PERGAMON

Phytochemistry 50 (1999) 1219–1223

PHYTOCHEMISTRY

Norterpenoid and sesquiterpenoid glucosides from *Juniperus phœnicea* and *Galega officinalis*

Yves Champavier[a], Gilles Comte[a,1], Joseph Vercauteren[b], Daovy P. Allais[a], Albert J. Chulia[a,*]

[a]*Biomolecules, Laboratoire de Pharmacognosie et de Phytochimie, UFR de Pharmacie, Université de Limoges, 2 rue Docteur Marcland, F-87025 Limoges Cedex, France*

[b]*Laboratoire de Pharmacognosie, UFR des Sciences Pharmaceutiques, Université de Bordeaux II, Bat. 3A (zone Nord), 146 rue Léo Saignat, F-33076 Bordeaux cedex, France*

Received in revised form 20 October 1998

Abstract

Four norterpenoid glucosides have been characterized along with a sesquiterpenoid glucoside from the aerial parts of *Juniperus phœnicea* and *Galega officinalis*. Among these five compounds, two norterpenoids which are 3-oxo-α-ionol glucosides named junipeionoloside and 6-hydroxy-junipeionoloside are new natural products. These new norterpenoids were isolated from *Juniperus phœnicea* together with an other known norterpenoid glucoside: roseoside and a sesquiterpenoid glucoside: dihydrophaseic acid 4′-*O*-β-D-glucopyranoside. We also have identified from *Galega officinalis* a rare norterpenoid glucoside: dearabinosyl pneumonanthoside.

Keywords: *Juniperus phœnicea*; Cupressaceae; *Galega officinalis*; Fabaceae; Norterpenoid glucoside; Sesquiterpenoid glucoside; 3-oxo-α-ionol glucoside; Junipeionoloside; 6-hydroxy-junipeionoloside; Roseoside; Dearabinosyl pneumonanthoside; Dihydrophaseic acid 4′-*O*-β-D-glucopyranoside

1. Introduction

In an effort to identify cytotoxic natural compounds in medicinal plants, we have for the first time purified and characterized in the leaves of *Juniperus phœnicea* the active principle sandaracopimaric acid, a cytotoxic and antilipoxygenasic diterpene acid (Comte et al., 1995). We also have reported the presence of seven phenylpropane glucosides in this plant: juniperoside, rosarin, skimmin, junipediol A 8-glucoside, junipediol B 8-glucoside, junipetrioloside A and junipetrioloside B (Comte, Chulia, Vercauteren, & Allais, 1996; Comte, Allais, Chulia, Vercauteren, & Pinaud, 1997; Comte, Vercauteren, Chulia, Allais, & Delage, 1997) and two furanone glucoside derivatives, psydrin and phœnicein (Comte, Allais, Chulia, Vercauteren, & Delage, 1996). More recently, we have demonstrated the presence of phœniceroside, a pseudo-dimer of the two previously cited furanones (Comte, Allais, Chulia, Vercauteren, & Bosso, 1996). In this paper, we report the isolation and the structural elucidation of two new 3-oxo-α-ionol glucosides: junipeionoloside (**2**) and 6-hydroxy-junipeionoloside (**3**), characterized along with: roseoside (**4**), dearabinosyl pneumonanthoside (**1**) and dihydrophaseic acid 4′-*O*-β-D-glucopyranoside (**5**). These compounds were isolated from a methanolic extract of *J. phœnicea*, except the rare ionol dearabinosyl pneumonanthoside which was purified from an ethyl acetate extract of an other toxic plant: *Galega officinalis*. Identification of these natural products was achieved by ^{1}H, ^{13}C, DEPT, *J* mod, COSY, HMQC and HMBC NMR experiments and by DCI and FAB mass spectral data.

