Available online at www.sciencedirect.com
ScienceDirect
Phytochemistry Letters 1 (2008) 125–129
PHYTOCHEMISTRY LETTERS
www.elsevier.com/locate/phytol

Acylated flavonol glycosides from *Delphinium staphisagria*

Jesús G. Díaz [a], Armando J. Carmona [a], Pedro Perez de Paz [b], Werner Herz [c,*]

[a] *Instituto Universitario de Bio-Orgánica "Antonio González", La Laguna, Tenerife, Spain*
[b] *Departamento de Botanica, Facultad de Farmacia, Universidad de La Laguna, Tenerife, Spain*
[c] *Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL 32306-4390, United States*

Received 16 April 2008; received in revised form 12 June 2008; accepted 16 June 2008
Available online 7 July 2008

Abstract

An ethanolic extract of the aerial parts of *Delphinium staphisagria* L. from Tenerife yielded four new flavonol glycosides 2″-acetylastragalin, 2″-acetylpaeonoside, quercetin 3-*O*-(2-acetyl-β-glucopyranoside)-7-*O*-β-glucopyranoside and 2″-acetylpetiolaroside in addition to astragalin, isoquercitrin, paeonoside, kaempferol 3-*O*-β-glucopyranoside-7-*O*-α-rhamnopyranoside, petiolaroside and rutin.

Keywords: *Delphinium staphisagria*; Ranunculaceae; Flavonol glycosides; 2″-Acetylastragalin; 2″-Acetylpaeonoside; Quercetin 3-*O*-(2-acetyl-β-glucopyranoside)-7-*O*-2″-acetylpetiolaroside

1. Introduction

The literature contains numerous publications on the diterpenoid alkaloids of *Delphinium* species but articles on *Delphinium* flavonoids are relatively rare (Arazashvili et al., 1973, 1974; Strzelecka and Dobrowolska, 1976; Lomadze et al., 1976; Yunusova and Nigmanova, 1976; Warnock et al., 1983; Özden et al., 1998; Yoshimitsu et al., 2007). Several years ago one of us, with others, reported new diterpene alkaloids from the aerial parts of *Delphinium staphisagria* L. (Díaz et al., 2000). The present article deals with flavonols in the extracts of the aerial parts of this species. Isolated were the kaempferol-based glycosides astragalin (**1**), 2″-acetylastragalin (**1a**), paeonoside (**3**), 2″-acetylpaeonoside (**3a**), kaempferol β-glucopyranoside-7-*O*-rhamnopyranoside (**5**) and the quercetin-based glycosides isoquercitrin (**2**) contaminated with rutin (**7**), quercetin 3-(2-acetyl-β-glucopyranoside)-7-*O*-β-glucopyranoside (**4**), petiolaroside (**6**) and 2″-acetylpetiolaroside (**6a**). Flavonol glucosides **1a**, **3a**, **4** and **6a** are new naturally occurring flavonoids and have not been described previously.

2. Results and discussion

The *n*-BuOH soluble fraction of the EtOH–H_2O (4:1) extract of the aerial parts of *D. staphisagria* was submitted to multiple chromatographic steps to afford the known flavonoids astragalin (**1**), isoquercitrin (**2**) contaminated with rutin, paeonoside (**3**), kaempferol 3-*O*-β-glucopyranoside-7-*O*-α-rhamnopyranoside (**5**, Özden et al., 1998), petiolaroside (**6**) and the new flavonol glycosides 2″-acetylastragalin (**1a**), 2″-acetylpaeonoside (**3a**), quercetin 3-*O*-(2-acetyl-β-glucopyranoside)-7-*O*-β-glucopyranoside (**4**) and 2″-acetylpetiolaroside (**6a**). Known flavonoids **1**–**3**, **5** and **6** were identified by HRMS, ^{1}H and ^{13}C NMR spectrometry and conversion to the known respective peracetates.

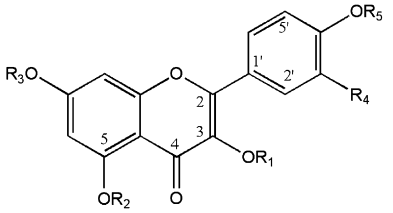
In the case of new compound **1a** location of the acetate function on C-2″ of the glucose moiety was deduced by comparing the ^{1}H and ^{13}C NMR spectra (see Section 3) with those of astragalin (**1**), the significant difference being the downfield shift of the H-2″ signal from δ 4.32 (in pyridine-d_5) for **1** to δ 5.89 for **1a**. In the ^{13}C NMR spectrum acetylation at C-2″ was evidenced by the upfield shifts of C-1″ and C-3″ from δ 104.5 resp. 79.0 in **1** to δ 101.2 resp. 76.3 in **1a**. To verify the structure further acetylation of monoacetate **1a** produced the known astragalin heptaacetate (**1d**) as well as two new isomeric astragalin hexaacetates **1b** and **1c** whose ^{1}H and ^{13}C NMR spectra (see Section 3) when compared with those of **1a** and **1d** indicated that **1b** was the 7,4′,2″,3″,4″,6″-hexaacetate of astragalin, i.e. kaempferol 3-*O*-β-glucopyranoside 7,4′,2″,3″,4″,6″-hexaacetate, and that **1c** was the isomeric kaempferol 3-*O*-β-glucopyranoside 5,4′,2″,3″,4″,6″-hexaacetate.

