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Phenolic constituents of the fern *Phegopteris connectilis*

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Abstract

The new compounds 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,4′,6′-tetraacetylglucoside, 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,6′-triacetylglucoside and 2,4,6-trihydroxybenzoic acid-4-*O*-3′,4′,6′-triacetylglucoside, 3-*O*-*p*-coumaroylshikimic acid and 2-(*trans*-1,4-dihydroxy-2-cyclohexenyl)-5-hydroxy-7-methoxychromone were isolated from the methanolic extract of fronds of *Phegopteris connectilis*, along with kaempferol and kaempferol-3-*O*-β-D-glucoside. Their structures have been elucidated by spectroscopic analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Phegopteris connectilis; Thelypteridaceae; Pteridophyta; Fern; Trihydroxybenzoic acid; Shikimic acid; *p*-coumaric acid; Flavone

1. Introduction

The circumboreal and north-temperate fern *Phegopteris connectilis* (Michx.) Watt, is one of the three species of the genus *Phegopteris*, Thelypteridaceae (Dostal, 1984; Smith, 1990). So far, the occurrence of the phloroglucides aspidin and aspidinol has been reported from *P. connectilis* (Molodozhnikova, Bankovskii & Nakaidze, 1970). Since there are no further records on the chemistry of the genus *Phegopteris*, we have analyzed the phenolic constituents of the methanolic extract of the fronds of *P. connectilis*.

2. Results and discussion

A combination of column chromatography (Sephadex LH-20), vacuum liquid chromatography and HPLC of the methanolic extract of fronds of *Phegopteris connectilis* afforded the five new compounds 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,4′,6′-tetraacetylglucoside (**1**), 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,6′-triacetylglucoside (**2**), 2,4,6-trihydroxybenzoic acid-4-*O*-3′,4′,6′-triacetylglucoside (**3**), 3-*O*-*p*-coumaroylshikimic acid (**4**) and 2-(*trans*-1,4-dihydroxy-2-cyclohexenyl)-5-hydroxy-7-methoxychromone (**5**), along with kaempferol and kaempferol-3-*O*-β-D-glucoside.

*2.1. 2,4,6-Trihydroxybenzoic acid-4-O-2′,3′,4′,6′-tetraacetylglucoside (**1**)*

Compound **1** was obtained as a brownish amorphous powder with the molecular formula $C_{21}H_{24}O_{14}$ as indicated by the FAB$^-$ mass spectrum (*m*/*z* 499.4, $[M-H]^-$). The ^{1}H NMR spectrum displayed four singlets of methyl groups (δ_H 1.98–2.08) (Table 1) assignable to four acetate residues, as confirmed by the presence of the corresponding signals in the ^{13}C NMR spectrum (δ_C 20.50–20.60 and δ_C 171.09–172.37) (Table 2). The signals in the range of δ_H 4.31–5.37 were attributed to a tetraacetylated sugar moiety that could be identified as 2,3,4,6-tetraacetylglucose by its characteristic ^{13}C NMR signals (Table 2). The coupling constant of 8.0 Hz of the anomeric proton (δ_H

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Table 1
^{1}H NMR data of **1**, **2** and **3** in MeOH-d_4, (J in Hz)

H	**1**	**2**	**3**
H-3/5	5.91 s	5.89 s	5.91 s
H-1′	5.28 d (8.0)	5.23 d (7.9)	5.08 d (7.9)
H-2′	5.11 dd (8.0, 9.5)	5.02 dd (7.9, 9.3)	3.68 dd (7.9, 9.4)
H-3′	5.37 t (9.5)	5.17 t (9.3)	5.20 t (9.4)
H-4′	5.06 t (9.5)	3.62 t (9.3)	4.94 t (9.4)
H-5′	4.08 ddd (2.2, 5.2, 9.5)	3.85 ddd (1.7, 6.9, 9.3)	4.04 ddd (2.0, 6.1, 9.4)
H-6α′	4.29 dd (5.2, 11.5)	4.26 dd (6.9, 11.9)	4.27 dd (6.1, 12.2)
H-6β′	4.13 dd (2.2, 11.5)	4.42 dd (1.7, 11.9)	4.10 dd (2.0, 12.2)
CH$_3$(acetyl)	2.08 s	2.09 s	2.06 s
CH$_3$(acetyl)	2.03 s	2.05 s	2.04 s
CH$_3$(acetyl)	2.02 s	2.01 s	2.01 s
CH$_3$(acetyl)	1.98 s	–	–