2. Results and discussion

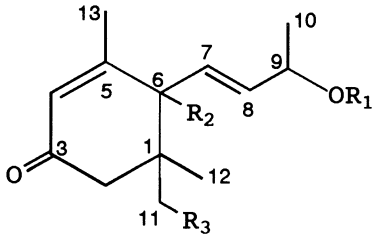
From an ethyl acetate extract of *G. officinalis*, we have first purified a norterpenoid glucoside (**1**), according to the procedures described in the experimental.

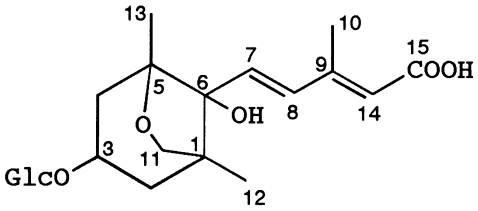
The ^{1}H NMR spectrum of compound **1** showed the presence of four methyls: two tertiary methyls (1.03 s, H_{11}; 1.00 s, H_{12}), a methyl attached to an olefinic carbon (1.93 s, H_{13}), a secondary methyl (1.29 d $J = 6.4$ Hz, H_{10});

[1] New address: Laboratoire de Biochimie, Végétale (Bat. 303), Université Claude Bernard Lyon I, 18 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France.

* Corresponding author. E-mail: jose.chulia@unilim.fr.

0031-9422/99/$ - see front matter
PII: S0031-9422(98)00697-9





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	R_1	R_2	R_3
1 :	Glc	H	H
2 :	H	H	OGlc
3 :	H	OH	OGlc
4 :	Glc	OH	H

Structure 1.

a methylene group attached to a carbonyl (2.04 d $J=16.8$ Hz, 2.42 d $J=16.8$ Hz, H_2); a methine group (2.67 d $J=9.1$ Hz, H_6); a secondary oxymethine group (4.40 m, H_9); three olefinic protons (5.88 s, H_4; 5.64 dd $J=15.5$ and 9.1 Hz, H_7; 5.77 dd $J=15.4$ and 6.4 Hz, H_8) and a β-D-glucopyranosyl moiety (Table 1). The ^{13}C NMR spectrum indicated the presence of 19 signals, 6 of which were assigned to a β-D-glucopyranosyl unit (Breitmaier & Voelter, 1989) and 13 to the aglycone moiety (Table 2). From ^{13}C and DEPT NMR experiments, these 13 signals were identified into three quaternary carbons: one aliphatic (37.3, C_1), one oxygenated (202.1, C_3) and one sp^2 (165.9, C_5); five tertiary carbons: (129.0, C_7; 138.4, C_8; 126.3, C_4; 77.1, C_9; 57.0, C_6); one secondary carbon (48.5, C_2) and four primary carbons (21.2, C_{10}; 27.7, C_{11}; 28.2, C_{12}; 23.9, C_{13}). Examination of the NMR data (Tables 1–2) and comparison with literature (Mpondo Mpondo, Garcia, Chulia, & Mariotte, 1989) allowed

Table 1
^1H NMR data for compounds **1**–**5** in CD_3OD/TMS 400 MHz[a] and CD_3OD 500 MHz[b]