In a quite similar fashion comparison of the ^{1}H and ^{13}C NMR spectra of new monoacetate **3a** with those of paeonoside

* Corresponding author. Tel.: +1 850 644 2774; fax: +1 850 644 8281.
E-mail addresses: jdulin@chem.fsu.edu, herz@chem.fsu.edu (W. Herz).

1874-3900/$ – see front matter
doi:10.1016/j.phytol.2008.06.005

(**3**), also a constituent of the extract, showed that the new acetoxy group esterified C-2″ of the glucoside on C-3 of the flavonol skeleton, the signal of the corresponding proton having shifted from δ 4.36 in **3** to δ 5.88 in **3a**, a change mirrored in the upfield shift of the C-1″ and C-3″ signals from δ 103.9 resp. 79.0 in **3** to δ 101.0 resp. 76.4 in **3a**, while peracetylation of **3a** produced paeonoside decaacetate (**3b**) identical with material prepared from paeonoside. Similarly in the ^{1}H and ^{13}C NMR spectra of new monoacetate **6a** the signal of H-2″ was shifted downfield from δ 4.34 m in petiolaroside (**6**) to δ 5. 87 dd and the C-1″ and C-3″ signals were shifted from δ 104.7 resp. 79.0 in **6** to δ 101.5 resp. 76.5, all indicating acetylation at C-2″, while peracetylation of **6a** produced petiolaroside undecaacetate (**6b**) identical with material prepared from petiolaroside itself. Finally, in the ^{1}H and ^{13}C NMR spectra of new monoacetate **4** the H-2″ signal occurred at δ 5.85 dd with the C-1″ and C-3″ signals being found at δ 102.1 resp. 75.2, all indicating location of the acetate on C-2″, while peracetylation of **4** yielded the known quercetin 3,7-diglucoside undecaacetate (**4a**).



(1) astragalin: R_1= Glc, R_2= R_3= R_4= R_5 = H
(1a) 2" acetylastragalin: R_1= Glc 2"-Ac; R_2= R_3 = R_4 = R_5= H
(1b) R_1= Glc-Ac; R_2 = R_4 = H, R_3= R_5 = Ac
(1c) R_1= Glc-Ac; R_2 = R_5 = Ac, R_3 = R_4 = H
(1d) astragalin heptaacetate: R_1= Glc-Ac; R_2 = R_3 = R_5 = Ac, R_4 = H
(2) isoquercitrin: R_1= Glc; R_2= R_3= R_5 = H, R_4= OH
(2a) isoquercitrin octaacetate: R_1= Glc-Ac; R_2= R_3= R_5 = Ac, R_4= OAc
(3) paeonoside: R_1= R_3 = Glc; R_2 = R_4 = R_5 = H
(3a) 2"-acetylpaeonoside: R_1= Glc 2"-Ac; R_3 = Glc, R_2 = R_4 = R_5 = H
(3b) paeonoside decaacetate: R_1= R_3 = Glc-Ac; R_2 = R_5 = Ac, R_4= H
(4) quercetin 3-O(2'-acetyl-β-glucopyranoside) -7-O-β-glucopyranoside:
(R_1= Glc 2"-Ac; R_3 = Glc, R_2 = R_5 = H, R_4 = OH)
(4a) quercetin 3-O-β-glucopyranoside -7-O - β - glucopyranoside undecaacetate:
(R_1= R_3 = Glc-Ac; R_2 = R_5 = Ac, R_4= OAc)
(5) kaempferol 3-O-β-glucopyranoside -7-O -α-rhamnopyranoside:
(R_1= Glc ; R_3 = Rha; R_2 = R_4 = R_5 = H)
(5a) kaempferol 3-O-β-glucopyranoside -7-O -α-rhamnopyranoside nonaacetate:
(R_1= Glc-Ac ; R_3 = Rha-Ac, R_2 = R_5 = Ac, R_4 = H)
(6) petiolaroside: R_1= Glc ; R_3 = Rha, R_2 = R_5 = H, R_4 = OH
(6a) 2" acetylpetiolaroside: R_1= Glc 2"-Ac; R_3 = Rha, R_2 = R_5 = H, R_4 = OH
(6b) petiolaroside decaacetate: R_1= Glc-Ac; R_3 = Rha-Ac; R_2 = R_5 = Ac, R_4 = OAc
(7) quercetin 3-O-rhamnosylglucoside decaacetate:
(R_1= 6-RhaGlc-Ac; R_2= R_3= R_5 = Ac, R_4= OAc)
Glc = -β-glucopyranosyl.
Rha = -α -rhamnopyranosyl.
6-RhaGlc = α-rhamnopyranosyl-(1 → 6)- β-glucopyranoside