5.28) indicated the presence of a β-glycosidic linkage to a aglycone characterized by a single aromatic proton signal at δ_H 5.91 integrating to two protons. Based on comparison of the respective ^{13}C NMR signals with literature data (Kielmann & Lauener, 1989), this singlet could be assigned to H-3/H-5 of a symmetrically substituted 2,4,6-trihydroxybenzoic acid moiety. The glycosylation of the phenolic hydroxyl group at C-4 of the trihydroxybenzoic acid unit could be deduced from the respective C-H long-range coupling of H-1′ of the tetraacetylglucose moiety to C-4. Thus, in agreement with the MS data, **1** is 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,4′,6′-tetraacetylglucoside.

Table 2
^{13}C NMR data of **1**, **2** and **3** in MeOH-d_4 and DMSO-d_6

C	**1**		**2**	**3**
	MeOH-d_4	DMSO-d_6	DMSO-d_6	DMSO-d_6
C-1	100.10	96.90 s	99.82 s	99.95 s
C-2, 6	164.45	162.50 s	163.48 s	163.65 s
C-3, 5	95.65	95.11 d	93.06 d	93.14 d
C-4	162.43	161.49 s	159.53 s	159.69 s
C-7	172.37[a]	172.29 s	172.18 s	172.15 s
C-1′	98.79	96.25 d	96.78 d	96.82 d
C-2′	72.52	70.64 d	71.28 d	70.68 d
C-3′	74.09	71.94 d	74.68 d	73.81 d
C-4′	69.86	68.13 d	67.78 d	67.95 d
C-5′	72.98	71.02 d	73.26 d	73.18 d
C-6′	63.18	61.69 t	62.75 t	62.17 t
COO(acetyl)	171.09	169.12 s	169.00 s	169.66 s
COO(acetyl)	171.29	169.38 s	169.47 s	169.20 s
COO(acetyl)	171.55	169.61 s	170.01 s	169.14 s
COO(acetyl)	172.37[a]	170.01 s	–	–
CH$_3$(acetyl)	20.60[b]	20.40[a] q	20.20 q	20.45 q
CH$_3$(acetyl)	20.60[b]	20.40[a] q	20.38 q	20.68 q
CH$_3$(acetyl)	20.50[c]	20.30[b] q	20.51 q	20.74 q
CH$_3$(acetyl)	20.50[c]	20.30[b] q	–	–

[a] Signals overlapped.
[b] Signals overlapped.
[c] Signals overlapped.

2.2. 2,4,6-Trihydroxybenzoic acid triacetylglucosides (**2** and **3**)

Chemical shifts and multiplicities of signals in the ^{1}H NMR spectra indicated compounds **2** and **3** to be acetylated glucosides of 2,4,6-trihydroxybenzoic acid as well. The major difference to **1** was the number of ^{1}H and ^{13}C NMR signals corresponding to only three acetyl groups in both compounds. This fact was confirmed by the molecular formula of $C_{19}H_{22}O_{13}$ as calculated from the respective FAB$^-$ mass spectra of **2** and **3** (m/z 457.4 [M-H]$^-$). The positions of the acetyl groups in the two isomeric triacetylglucosides at C-2′, C-3′, C-6′ in **2** and C-3′, C-4′, C-6′ in **3** could be obtained from the analysis of the ^{1}H-^{1}H-COSY correlations of the signals of the sugar moiety. Accordingly, **2** was the 2,4,6-trihydroxybenzoic acid-4-*O*-2′,3′,6′-triacetylglucoside and **3** the 2,4,6-trihydroxybenzoic acid-4-*O*-3′,4′,6′-triacetylglucoside.