H	**1**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[b]
2	2.04 d (16.8)	2.27 d (17.0)	2.37 d (17.3)	2.18 d (17.0)	1.98 m
	2.42 d (16.8)	2.47 d (17.0)	2.62 d (17.3)	2.60 d (17.0)	2.19 m
3					4.25 m
4	5.88 s	5.89 dq (1.3)	5.89 se	5.87 s	1.80 m
					1.98 m
6	2.67 d (9.1)	ca. 3.20[c] m			
7	5.64 dd (15.5; 9.1)	5.56 ddd (15.4; 9.6; 1.3)	5.74 d (15.5)	5.97 d (15.6)	6.49 d (15.9)
8	5.77 dd (15.5; 6.4)	5.79 ddd (15.4; 6.0; 0.6)	5.82 dd (15.5; 5.6)	5.73 dd (15.6; 7.2)	7.96 d (15.9)
9	4.40 m	4.29 dq (6.2; 1.3)	4.32 dq (6.4; 5.6)	4.53 m	
10	1.29 d (6.4)	1.25 d (6.5)	1.23 d (6.4)	1.29 d (6.6)	2.07 s
11	1.03[d] s	3.32 d (9.6)	3.58 d (9.9)	1.04[d]s	3.75 d (7.4)
		3.69 d (9.6)	3.95 d (9.9)		3.80 dd (7.4; 2.1)
12	1.00[d] s	0.97 s	1.05 s	1.02[d] s	0.94 s
13	1.93 s	1.95 q (0.6)	1.91 d (1.0)	1.94 s	1.17 s
14					5.78 se
1′	4.35 d (7.8)	4.17 d (7.7)	4.13 d (7.8)	4.28 d (7.8)	4.36 d (7.8)
2′	3.17 m	3.18 dd (9.1; 7.7)	3.13 t (8.3)	3.19 dd (8.8; 7.8)	3.14 dd (9.1; 7.8)
3′	ca. 3.32 m	3.33 t (8.9)	3.30 m	ca. 3.35 m	ca. 3.30[d] m
4′	ca. 3.27 m	3.28 t (9.1)	3.25 t (9.0)	ca. 3.26 m	ca. 3.30[d] m
5′	3.21 m	3.21 m	3.20 m	ca. 3.14 m	3.28 m
6′	3.66 dd (11.8; 5.4)	3.65 dd (11.9; 5.6)	3.64 dd (11.9; 5.5)	3.63 dd (11.9; 6.2)	3.67 dd (11.9; 5.5)
	3.82 dd (11.8; 2.4)	3.84 dd (11.9; 2.3)	3.83 dd (11.9; 2.3)	3.85 dd (11.9; 2.2)	3.87 dd (11.9; 1.5)

[c] Assignments were based on HMQC and HMBC experiments.
[d] Assignments may be reversed.

Table 2
^{13}C NMR data for compounds **1**–**5** in CD_3OD/TMS 100 MHz[a] and CD_3OD 125 MHz[b]

C	1[a]	2[b]	3[b]	4[b]	5[b]
1	37.3	41.8	46.3	42.4	49.9
2	48.5	45.3	45.5	50.8	42.8
3	202.1	201.8	202.1	201.2	73.9
4	126.3	126.3	128.5	127.1	42.9
5	165.9	166.1	168.2	167.1	87.6
6	57.0	50.6	79.4	80.0	83.2
7	129.0	126.4	130.6	133.8	134.6
8	138.4	141.2	138.0	133.7	132.0
9	77.1	68.8	68.7	75.0	150.4
10	21.2	23.8	23.8	22.2	21.2
11	27.7[c]	76.1	74.6	23.5[c]	77.2
12	28.2[c]	21.3	20.1	24.7[c]	16.3
13	23.9	23.8	19.5	19.5	19.7
14					ca. 120.5[d]
15					n.d.
1′	102.6	104.8	104.6	101.3	103.1
2′	75.4	75.1	75.1	74.7	75.1
3′	78.3	78.2	78.1	78.4	78.1
4′	71.7	71.7	71.5	71.7	71.7
5′	78.1	77.9	78.0	78.2	78.0
6′	62.9	62.8	62.7	62.9	62.8

[c] Assignments may be reversed.
[d] Assignments were based on HMQC and HMBC experiments.

identification of the compound **1** as dearabinosyl pneumonanthoside. This compound **1** has been described for the first time from *Gentiana pneumonanthe* (Gentianaceae) and among *Rubus idaeus* (Rosaceae), *Salvia nemorosa* (Labiatae) (Pabst, Barron, Sémon, & Schreier, 1992; Takeda et al., 1997), but not previously in the genus *Galega*.