3. Experimental

3.1. General experimental procedures

M.p.s are uncorrected and were taken on a Reichert Thermovar apparatus. IR spectra were measured on a Bruker TFS-55 spectrometer. Optical rotations were determined using a PerkinElmer 2H polarimeter with a 1 dm cell. ^{1}H and ^{13}C NMR spectra were measured using a Bruker AMX-400 instrument. FAB MS and exact mass measurements were determined using a Micromass Autospec instrument at 70 eV. Column chromatograms used Sephadex LH-20 (Pharmacia ref. 17-0090-01), silica gel 60 (Merck 230–400 mesh), octadecyl-functionalized silica gel (Aldrich 377635-1006) and for analytical TLC, Merck Kieselgel 60 F_{254}. HPLC separations were performed on a JASCO Pu-980 series pumping system equipped with a JASCO UV-975 ultraviolet detector and with a Waters Kromasil Si 5 mm (10 mm × 250 mm) column. A Macherey–Nagel VP 250/10 nuclear Sphinx RP, 5 μm column was used for HPLC-RP chromatography. Chromatograms were visualized under UV light at 255 and 366 nm and/or sprayed with oleum followed by heating. All solvents were distilled before use; the purity of all compounds was 99.0% as judged by high-performance liquid chromatography.

3.2. Plant material

Aerial parts of *Delphinium staphisagria* L. were collected in May 2006 in the Teno area, Tenerife, at an altitude of 120 m and identified by Prof. Pedro Perez de Paz, Botany Department, Faculty of Pharmacy, University of La Laguna, where a voucher specimen (TFC 46-325) has been deposited.

3.3. Extraction and isolation of the flavonoids

Chopped whole fresh plant (8 kg) was repeatedly extracted with 80% ethanol (12 l) at room temperature for 2 weeks. The extract was filtered and concentrated under reduced pressure until only H_2O remained. The remaining solution was extracted exhaustively with *n*-BuOH. The latter on removal of solvent afforded 35 g of residue. This was fractionated on a 50 cm × 8 cm column packed with Sephadex LH-20 and eluted with hexane–CH_2Cl_2–MeOH, 2:1:1, twenty-five 500 ml fractions being collected. Frs DS_1–DS_{12} (13.8 g) contained mainly alkaloids and other components exhibiting no UV absorption while frs DS_{13}–DS_{25} (9.5 g) contained primarily a mixture of glycosides and were subjected to low pressure chromatography on a RP C-18 7 cm × 40 cm column using a linear gradient of 250 ml MeOH–H_2O mixtures ranging from 0 to 100% MeOH, 52 frs (DSA_1–DSA_{52}) being collected. Frs $DSA_{15–21}$ (284 mg) were chromatographed over a polyamide column (35 cm × 1 cm) and eluted with MeOH–EtOAc (3:2) to give in subfrs 14–20 after purification by crystallization from MeOH–EtOAc (2:1) 120 mg of paeonoside (**3**) identified by HRMS, ^{1}H and ^{13}C NMR spectrometry (Kamiya et al., 1997; Khetwal et al., 1988; Markham et al., 1978). Frs $DSA_{23–24}$ (288 mg) were subjected to gel filtration on Sephadex LH-20 using CH_2Cl_2–MeOH (1:1) as eluent, fifty 200 ml subfrs being collected. Subfrs 16–29 on crystallization from MeOH–EtOAc afforded 76 mg of 2″-acetylpaeonoside (**3a**). Subfrs 36–42 on crystallization from MeOH–EtOAc afforded 22 mg of **4**; the material from the mother liquors on rechromatography over polyamide using EtOAc–MeOH 3:2 gave 29 mg of petiolaroside (**6**) identified by HRMS, ^{1}H and ^{13}C NMR spectrometry

(Akhov and Barl, 2003; Aly et al., 1975; Kerhoas et al., 2006; Shi et al., 1995). Frs $DSA_{25–27}$ after cc over polyamide using MeOH–EtOAc (1:1) gave 150 mg of 2″-acetylpaeonoside (**3a**). Chromatography of frs $DSA_{28–30}$ over a 35 cm × 1 cm polyamide column and elution with EtOAc–MeOH (3:2) afforded 24 mg of impure isoquercitrin (**2**) in subfrs 20–26 and in subfrs 6–12 18 mg of **5** after purification by RP HPLC chromatography (T_R 10.5 mm, H_2O–MeOH–CH_3CN 3:1:1). The latter was identified by HRMS, ^1H and ^{13}C NMR spectrometry and comparison with the literature (Özden et al., 1998). Acetylation of 18 mg of impure **2** in 0.5 ml of pyridine with 1 ml of Ac_2O overnight followed by the usual work-up and HPLC (hexane–EtOAc 2:3, flow rate 2 ml min^{-1}) furnished 8 mg of isoquercitrin octaacetate (**2a**), T_R 21 min, and 3 mg of rutin decaacetate (**7**), both identified by MS, ^1H and ^{13}C NMR spectrometry (Demetzos et al., 1989; Jayasinghe et al., 2004).