The tetraacetylglucoside **1** is the main constituent among the three acetylglucosides **1**, **2** and **3** with a ratio of 84:8:8 as estimated by TLC. The genuine presence of both triacetates in the plant was shown by TLC of a methanol extract of lyophilized fresh plant material that had been shock frozen in liquid N_2. However, the tetraacetate **1** proved to be unstable to traces of formic acid in methanolic solution under formation of the isomeric triacetates **2** and **3** after several weeks of exposition.

2.3. 3-*O*-*p*-coumaroylshikimic acid (**4**)

Compound **4** was obtained as an amorphous powder. The pseudo-molecular ion peak at m/z 319.3, [M-H]$^-$ in the CI$^-$ mass spectrum was in agreement with the molecular formula of $C_{16}H_{16}O_7$. The ^{1}H NMR in MeOH-d_4 showed compound **4** to contain 12 non-exchangeable protons. Among these, four could be assigned to aromatic and three to olefinic protons. The signals of two olefinic protons at δ_H 6.49 and 7.69 in *trans*-configuration as shown by their coupling constant of 15.9 Hz, and four aromatic protons with an AA′–BB′ spin system [δ_H 6.80 (2H, d (br), $J = 7.8$ Hz, H-2′/6′), 7.47 (2H, d (br), $J = 7.8$ Hz, H-3′/5′)] indicated the presence of a *p*-coumaric acid moiety. The remaining olefinic proton signal at δ_H 6.75 (s, H-2), the signals of a CH_2-group (δ_H 2.29, H-6α; 2.75, H-6β) and the three methine proton appearing at δ_H 3.95 (H-4), δ_H 4.08 (H-5) and δ_H 5.68 (H-3), were attributed to a shikimic acid residue (Fukuoka, 1982). The assignment of the individual signals was confirmed by the respective correlations in the ^{1}H–^{1}H-COSY spectrum. The ester linkage of both units via the hydroxyl group at C-3 of the shikimic acid unit could be deduced from the characteristic low-field shift of H-3. Accordingly, the structure of compound **4** could be established as 3-*O*-*p*-cumaroylshikimic acid. So far, two *p*-coumaroylshikimic acid conjugates have been described. One from the cambium of Western hemlock (*Tsuga heterophylla*); but in this study the linkage of *p*-coumaric acid to shikimic acid has not been specified (Goldschmid & Hergert, 1961). The second compound is 4-*O*-*p*-cumaroylshikimic acid from the fern Dicksonia antarctica (Saito, Yamane, Muropushi, Takahashi & Phinney, 1997).

2.4. 2-(*trans*-1,4-dihydroxy-2-cyclohexenyl)-5-hydroxy-7-methoxychromone (**5**)

Compound **5** consisted of a pale yellow amorphous powder with a molecular formula $C_{16}H_{16}O_6$, obtained from the CI$^+$ mass spectrum (m/z 305.3, $[M+H]^+$). The ^{1}H and ^{13}C NMR spectra showed two sets of signals, suggesting that compound **5** exits as a mixture of two conformers A and B. The presence of conformers instead of a mixture of isomers was also supported by the fact that **5** could not be further separated by HPLC on various stationary phases (Si, Diol, RP-8, RP-18). The assignment of the signals to the two separate data sets A and B could be deduced from the ^{1}H-^{1}H-COSY, HSQC and HMBC spectra of **5**. In the ^{1}H NMR spectrum each set showed signals assignable to two *meta*-coupled aromatic protons (δ_H 6.24/6.51 (d, $J = 2.3$ Hz, A), 6.24/6.49 (d, $J = 2.3$ Hz, B), H-6/H-8), an olefinic proton (δ_H 6.37 (s, A), 6.40 (s, B), H-3), an aromatic methoxy group (δ_H 3.84, s). Together with the corresponding ^{13}C signals these data indicated the presence of a 5-hydroxy-7-methoxychromone moiety. The eight signals in the range δ_H 1.66–2.37 (H-5′, H-6′) could be assigned to two sets of a -CH_2–CH_2-substructure that is linked to a methine proton with hydroxyl shift (δ_H 4.23 (m, A), 4.01 (m, B), H-4′) which in turn couples with two olefinic protons (δ_H 5.76 (d, $J = 10.1$ Hz, H-2′), 6.06 (dd, $J = 3.3$, 10.1 Hz, H-3′)) assignable to a *cis*-double bond. Based on the analysis of ^{1}H–^{1}H-COSY, HSQC and HMBC spectra this substructure could be recognized as 1,4-dihydroxy-2-cyclohexenyl moiety, linked to the 5-hydroxy-7-methoxychromone moiety via C-2.