The MeOH extract of leaves of *J. phœnicea* was solubilized in water and then extracted by EtOAc and *n*-BuOH. The aqueous residual phase was fractionated according to the procedures described in the experimental, yielding three norterpenoids and one sesquiterpenoid.

The molecular formula $C_{19}H_{30}O_8$ of compound **2** was deduced from FAB and DCI mass spectrometry which showed quasimolecular ion peaks at m/z 387 $[M+H]^+$ and 385 $[M-H]^-$. The ^1H and ^{13}C NMR data for compound **2** were very similar to those of **1** (Tables 1–2) and showed the presence of a glucosyl moiety in the β-pyranose form. The glucosyl unit of **2** was also identified after acid hydrolysis (Hansen, 1975) and confirmed by the respective ions in the DCI mass spectra at m/z 225 $[M-Glc+H]^+$, 207 $[M-OGlc+H]^+$. The main difference between the compound **1** and **2** was based on the site of glucosylation. Indeed, the NMR data showed the absence of the signals corresponding to a methyl group (δ_H 1.03 s, H_{11} and δ_c 27.7 C_{11}) and the appearance of signals for a further methyleneoxy function (δ_H 3.32 d $J=9.6$ Hz, δ_H 3.69 d $J=9.6$ Hz, H_{11} and δ_c 76.1, C_{11}) (Tables 1–2). This observation was confirmed by HMBC experiment with correlations H_{11}/C_{12}, H_{11}/C_2, H_{11}/C_1, $H_{11}/C_{1'}$, H_{11}/C_6, H_{12}/C_{11} and H_2/C_{11}. The linkage between the sugar residue and the aglycone part was deduced from HMBC experiment on the basis of ^3J correlations between the anomeric osidic proton (δ_H 4.17, $H_{1'}$) and the methyleneoxy carbon (δ_c 76.1, C_{11}). Thus, **2** was identified as 3-oxo-α-ionol 11-*O*-β-D-glucopyranoside, a new natural product named junipeionoloside.

The M_r 402 and the molecular formula $C_{19}H_{30}O_9$ for **3** were deduced from FAB and DCI mass spectrometry which showed quasimolecular ion peaks at m/z 403 $[M+H]^+$, 401 $[M-H]^-$ and 420 $[M+NH_4]^+$, respectively. Moreover, the base peaks at m/z 241 $[M-Glc+H]^+$, 239 $[M-Glc-H]^-$, 223 $[M-OGlc+H]^+$ and 221 $[M-OGlc-H]^-$ were due to the aglycone unit. Both ^1H and ^{13}C NMR spectra of **3** showed some great similarities to those of junipeionoloside (**2**) (Tables 1–2). The most important difference was the appearance of a quaternary hydroxylated carbon for the position 6 (δ_c 79.4), instead of a methine signal (δ_H 3.20 m; δ_c 50.6) for the junipeinoloside. This observation was confirmed by the gain in 16 atomic mass units noted in the DCI mass spectra, by the absence of correlation with the H_7 in the COSY NMR experiment and by the absence of correlation with C_5, C_1, C_7, C_8 in the HMBC NMR experiment which were observed in the case of the junipeionoloside. The compound **3** was identified as 3-oxo-6-hydroxy-α-ionol 11-*O*-β-D-glucopyranoside, a new natural compound and named 6-hydroxy-junipeionoloside. Finally, from the same MeOH extract of *J. phœnicea*, we have characterized an other norterpenoid and a sesquiterpenoid glucoside which were identified to be 3-oxo-6-hydroxy-α-ionol 9-*O*-β-D-glucopyranoside or roseoside (**4**) and dihydrophaseic acid 4′-*O*-β-D-glucopyranoside (**5**) respectively by comparison of NMR with the structural data given in the literature (Bhakuni, Joshi, Uprety, & Kapil, 1974; Milborrow, & Vaughan, 1982; Cui, Nakamura, Kinjo, & Nohara, 1993; Otsuka, Yao, Kamada, & Takeda, 1995). These two compounds have been described for the first time in this plant.