Frs $DSA_{35–37}$ on chromatography over a polyamide column (35 cm × 1 cm) and elution with EtOAc–MeOH (3:2) gave in subfrs 6–14 2″-acetylpetiolaroside (**6a**, 45 mg) and in subfrs 23–29 38 mg of astragalin (**1**), the latter being identified by HRMS, ^1H and ^{13}C NMR spectrometry (Kamiya et al., 1997; Lee et al., 1981; Markham et al., 1978). Frs $DSA_{45–48}$ on recrystallization from H_2O–MeOH (3:1) furnished 85 mg of 2″-acetylastragalin (**1a**)

3.3.1. Kaempferol 3-O-β-(2″-acetyl)-glucopyranoside (2″-acetylastragalin) (1a)

Yellow powder, mp 152–153 °C (H_2O–MeOH 3:1), $[\alpha_D{}^{20}]$ −76.2 (MeOH, $c = 0.04$), IR γ_{max}^{NaCl} 3395 (OH), 1735, 1653, 1605, 1506, 1361, 1255, 1179, 1074, 670 cm^{-1}, UV λ_{max} (MeOH) nm (log ε) 266 (4.0), 348 (3.9), FAB MS *m/z*: 513 (78) $[M+Na]^+$, 471 (6) $[M+Na-C_2H_2O]^+$, 439 (5), 406 (7), 366 (11), HR FAB MS *m/z* 513.0997 (calcd for $C_{23}H_{22}O_{12}Na$ 513.1009), 471.0890 (calcd for $C_{21}H_{20}O_{11}Na$, 471.0903); ^1H NMR (400 MHz, pyridine-d_5) δ 6.72 (brs, 2H, H-6, H-8), 7.26 (d, $J = 9$ Hz, 2H, H-3′,5′), 8.47d (d, $J = 9$ Hz, 2H, H-2′,6′), 6.48 (d, $J = 7.5$ Hz, 3-*O*-Glc-1), 5.89 (dd, $J = 9.5$, 7.5 Hz, 3-*O*-Glc-2), 4.43 (t, $J = 9.5$ Hz, 3-*O*-Glc-3), 4.24 (dd, $J = 10$, 9.5 Hz, 3-*O*-Glc-4), 4.06 (ddd, $J = 10$, 5, 2.2 Hz, 3-*O*-Glc-5), 4.38 (dd, $J = 11.8$, 2.2 Hz, 3-*O*-Glc-6a), 4.22 (dd, $J = 11.8$, 5 Hz, 3-*O*-Glc-6b), 2.17 (s, 3p, Ac–Me); ^{13}C NMR (100 MHz, pyridine-d_5) δ 157.6 (C-2), 134.9 (C-3), 178.9 (C-4), 163.4 (C-5), 100.3 (C-6), 166.4 (C-7), 95.1 (C-8), 157.9 (C-9), 105.2 (C-10), 122.4 (C-1′), 132.4 (C-2′), 116.7 (C-3′), 162.2 (C-4′), 116.7 (C-5′), 132.4 (C-6′), 101.2 (C-1-Glc), 76.3 (C-2-Glc), 76.5 (C-3-Glc), 72.1 (C-4-Glc), 79.6 (C-5-Glc), 62.8 (C-6-Glc) 171.0, 21.8 (Ac).

Acetylation of **1a** (16 mg) with 1.5 ml of Ac_2O and 1 ml of pyridine, stirring at r.t. overnight and work-up by pouring into cold H_2O, extraction with $CHCl_3$, drying ($MeSO_4$) and removal at solvent afforded 14 mg of crude product. Chromatography on silica coated preparative plates (hexane–EtOAc 1:1, twice) resulted in two bands the upper one of which yielded **1b** (4 mg), a new flavonol derivative. The lower zone was extracted with EtOAc to give after HPLC rechromatography (hexane–EtOAc 1:1, flow rate 1.9 ml mm^{-1}), 3.6 mg of **1c**, another new flavonol derivative, T_R 20.5 min, and 8 mg of known **1d**, T_R 26 min), the latter being identified by HR FAB MS, ^1H and ^{13}C NMR spectrometry (Lee et al., 1981; Matsuura and Iinuma, 1978).

3.3.2. Kaempferol 3-O-β-(glucopyranoside)-7,4′,2″,3″,4″,6″-hexaacetate (1b)

Yellow gum, $[\alpha_D{}^{20}]$ −84.8° ($CHCl_3$, $c = 0.066$); IR γ_{max}^{NaCl} 2922, 1754 (strong), 1653, 1609, 1370, 1212 (strong), 1068, 1039, 908, 756 cm^{-1}, UV λ_{max} ($CHCl_3$) nm (log ε) 269 (3.84), 354 (3.56); FAB MS *m/z* 723 (39) $[M+Na]^+$, 685 (10) $[M-CH_3]^+$, 683 (7), $[M+H-H_2O]^+$, 663 (19), 521 (16), 369 (17), 331 (37) HR FAB MS *m/z* 723.1547 (calcd for $C_{33}H_{32}O_{17}Na$ 723.1537), 693.1420 (calcd for $C_{32}H_{30}O_{16}Na$, 693.1432), 685.1405 (calcd for $C_{32}H_{29}O_{17}$, 685.1405), 683.1644 (calcd for $C_{33}H_{31}O_{16}$, 683.1612); ^1H NMR (400 MHz, C_6D_6 at 65 °C) δ 6.71 (d, $J = 1.8$ Hz, H-6), 6.73 (d, $J = 1.8$ Hz, H-8), 7.26 (d, $J = 8.9$ Hz, H-3′,5′), 8.12 (d, $J = 8.9$ Hz, H-2′,6′), 5.88 (brd, $J = 6.75$ Hz, 3-*O*-Glc-1), 5.57 (brdd, $J = 9.4$, 6.7 Hz, 3-*O*-Glc-2), 5.56 (brt, $J = 9.4$ Hz, 3-*O*-Glc-3), 5.25 (brt, $J = 9.4$ Hz, 3-*O*-Glc-4), 3.36 (*m*, 3-*O*-Glc-5), 4.07 (dd, $J = 12.5$, 2.3 Hz), and 3.92 dd (12.5, 2.3 Hz, 3-*O*-Glc-6a,b), 2.00 (s, 3p), 1.88 (s, 3p), 1.84 (s, 3p), 1.83 (s, 3p), 1.76 (s, 3p), 1.75 (s, 3p)-Ac–Mes); ^{13}C NMR (100 MHz, pyridine-d_5) δ 157.6 (C-2), 135.5 (C-3), 178.5 (C-4), 156.3 (C-5), 101.5 (C-6), 156.9 (C-7), 105.5 (C-8), 162.8 (C-9), 109.8 (C-10), 128.7 (C-1′), 131.3 (C-2′), 122.2 (C-3′), 153.8 (C-4′), 122.2 (C-5′), 131.3 (C-6′), 100.1 (C-1-Glc), 72.5 (C-2″-Glc), 73.5 (C-3″-Glc), 68.8 (C-4″-Glc), 72.8 (C-5″-Glc), 61.4 (C-6″-Glc); acetates 20.88, 20.82, 20.77, 20.54, 20.47, 20.43, 20, 170.1, 170.08, 169.8, 169.4, 168.2, 167.8.

