AlCl_3$/HCl), 267, 300, 362, 401; (+NaOAc), 274, 323, 402; (+NaOAc/$H_3BO_3$), 256, 269 sh, 292 sh, 359. FABMS, *m/z*: 639 $[M-H]^-$, 477 $[M-\text{hexose}]^-$, 315 $[M-2\times\text{hexose}]^-$. For NMR spectra, see Tables 1–3.

*Peracetylated derivative of* **8**. Compound **8** was acetylated in the usual way ($Ac_2O$–pyridine, room temp. overnight). After aqueous work-up, the product was chromatographed on silica gel (elution with $Et_2O$–dichloromethane 1:1). $^1H$ NMR ($CDCl_3$), $\delta$ppm: 7.67 (*d*, $J=2$ Hz, H-2'), 7.61 (*dd*, $J=8.3$ and 2 Hz, H-6'), 7.29 (*d*, $J=2.2$ Hz, H-8), 7.14 (*d*, $J=8.3$ Hz, H-5'), 6.82 (*d*, $J=2.2$ Hz, H-6), 5.84 (*d*, $J=7.7$ Hz, H-1''), 5.35–5.00 (*m*, 5H), 4.25–3.70 (*m*, 8H), 3.94 (*s*, 3H, OMe), 2.44, 2.33 (× 2), 2.08, 2.03, 1.97 (× 3), 1.95, 1.88 (acetate singlets). $^{13}C$ NMR ($CDCl_3$), $\delta$ppm: 172.01 (C-4), 170.59, 170.26, 170.17, 169.86, 169.68, 169.23, 169.21, 169.19, 168.51, 167.95 (acetate carbonyls), 156.51, 155.40, 153.83, 150.78, 150.23, 141.70 (C-2, 5, 7, 9, 3', 4'), 135.99 (C-3), 128.98, 122.55, 121.85 (C-1', 5', 6'), 115.10 (C-10), 113.49, 113.41, 108.88 (C-6, 8, 2'), 99.43, 98.26 (C-1'', C-1'''), 75.59, 73.06, 72.09, 71.75, 71.66, 70.87, 68.21, 67.32 (C-2'' to C-5'', C-2''' to C-5'''), 61.62, 60.51 (C-6'', C-6'''), 56.15 (OMe), 21.10, 21.01, 20.57 (× 3), 20.50 (× 3), 20.42 (× 2) (acetyl Me groups).

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