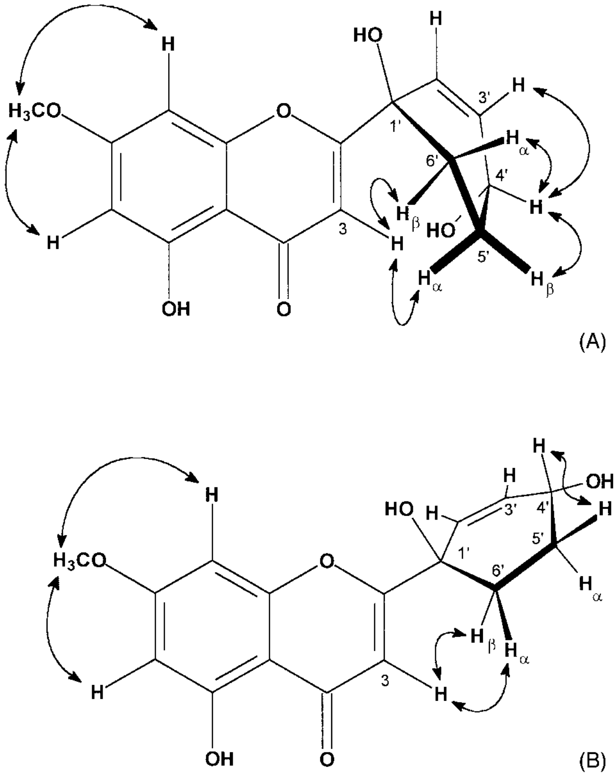


Fig. 1. Significant NOEs of both conformers of **5**, shown on the possible 1′*R*,4′*R* enantiomer.

The NOESY spectrum allowed the determination of the stereo structure of the two conformers and their assignment to the individual sets of NMR signals. Conformer A, corresponding to the signal set A, is the form with the chromone moiety in pseudoaxial position at C-1′ of the cyclohexene ring, as deduced from specific NOEs: Correlations are present between H-3 and both H-5′α and H-6′β and between H-4 (pseudoequatorial) and the olefinic proton H-3′. The latter correlation as well as the cross peaks of H-4′ with H-5′β and H-6′α indicate the *trans*-configuration of the hydroxyl groups at C-1′ and C-4′ (Fig. 1(A)) Conformer B with the signal set B is the form with the chromone moiety in pseudoequatorial position at C-1′ of the cyclohexene ring, as obtained from the respective NOESY correlations: H-3 correlates with both H-6′α and H-6′β. H-4′, now in pseudoaxial position, shows only an effect on H-5′β and not on H-3′ what is in agreement with the dihedral angle of about 90° between H-4′ and H-3′. This fact and the correlation of H-4′ to H-5′β also confirms the *trans*-configuration of the hydroxyl groups of the cyclohexene ring (Fig. 1(B)). Dreiding models of both *trans* and *cis* configured molecules showed that only the *trans* configuration (1′*R*,4′*R* or 1′*S*,4′*S*) is in agreement with the observed NOESY data and the line doubling of **5** is not due to a mixture of the spectroscopically differentiable 1′*R*,4′*R* (1′*S*,4′*S*) and 1′*R*,4′*S* (1′*S*,4′*R*) stereoisomers.