In the past, a considerable number of norisoprenoid compounds such as 3-oxo-α-ionol 9-*O*-β-D-glucoside have been isolated and characterized from various plants. The aglycones of these compounds are important contributors to the flavour of plants and fruits, and several of them are highly esteemed in the perfume and flavour industry (Naves, 1971; Schreier, 1984; Williams, Sefton, & Marinos, 1993).

For the first time we describe in this article, ionols with a site of glucosylation at C_{11}. The biogenesis of such products has been attributed to the degradation of higher molecular weight terpenoids such as carotenoids; but in fact, sesquiterpenoids containing the ionone skeleton in their structure, e.g. dihydrophaseic acid 4′-*O*-β-D-gluco-

pyranoside can be considered as the biological source of ionols and ionones.

3. Experimental

3.1. Plant material

Leaves of *J. phœnicea* were collected near Roquemaure (Vaucluse, France). A voucher specimen (No. 103) has been deposited at our Laboratory of Pharmacognosy and Phytochemistry of the University of Limoges, France. *G. officinalis* has been harvested in flowering period times by a pharmaceutical Laboratory (Pharma et Plantes, Chanzeaux, France). This Laboratory has supplied the aerial part of *G. officinalis* in powder form with its control certificate.

3.2. General

TLC was carried out on pre-coated microcrystalline cellulose plastic sheets (Merck), polyamide 11-F254 aluminium sheets (Merck) and silica gel 60F-254 aluminium sheets (Merck), using vanilline sulphuric acid detection. For analytical HPLC a Waters model equipped with 501 and 510 model pumps and a variable wavelength photodiode array detector (Waters PDA 996) as well as a radial Novapak C18 cartridge (4 μm, 8 × 100 mm) was used. CC was achieved on polyamide SC-6 (Macherey–Nagel) and Sephadex LH20 (Pharmacia). Prep. HPLC was performed on a Merck model (Prep Septech) with Lichroprep DIOL (25–40 μm) and Lichroprep RP18 (15–25 μm) columns and semiprep. HPLC on a Waters Assoc. system with μBondapak C18 column (10 μm, 8 × 100 mm). Chromatographic mobilities were recorded in six systems: system 1 (Silica gel F-254, EtOAc–H_2O–HCO_2H–HOAc, 20:2:1:1), system 2 (cellulose F-254, *n*-BuOH–HOAc–H_2O, 4:1:5 (upper phase)), system 3 (polyamide, Toluene–MeOH, 4:1), system 4 (Waters radial μBondapak C18 (10 μm, 8 × 100 mm), H_2O–MeOH, 85:15, 1 ml·min^{-1}), system 5 and 6 (identical to system 4 but with respectively H_2O–MeOH, 80:20 and H_2O–MeOH, 75:25). Acid hydrolysis was made in 2N HCl under reflux. Glucose was identified by TLC on silica gel (EtOAc–H_2O–MeOH–HOAc 13:3:3:4) after pulverization of *p*-anisidine phthalate reagent (Hansen, 1975). UV spectra were recorded on a Jasco V-560 spectrophotometer. NMR spectra were measured at 400 or 500 MHz for ^1H and 100 or 125 MHz for ^{13}C on a Bruker apparatus and the solvent signal used as reference was CD_3OD (δ_H 3.32; δ_C 49.O ppm) or TMS. The complete proton and carbon assignments were based on 1-D (^1H standard, ^{13}C *J* mod and ^{13}C DEPT), 2-D (^1H–^1H COSY, ^1H–^{13}C HMQC and ^1H–^{13}C HMBC) NMR experiments. FAB and DCI-MS were recorded with a Nermag Sidar V 3.1, spectrometer (70 eV).