3.3.3. Kaempferol 3-O-β (glucopyranoside)-5,4′,2″,3″,4″,6″-hexaacetate (1c)

Colorless gum, $[\alpha_D{}^{20}]$ −33.3° ($CHCl_3$, $c = 0.07$); IR γ_{max}^{NaCl} 2918, 1753 (strong), 1631, 1369, 1211, 1070, 1038 cm^{-1}, UV λ_{max} ($CHCl_3$) nm (log ε) 254 (3.97), 307 (3.98); FAB MS *m/z* 723 (15) $[M+Na]^+$, 708 (1) $[M+Na-CH_3]^+$, 682 (1), $[M+Na+H-CH_2H_2O]^+$, 663 (15), 552 (17), 519 (27), 331 (37) HR FAB MS *m/z* 723.1543 (calcd for $C_{33}H_{32}O_{17}Na$ 723.1537), 708.1287 (calcd for $C_{32}H_{29}O_{17}Na$, 708.1302), 682.1476 (calcd for $C_{31}H_{31}O_{16}Na$, 682.1510); ^1H NMR (400 MHz, C_6D_6) δ 6.37 (d, $J = 2.1$ Hz, H-6), 6.48 (d, $J = 2.1$ Hz, H-8), 8.17 (d, $J = 8.9$ Hz, H-2′), 7.24 (d, $J = 8.9$ Hz, H-3′, 5′), 8.17 (d, $J = 8.9$ Hz, H-6′), 6.07 (d, $J = 7.8$, 3-*O*-Glc-1), 5.68 (dd, $J = 9.6$, 7.8 Hz, 3-*O*-Glc-2), 5.58 (t, $J = 9.6$ Hz, 3-*O*-Glc-3), 5.34 (dd, $J = 10$, 9.6 Hz, 3-*O*-Glc-4), 3.08 (ddd, $J = 10$, 3.5, 2.3 Hz, 3-*O*-Glc-5), 4.03 (dd, $J = 12.5$, 2.3 Hz, 3-*O*-Glc-6a), 3.92 (dd, $J = 12.5$, 2.3 Hz, 3-*O*-Glc-6b), 2.39 (s, 3p), 2.00 (s, 3p), 1.82 (s, 3p) 1.80 (s, 3p), 1.76 (s, 3p) 1.72 (s, 3p)-Ac–Mes); ^{13}C NMR (100 MHz, C_6D_6) 155.3 (C-2), 136.8 (C-3), 172.8 (C-4), 158.3 (C-5), 101.6 (C-6), 161.2 (C-7), 109.3 (C-8), 151.8 (C-9), 112.1 (C-10), 127.7 (C-1′), 131.0 (C-2′), 121.9 (C-3′), 153.4 (C-4′), 121.9 (C-5′), 131.0 (C-6′), 99.6 (1″-Glc), 72.7 (2″-Glc), 73.6 (3″-Glc), 68.7 (4″-Glc), 72.5 (5″-Glc), 61.2 (6″-Glc); acetates δ 21.5, 20.09, 20.87, 20.84, 20.55, 20.45, 170.4, 170.1, 170.0, 169.7, 169.4, 168.5.