Furthermore, the position of the methoxy group at C-7 of the chromone moiety could be confirmed by NOESY-correlations of the methoxyl signal to the signals of both *meta*-coupled protons H-6 and H-8. Thus, compound **5** is 2-(*trans*-1,4-dihydroxy-2-cyclohexenyl)-5-hydroxy-7-methoxychromone, a flavone with a partially hydrogenated B-ring.

Only a few flavonoids with a hydrogenated B-ring are known, mainly from some ferns of the genus *Pseudophegopteris* (Wada, Fujita, Murakami, Saiki & Chen, 1987) and the horsetail species *Equisetum arvense* (Hauteville, Chopin, Geiger & Schuler, 1981). From a chemotaxonomical point of view the occurrence of such unusual flavonoids in *Phegopteris* and *Pseudophegopteris* species underlines the close relationship of both genera within the family Thelypteriadaceae (Smith, 1990).

3. Experimental

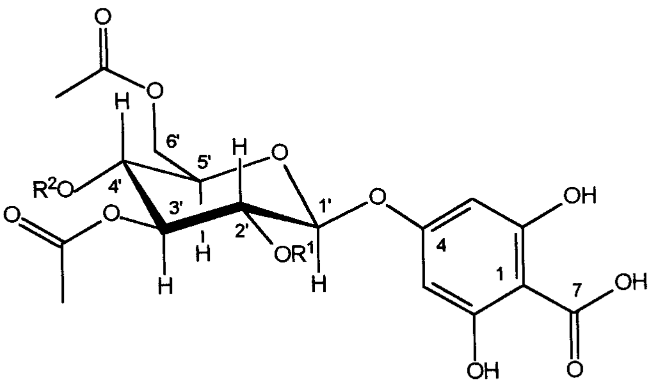
NMR spectra were recorded in MeOH-d_4, DMSO-d_6 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100.5 MHz, 125 MHz for 1D spectra; 500 MHz, 125 MHz for 2D spectra, respectively) relative to MeOH-d_4 at δ_H 3.30, δ_C 49.05, DMSO-d_6 at δ_H 2.50, δ_C 39.43. ^{13}C multiplicities were determined using the DEPT pulse sequence. Optical rotations were measured in MeOH.

3.1. Plant material

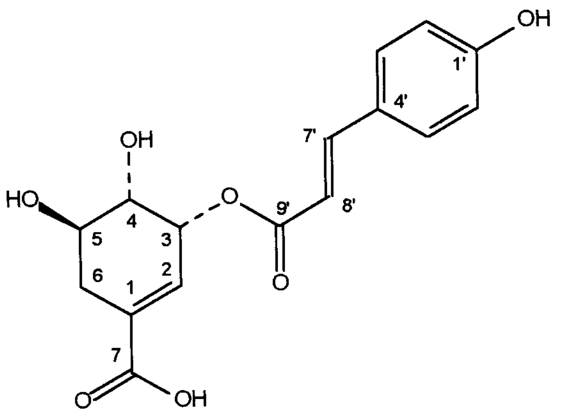
P. connectilis (Michx.) Watt was collected in Börfink, Germany in June 1997 and identified by K.-P.A. A voucher specimen is retained at the institute.