3.3. Extraction and isolation of compound *1*

Nine kg of powdered aerial part of *G. officinalis* were placed in a percolator and were successively extracted at room temperature with different solvents of increasing polarity: 57 l hexane (110 g), 200 l CH_2Cl_2 (120 g), 140 l EtOAc (52 g) and 100 l MeOH (500 g). The EtOAc extract was adsorbed to 100 g of polyamide MN SC-6 and chromatographied on a 700 × 90 mm polyamide column. For elution, a gradient of MeOH in toluene was applied. Fractions eluted with 10% of MeOH were joined (8 g) and submitted to a silica gel MPLC (460 × 26 mm with an increase of % MeOH in a mix of toluene–Et_2O–HOAc 50:50:1). Fractions eluted with 50% MeOH were kept for further investigations (910 mg). The third step of purification was carried out on a silica gel MPLC (460 × 15 mm with MeOH gradient in EtOAc to 1% of HOAc). Fractions corresponding to 5% MeOH (500 mg) were subjected to a MPLC (Merck Lichroprep DIOL column, 25–40 μm, 230 × 15 mm with a fine gradient of *iso*-PrOH in hexane). Fractions eluted with hexane–*iso*-PrOH (75:25) (82 mg) were finally purified on a semiprep. HPLC (μBondapak C18 10 μm, 25 × 100 mm, MeOH–H_2O–HOAc, 35:64:1, 5 ml·min^{-1}) yielding 13 mg pure **1**.

3.4. Extraction and isolation of compounds *2–5*

Air dried leaves of *J. phœnicea* (637 g) were successively extracted at room temperature with different solvents of increasing polarity: petrol (53.5 g), $CHCl_3$ (45 g), EtOAc (11 g), Me_2CO (52 g) and MeOH (130 g). The MeOH extract was suspended in 300 ml of water and then shared by three-fold 100 ml each of EtOAc and *n*-BuOH. After concn, residues were 10 g of the EtOAc part and 50 g in the *n*-BuOH part. The aq. residual phase (70 g) was then fractionated on a 900 × 90 mm column using Sephadex LH20 eluted with an aq. MeOH stepped gradient and on a prep. HPLC (Merck 200 × 40 mm Prep Septech column using Lichroprep 100 RP18 15–25 μm as stationary phase with an aq. MeOH stepped gradient). Six frs were obtained and only fr 4 (1.5 g) and fr 5 (1.5 g) were kept for further investigations. Fr 4 (1.5 g) was fractionated on a 570 × 25 mm column using Sephadex LH20 eluted with MeOH and by a MPLC (230 × 15 mm on a Merck Lichroprep 100 RP18 25–40 μm, 10% MeOH in H_2O) to give four frs (A, B, C, D). Compound **3** was present in the fr B and was purified by a MPLC (230 × 15 mm on a Merck Lichroprep 100 RP18 25–40 μm with 10% MeOH in H_2O) affording 25 mg pure **3**. Fr C was submitted to a MPLC (230 × 15 mm, Lichroprep 100 RP18 25–40 μm, 10% MeOH) and to a semiprep. HPLC (μBondapak C18 10 μm, 25 × 100 mm, MeOH–H_2O, 12:88) yielding 5 mg pure **5**. Fr 5 (1.5 g) was fractionated by a MPLC (Merck Lichroprep DIOL column, 15–25 μm, 460 × 15 mm, MeOH–H_2O, 20:80) to give five frs (I, II, III, IV, V). Compound **4** was present in the fr III and its final puri-

fication was carried out by a MPLC (230 × 15 mm on a Merck Lichroprep 100 RP18 25–40 μm, MeOH–H_2O, 20:80) and by a CC Sephadex LH20 (200 × 20 mm, MeOH), resulting in 17 mg of pure **4**. The purification of compound **2** present in the fr IV was performed by a MPLC (250 × 15 mm on a Merck Lichroprep 100 RP18 25–40 μm, MeOH–H_2O, 15:85), by a CC Sephadex LH20 (200 × 20 mm, MeOH) and by a semiprep. C18 HPLC (Novapak 4 μm, 8 × 100 mm, isocratic operation MeOH–H_2O, 17:83) yielding 8 mg of pure **2**.