*3.3.4. Kaempferol 3-O-β-(2″-acetylglucopyranoside)-7-O-β-glucopyranoside (2″-acetylpaeonoside) (**3a**)*

Yellow powder, mp 198–200 °C (MeOH–EtOAc), $[\alpha_D^{20}]$ −99.5° (MeOH, *c* = 0.18); IR γ_{max}^{NaCl} 3354, 1727, 1657, 1598, 1488, 1207, 1179, 1070, cm^{-1}, UV λ_{max} (MeOH) nm (log ε) 266 (3.9), 348 (3.9). FAB MS *m/z* 675 (24) $[M+Na]^+$, 642 (11), 637 (16) $[M-CH_3O]^+$, 505 (11), 449 (10); HR FAB MS *m/z* 675.1531 (calcd for $C_{29}H_{32}O_{17}Na$ 675.1537); ^1H NMR (pyridine-d_5) δ 6.80 (d, *J* = 2.5 Hz, H-6), 7.00 (d, *J* = 2.5 Hz, H-8), 7.25 (d, *J* = 9 Hz, H-3′,5′), 8.44 (d, *J* = 9 Hz, H-2′,6′) 6.47 (d, *J* = 8.2 Hz, 3-*O*-Glc-1), 5.88 (dd, *J* = 9.5, 8.2 Hz, 3-*O*-Glc-2), 4.43 (t, *J* = 9.5 Hz, 3-*O*-Glc-3), 4.22 (t, *J* = 9.5 Hz, 3-*O*-Glc-4), 4.06 (ddd, *J* = 9.5, 5.5, 2.2 Hz, 3-*O*-Glc-5), 4.41 m and 4.20 m (3-*O*-Glc-6a,b), 5.84 (d, *J* = 7.5 Hz, 7-*O*-Glc-1), 4.37 (m, 7-*O*-Glc-2), 4.43 (m, 7-*O*-Glc-3) 4.36 (m, 7-*O*-Glc-4), 4.21 (m, 7-*O*-Glc-5), 4.61 (dd, *J* = 12, 2 Hz, 7-*O*-Glc-6a), 4.42 (m, 7-*O*-Glc-6b), 2.16 (s, 3p, Ac–Me); ^{13}C NMR (100 MHz, pyridine-d_5) δ 158.1 (C-2), 135.1 (C-3), 179.0 (C-4), 162.7 (C-5), 100.9 (C-6), 164.4 (C-7), 95.5 (C-8), 157.3 (C-9), 107.3 (C-10), 122.1 (C-1′), 132.4 (C-2′,6′), 116.7 (C-3′,5′), 162.7 (C-4′), 101.0 (3-Glc, C-1′), 72.3 (3-Glc, C-2′), 76.4 (3-Glc, C-3′), 72.1 (3-Glc, C-4′), 79.8 (3-Glc, C-5′) 63.0 (3-Glc, C-6′), 102.2 (7-Glc, C-1″) 75.3 (7-Glc, C-2″), 78.9 (7-Glc, C-3″), 71.5 (7-Glc, C-4″), 79.7 (7-Glc, C-5″), 62.8 (7-Glc, C-6″), 171.1, 21.9 (Ac). Peracetylation of **3a** furnished the known paeonoside decaacetate **3b** (Nikolov et al., 1986; Akhov and Barl, 2003).

*3.3.5. Quercetin 3-O-β-(2″-acetylglucopyranoside)-7-O-β-glucopyranoside (**4**)*

Yellow powder, mp 168–170 °C (MeOH–EtOAc), $[\alpha_D^{20}]$ −96° (MeOH, *c* = 0.1); IR γ_{max}^{NaCl} 3360 (OH), 1734, 1652, 1600, 1558, 1204, 1070, cm^{-1}, UV λ_{max} (MeOH) nm (log ε) 259 (3.95), 356 (3.96). FAB MS *m/z* 691 (45) $[M+Na]^+$, 669 (20), 649 (20) $[M+C_2H_2O]^+$, 346 (65), 313 (100); HR FAB MS *m/z* 691.1459 (calcd for $C_{29}H_{32}O_{18}Na$ 691.1486), 669.1671 (calcd for $C_{29}H_{33}O_{18}$, 669.1667), 668.1588 (calcd for $C_{29}H_{32}O_{18}$, 668.1589). ^1H NMR (pyridine-d_5) δ 6.79 (d, *J* = 2 Hz, H-6), 6.89 (d, *J* = 2 Hz, H-8), 8.33 (d, *J* = 2.2 Hz, H-2′), 7.34 (d, *J* = 8.5 Hz, H-5′) 8.13 (dd, *J* = 8.5, 2.2 Hz, H-6′), 6.36 (d, *J* = 8. Hz, 3-*O*-Glc-1), 5.85 (dd, *J* = 9.5, 3-*O*-Glc-2), 4.41(t, *J* = 9.5 Hz, 3-*O*-Glc-3), 4.15 (dd, *J* = 10, 9.5 Hz, 3-*O*-Glc-4), 4.06 (ddd, *J* = 10, 5.5, 2.2 Hz, 3-*O*-Glc-5), 4.41 (dd, *J* = 12, 2.2 Hz, 3-*O*-Glc-6a), 4.21 (dd, *J* = 12, 5.5 Hz, 3-*O*-Glc-6b), 5.80 (d, *J* = 7.5 Hz, 7-*O*-Glc-1), 4.35 (m, 7-*O*-Glc-2), 4.43 (m, 7-*O*-Glc-3), 4.36 (m, 7-*O*-Glc-4), 4.21 (m, 7-*O*-Glc-5), 4.58 (dd, *J* = 4.5, 2.5 Hz, 7-*O*-Glc-6a), 4.48 (m, 7-*O*-Glc-6b), 2.15 (s, 3p, Ac); ^{13}C NMR (100 MHz, pyridine-d_6) δ 158.4 (C-2), 135.4 (C-3), 178.9 (C-4), 162.7 (C-5), 100.7 (C-6), 164.3 (C-7), 95.4 (C-8), 157.2 (C-9), 107.3 (C-10), 122.6 (C-1′), 118.1 (C-2′), 147.3 (C-3′), 151.4 (C-4′), 116.8 (C-5′), 123.4 (C-6′), 101.4 (3-Glc, C-1′), 76.2 (3-Glc, C-2′), 78.9 (3-Glc, C-3′), 72.0 (3-Glc, C-4′), 79.6 (3-Glc, C-5′), 62.8 (3-Glc, C-6′), 102.1 (7-Glc, C-1″), 75.2 (7-Glc, C-2″), 76.4 (7-Glc, C-3″), 71.5 (7-Glc, C-4″), 79.7 (7-Glc, C-5″), 62.8 (7-Glc, C-6″), 170.9, 21.7 (Ac). Peracetylation of monoacetate **4** furnished the known quercetin 3,7-diglycoside undecaacetate **4a** (Kato et al., 1990).