3.2. Extraction and isolation

Powdered air dried plant material (520 g) was sequentially extracted with CH_2Cl_2 and MeOH at room temp. The MeOH extract (47 g) was dissolved in H_2O (500 ml) and washed with EtOAc (500 ml, ×3)



	R1	R2
1	Ac	Ac
2	Ac	H
3	H	Ac



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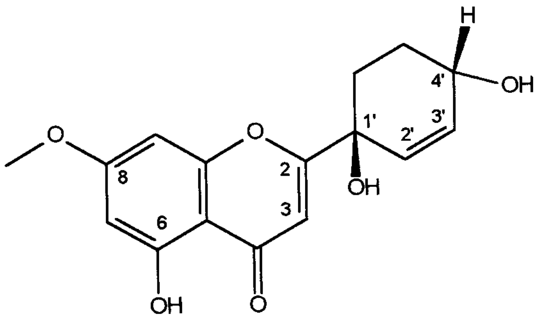

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Table 3
^{1}H and ^{13}C NMR data of **5** in MeOH-d_4

5	Conformer A		Conformer B	
H/C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
2	–	177.84, s	–	174.55, s
3	6.37, s	106.29, d	6.40, s	107.88, d
4	–	184.62, s	–	184.92, s
4a	–	106.63, s	–	106.54, s
5	–	163.28, s	–	163.28, s
6	6.24, d (2.3)	99.79, d	6.24, d (2.3)	99.71, d
7	–	167.81, s	–	167.75, s
8	6.51, d (2.3)	93.92, d	6.49, d (2.3)	93.84, d
8a	–	159.99, s	–	159.92, s
1′	–	72.30, s	–	73.64, s
2′	5.76, d (10,1)	131.48, d	5.76, d (10,1)	131.48, d
3′	6.06, dd (3.3, 10.1)	136.27, d	6.06, dd (3.3, 10.1)	136.27, d
4′	4.23, m	66.00, d	4.01, m	66.30, d
5′α	1.72, m	30.05, t	1.66, m	29.24, t
5′β	2.10, m		1.98, m	
6′α	1.82, m	33.61, t	1.55, m	30.60, t
6′β	2.37, m		2.33, m	
OMe	3.84, s	56.98, q	3.84, s	56.98, q

and extracted with *n*-BuOH (300 ml, ×3). The EtOAc soln was evapd. under red. pres. to afford 8 g of residue. The conc. EtOAc extract was chromatographed on Sephadex LH-20 (1500 mm × 25 mm i.d.) with MeOH–CH$_2$Cl$_2$ (80:20) as eluent to give five fractions (EP 1–5). CC of fr. EP-1 on SiO$_2$ (1500 mm × 25 mm i.d), with CH$_2$Cl$_2$–acetone–HCOOH, (80:10:5) yielded 230 mg of **1** and a mixture of **2** and **3** that was separated by HPLC (Phenyl, 250 mm × 8 mm i.d., MeCN–H$_2$O–HCOOH, 15:80:5) to afford 25 mg of **2** and 23 mg of **3**. Fr. EP-2 was further separated by VLC (RP 8, 60 × 35 mm i.d., MeOH–H$_2$O (10% steps from 20:80 to 50:50) in frs. EP-2.1, EP-2.2. HPLC of EP-2.2 (RP18, 250 mm × 8 mm i.d., MeOH–H$_2$O–HCOOH (25:75:10)] afforded **5** (90 mg) and kaempferol-3-*O*-glucoside (45 mg). VLC of EP-2.2 (Diol, 60 mm × 35 mm i.d., *n*-hexane–EtOAc, 10% steps from 20:80 to 100% EtOAc; EtOAc–acetone, 10% steps from 90:10 to 70:30) yielded kaempferol-3-*O*-glucoside (165 mg) and **4** (13 mg). VLC of fr. EP-3 (Diol, 60 mm × 35 mm i.d., *n*-hexane–EtOAc, 10% steps from 20:80 to 100% EtOAc) afforded kaempferol (15 mg). R_f (CHCl$_3$–acetone–HCOOH, 150:33:17) **1** (0.24), **2** (0.15) **3** (0.13).

*3.3. 2,4,6-Trihydroxybenzoic acid-4-O-2′,3′,4′,6′-tetraacetylglucoside (**1**)*

$[\alpha]_D^{20}$ −33.8° (MeOH; c = 0.63); FAB$^-$-MS *m*/*z*: 499.4 [M]$^-$; UV λ_{max}^{MeOH}: 252; IR ν_{max}^{KBr}: cm^{-1}: 3450, 2960, 1755, 1645, 1600, 1425, 1375, 1295, 1265, 1235, 1178, 1137, 1080, 1040, 1003, 840, 710; ^{1}H NMR; see Table 1; ^{13}C NMR: see Table 2.