3.5. Dearabinosyl pneumonanthoside (*1*)

UV λ_{max}^{MeOH} = 240 nm. Chromatographic behaviour: R_f 0.41 (system 1), R_f 0.80 (system 2), R_f 0.61 (system 3).

3.6. Junipeionoloside (*2*)

UV λ_{max}^{MeOH} = 245 nm. FAB$^+$MS (glycerol): *m/z* 387 $[M+H]^+$. FAB$^-$MS (glycerol): *m/z* 385 $[M-H]^-$. DCI$^+$MS (NH_3 + isobutane): *m/z* 387 $[M+H]^+$; 225 $[M-Glc+H]^+$; 207 $[M-OGlc+H]^+$. Chromatographic behaviour: R_f 0.16 (system 1), R_f 0.52 (system 2), R_f 0.51 (system 3), R_t 22 min (system 5).

3.7. 6-Hydroxy-junipeionoloside (*3*)

UV λ_{max}^{MeOH} = 241 nm. FAB$^+$MS (glycerol) *m/z* (rel. int.): 403 $[M+H]^+$ (82); 241 $[M-Glc+H]^+$ (66); 223 $[M-OGlc+H]^+$ (86). FAB$^-$MS (glycerol) *m/z* (rel. int.): 401 $[M-H]^-$ (100); 239 $[M-Glc-H]^-$ (14); 221 $[M-OGlc-H]^-$ (6). FAB$^+$MS (glycerol + NaCl) *m/z* (rel. int.): 425 $[M+Na]^+$ (96); 403 $[M+H]^+$ (100); 241 $[M-Glc+H]^+$ (43); 223 $[M-OGlc+H]^+$ (80). FAB$^-$MS (glycerol + NaCl) *m/z* (rel. int.): 437 $[M+Cl]^-$ (30); 401 $[M-H]^-$ (100); 239 $[M-Glc-H]^-$ (20); 221 $[M-OGlc-H]^-$ (9). DCI$^+$MS (NH_3 + isobutane) *m/z* (rel. int.): 420 $[M+NH_4]^+$ (3); 403 $[M+NH_4-H_2O]^+$ (29); 241 $[M-Glc+H]^+$ (16); 223 $[M-OGlc+H]^+$ (27); 180 $[OGlc]^+$ (100). Chromatographic behaviour: R_f 0.23 (system 1), R_f 0.34 (system 2), R_f 0.30 (system 3), R_t 14 min. (system 4).

3.8. Roseoside (*4*)

UV λ_{max}^{MeOH} = 242 nm. Chromatographic behaviour: R_f 0.29 (system 1), R_f 0.67 (system 2), R_f 0.57 (system 3), R_t 12 min (system 6).

3.9. Dihydrophaseic acid 4′-o-β-D-glucopyranoside (**5**)

UV λ_{max}^{MeOH} = 268 nm. FAB$^+$MS (glycerol + NaCl): *m/z* 467 $[M+Na]^+$; 445 $[M+H]^+$; 265 $[M-OGlc+H]^+$. DCI$^+$MS (NH_3 + isobutane): *m/z* 462 $[M+NH_4]^+$; 445 $[M+NH_4-H_2O]^+$; 265 $[M-OGlc+H]^+$. Chromatographic behaviour: R_f 0.15 (system 1), R_f 0.68 (system 2), R_f 0.07 (system 3), R_t 20 min (system 4).

Acknowledgements

The authors are grateful to Mrs S. Bourrut for technical assistance, to Mrs C. Oriol (service commun de RMN, Faculté de Pharmacie, 2 rue du docteur Marcland, 87025 Limoges cedex, France) for recording 400 MHz NMR spectra and to the Region Limousin for financial assistances.

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