*3.3.6. Quercetin-3-O-β-(2″-acetylglucopyranoside)-7-O-α-rhamnopyranoside (2″-acetyl-petiolaroside) (**6a**)*

Yellow powder, mp 250–252 °C (MeOH–EtOAc), $[\alpha_D^{20}]$ −113.6° (MeOH, *c* = 0.04); IR γ_{max}^{NaCl} 3410 (OH), 1724, 1657, 1595, 1481, 1300, 1206, 1075 cm, UV λ_{max} (MeOH) nm (log ε) 257 (4.11), 356 (4.0). FAB MS *m/z* 675 (45) $[M+Na]^+$, 652 (6) $[M]^+$, 638 (32), 582 (26), 446 (46), 346 (72) HR FAB MS *m/z* 675.1550 (calcd for $C_{29}H_{32}O_{17}Na$ 675.1537) $[M+Na]^+$, 652.1647 (calcd for $C_{29}H_{32}O_{17}$, 652.1640) $[M]^+$. ^1H NMR (400 MHz, pyridine-d_5) δ 6.74 (d, *J* = 2 Hz, H-6), 6.80 (d, *J* = 2Hz, H-8) 8.28 (d, *J* = 2.2 Hz, H-2′), 7.40 (d, *J* = 8.5 Hz, H-5′), 8.22 (dd, *J* = 8.5, 2 Hz, H-6′), 6.39 (d, *J* = 8 Hz, 3-Glc-1), 5.87 (dd, *J* = 9.3, 8 Hz, 3-Glc-2), 4.41 (t, *J* = 9.3 Hz, 3-Glc-3) 4.19 (t, *J* = 9.3 Hz, 3-Glc-4), 4.07 (ddd, *J* = 9.3, 5.3, 2.3 Hz, 3-Glc-5), 4.40 (dd, *J* = 12.2, 2.3 Hz, 3-Glc-6a), 4.23 (dd, *J* = 12.2, 5.3 Hz, 3-Glc-6b), 6.21 (brs, 7-Rha-1), 4.72 (brs, 7-Rha-2), 4.67 (brd, *J* = 9.3 Hz, 7-Rha-3), 4.41 (t, *J* = 9.2, 7-Rha-4), 4.27 (dq, *J* = 9.2, 6 Hz, 7-Rha-5), 1.66 (d, 6, 3p, 7-Rha-6), 2.16 (s, 3p, Ac–Me), ^{13}C NMR (100 MHz, pyridine-d_5) δ 158.3 (C-2), 135.5 (C-3), 179.0 (C-4), 162.8 (C-5), 100.8 (C-6), 163.15 (C-7), 95.1 (C-8), 157.3 (C-9), 107.3 (C-10), 122.5 (C-1′), 117.9 (C-2′), 147.5 (C-3′), 151.6 (C-4′), 116.9 (C-5′), 123.7 (C-6′), 101.5 (3-Glc, C-1′), 76.2 (3-Glc, C-2′), 76.5 (3-Glc, C-3′), 72.0 (3-Glc, C-4′), 79.6 (3-Glc, C-5′), 62.9 (3-Glc, C-6′), 100.4 (7-Rha, C-1), 72.1 (7-Rha, C-2), 72.9 (7-Rha, C-3), 74.1 (7-Rha, C-4), 71.9 (7-Rha, C-5), 19.3 (7-Rha, C-6), 21.7, 171.10 (Ac). Peracetylation of **6a** afforded the known petiolaroside decaacetate **6b** (Díaz et al., 2005).

References

Akhov, L., Barl, B., 2003. Isolation of quercetin glycosides from leaves of sea buckthorn (*Hippophae rhamnoides* ssp *mongolica*). Acta Horti. 626, 384–395.

Aly, H.F., Geiger, H., Schuecker, U., Waldrum, H., Vander Velde, G., Mabry, T.J., 1975. Flavonol glycosides from *Equisetum silvaticum*. Phytochemistry 14, 1613–1615.

Arazashvili, A.I., Moniava, I.T., Kemertelidze, E.P., 1973. Flavonoids of *Delphinium flexuosum* and *Delphinium elisabethae*. Khim. Prir. Soedin. 9, 556–557.