*3.4. 2,4,6-Trihydroxybenzoic acid-4-O-2′,3′,6′-triacetylglucoside (**2**)*

$[\alpha]_D^{20}$ −30.2° (MeOH; c = 0.84); FAB$^-$-MS *m*/*z*: 457.4 [M]$^-$; UV λ_{max}^{MeOH}: 252; IR ν_{max}^{KBr}: cm^{-1}: 3430, 2970, 1740, 1635, 1598, 1425, 1375, 1285, 1250, 1238, 1210, 1180, 1137, 1081, 1045, 1000, 837, 800, 705; ^{1}H NMR; see Table 1; ^{13}C NMR: see Table 2.

*3.5. 2,4,6-Trihydroxybenzoic acid-4-O-3′,4′,6′-triacetylglucoside (**3**)*

$[\alpha]_D^{20}$ −33.8° (MeOH; c = 0.42); FAB$^-$-MS *m*/*z*: 457.4 [M]$^-$; UV λ_{max}^{MeOH}: 252; IR ν_{max}^{KBr}: cm^{-1}: 3440, 2970, 1745, 1635, 1600, 1421, 1380,1352, 1290, 1255, 1235, 1175, 1075, 1045, 832, 765, 705; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2.

*3.6. 3-O-p-coumaroylshikimic acid (**4**)*

$[\alpha]_D^{20}$ −129.8° (MeOH; c = 0.64); CI$^-$-MS *m*/*z*: 319.3 [M]$^-$; UV λ_{max}^{MeOH}: 310; IR ν_{max}^{KBr}: cm^{-1}: 3450, 2940, 1705, 1695, 1610, 1595, 1522, 1515, 1450, 1355, 1270, 1210, 1175, 1040, 840; ^{1}H NMR (MeOH-d_4): δ_H 7.69 (1H, d, J = 15.9 Hz, C-8′), 7.47 (2H, d (br), J = 7.8 Hz, H-3′/5′), 6.80 (2H, d (br), J = 7.8 Hz, H-2′/6′), 6.75 (1H, s, H-2), 6.49 (1H, d, J = 15.9 Hz, C-7′), 5.68 (s (br), H-3), 4.08 (m, H-5), 3.95 (1H, dd, J = 6.5, 4.0 Hz, H-4), 2.75 (1H, d (br) J = 18.1 Hz, H-6β), 2.29 (1H, dd, J = 18.1 Hz, 4.0, H-6α); ^{13}C NMR (MeOH-d_4): δ_C 31.6 (t, C-6), 68.7 (d, C-3), 70.7[1] (d, C-5), 70.9[1] (d, C-4), 115.1 (d, C-8′), 116.9 (d, C-3′/C-5′), 127.3 (s, C-1), 131.1 (d, C-3′/C-5′), 133.5 (s, C-4′), 134.5 (d, C-2), 147.0 (d, C-7′), 161.3 (s, C-1′), 168.5, 168.6 (s × 2, C-7, C-9′).

*3.7. 2-(trans-1,4-dihydroxy-2-cyclohexenyl)-5-hydroxy-7-methoxychromone (**5**)*

$[\alpha]_D^{20}$ +47.8° (MeOH; c = 1.4);CI$^+$-MS *m*/*z*: 305.3, [M+H]$^+$; UV: 230, 255, 292, 319; IR ν_{max}^{KBr}: cm^{-1}: 3400, 2950, 1670, 1625, 1585, 1510, 1440, 1350, 1265, 1210, 1195, 1070, 1060, 1020, 765; ^{1}H NMR: see Table 3; ^{13}C NMR: see Table 3.

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[1] Signals may be interchanged.

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