Arazashvili, A.I., Moniava, I.T., Kemertelidze, E.P., 1974. Flavonoids from some species of *Delphinium*. Khim. Prir. Soedin. 10, 251.

Demetzos, C., Mitaku, S., Hotellier, F., Harvala, A., 1989. Polyphenolic glycosides from *Cistus creticus* leaves. Ann. Pharm. France 47, 314–318 Chem. Abstr. 113, 37728 (1990).

Díaz, J.G., Ruiz, J.G., De La Fuente, G., 2000. Alkaloids from *Delphinium staphisagria* J. Nat. Prod. 63, 1136–1139.

Díaz, J.G., Ruiz, J.G., Días, B.R., Sazatornil, J.A.G., Herz, W., 2005. Flavonol 3,7-glycosides and dihydrophenethyl glycosides from *Aconitum napellus* ssp. *lusitanicum*. Biochem. Syst. Ecol. 33, 201–205.

Jayasinghe, U.L.B., Balasooriya, B.A.I.S., Bandara, A.G.D., Fujimoto, Y., 2004. Glycosides from *Grewia damine* and *Filicium decipiens*. Nat. Prod. Res. 18, 499–502 Chem. Abst. 142, 352103 (2005).

Kamiya, K., Yoshioka, K., Saiki, Y., Ikuta, A., Satake, T., 1997. Triterpenoids and flavonoids from *Paeonia lactiflora*. Phytochemistry 44, 141–144.

Kato, T., Yamane, F., Morita, Y., 1990. Flavonol glycosides and other constituents from the leaves of *Ampelopsis brevipedunculata* Trutv. Shoyakugaku Zasshi. 44, 138–142 Chem. Abstr. 114:58890 (1991).

Kerhoas, L., Aouak, D., Cingoz, A., Routaboul, J.-M., Lepiniac, L., Einhorn, J., Birlirakis, N., 2006. Structural characterization of the major flavone glycosides from *Arabidopsis thaliana* seeds. J. Agric. Food Chem. 54, 6603–6612.

Khetwal, K.S., Manral, K., Verma, D.L., 1988. Flavonoids from the roots of *Sedum cressipes*. Planta Med. 54, 89–90.

Lee, K.H., Tagahara, K., Suzuki, H., Wu, R.Y., Haruna, M., Hall, I.H., Huang, H.C., Ito, K., Iida, T., Lai, J.S., 1981. Antitumor agents 49. Tricin, kaempferol 3-*O*-β-D-glucopyranoside and (+)-nortrachelogenin, antileukemic principles from *Wikstroemia indica*. J. Nat. Prod. 44, 530–535.

Lomadze, I.A., Dzhagamadze, N.N., Moniava, I.I., Bostoganashvili, V.S., 1976. Quantitative determination of some flavonoids in plants. Soobshcheniya Akad. Nauk. Gruzinskoi SSR 84, 369–371 Chem. Abstr. 86, 86154 (1977).

Markham, K.R., Ternai, B., Stanley, R., Geiger, H., Mabry, T.J., 1978. Carbon-13 NMR studies of flavonoids. III. Naturally occurring flavonoid glycosides and their acylated derivatives. Tetrahedron 34, 1389–1397.

Matsuura, S., Iinuma, M., 1978. Studies on the constituents of useful plants VI. Constituents of the calyx of *Diospyros kaki* and carbon-13 nuclear magnetic resonance spectra of flavonol glycosides. Chem. Pharm. Bull. 26, 1936–1941.

Nikolov, N., Seligmann, O., Wagner, H., 1986. New flavonol glycosides from *Mespilus germanica* L. In: Studies in Organic Chemistry, Amsterdam, pp. 251–260.

Özden, S., Dürüst, N., Toki, K., Saito, N., Honda, T., 1998. Acylated kaempferol glycosides from flowers of *Delphinium formosum*. Phytochemistry 49, 241–245.

Shi, Q., Chen, K., Li, L., Chang, J.J., Autry, C., Kuzuka, M., Konoshima, T., Estes, J.R., Lin, C.M., Hamil, E., McPhail, A.T., McPhail, D.M., Lee, K.-H., 1995. Antitumor agents 154. Cytotoxic and antimitotic flavonols from *Polanisia dodecandra*. J. Nat. Prod. 58, 475–482.

Strzelecka, H., Dobrowolska, B., 1976. Flavonoid compounds in *Delphinium grandiflorum*. Acta Pol. Pharm. 33, 135 Chem. Abstr. 85, 189225 (1976).

Warnock, M.J., Liu, Y.-L., Mabry, T.J., 1983. Acylated flavonols from *Delphinium carolinianus*. Phytochemistry 22, 1834–1835.

Yoshimitsu, H., Nishida, M., Hashimoto, F., Tanaka, M., Sakata, Y., Okawa, M., Nohara, T., 2007. Chromone and flavonol glycosides for *Delphinium hybridum* cv. ''Belladonna Casablanca'' J. Nat. Med. 61, 334–338.

Yunusova, M.S., Nigmanova, A., 1976. Flavonoids of *Delphinium semibarbatum* growing in Uzbekistan. Vapr. Farmacol. Farmatsii 75–76 Chem. Abstr. 88, 86056 (1978).