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AROMATIC GLYCOSIDES FROM *BERCHEMIA RACEMOSA*

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Key Word Index—*Berchemia racemosa*; Rhamnaceae; lignan; aromatic glycoside; nudiposide; secoisolariciresinol glucoside; isotachioside; tachioside; syringic acid glucosyl ester; ^{13}C NMR.

Abstract—Two new aromatic glucosides have been isolated from the stems of *Berchemia racemosa* together with the known glycosides, nudiposide, (−)-secoisolariciresinol-*O*-*β*-D-glucopyranoside and methoxyhydroquinone-1-*O*-*β*-D-glucopyranoside (isotachioside). The structures of the new glucosides were found to be *β*-D-glucopyranosyl syringate, and methoxyhydroquinone-4-*O*-*β*-D-glucopyranoside on the basis of chemical and spectral evidences.

INTRODUCTION

The stems of *Berchemia racemosa* Sieb. et Zucc. are used in Japan for the treatment of gall stones, liver diseases, neuralgia and stomach cramp. The related plant, *B. floribunda*, has been used in traditional Chinese medicine as an antipyretic, a diuretic and for the treatment of rheumatism and lumbago [1].

From the methanol extract of the stems of *B. racemosa*, we have recently isolated 2,6-dimethoxybenzoquinone (**1**) as the physiologically active constituent which inhibits histamine release from rat mast cells induced by compound 48/80 and by concanavalin A [2]. In the course of further studies on the constituents of the above plant, two new aromatic glucosides (**4** and **6**) along with three known glycosides (**2**, **3** and **5**) have been isolated from the butanol-soluble fraction of the methanol extract.

RESULTS AND DISCUSSION

Compound **2**, $C_{27}H_{36}O_{12}$, showed ^{13}C NMR signals for tetra- and penta-substituted benzene rings, four methoxyl carbons, pentose carbons and six sp^3 carbons, two of which were *O*-substituted (Table 1). This strongly suggested that **2** had a lignan glycoside skeleton. The carbon signals of the aglycone portion were similar to those reported for lyoniresinol 3*α*-*O*-*β*-D-glucopyranoside (**2c**) [3]. Methanolysis of **2** followed by GC analysis of the TMS derivative established that the sugar moiety was xylose.

Nudiposide (**2a**) and lyoniside (**2b**) are diastereomeric xylosides of enantiomeric lyoniresinols, isolated from *Enkianthus nudipus* and reported without ^{13}C NMR data [4]. A comparison of the ^{13}C NMR spectra of **2** with authentic samples of **2a**, **2b** and **2c** was undertaken. In referring to the spectral data of **2c**, (in pyridine-d_5) [3], we assigned ^{13}C NMR signals of **2a** and **2b** as listed in Table 1 using CD_3OD as solvent. The data of **2a** is identical with that of **2** within a difference of 0.1 ppm for each corresponding carbon signal, while in the data of **2b**, small but significantly different shifts from the data of **2** are observed for C-4 (upfield shift by 0.5 ppm) and the anomeric carbon, C-1″ (downfield shift by 0.4 ppm).

The specific optical rotation of **2** (−66.3°) is virtually the same as that of **2a** (−68.9°) and differs from that of **2b** (+28.5°). Other physicochemical properties of **2**, such as ^{1}H NMR, IR, UV, melting point and R_f value on TLC are consistent with those of **2a**. Consequently, **2** is identified with 3-*α*-*O*-*β*-D-xylopyranoside of (−)-lyoniresinol (nudiposide, **2a**).

Compound **3** showed ^{13}C NMR signals for two sets of 1,2,4-trisubstituted benzene rings, two CH_2O– (*δ*70.4 and 62.8), and four sp^3 carbons [*δ*44.0 (*d*), 41.6 (*d*), and 35.5 (*t* × 2)]. In addition, one set of *β*-glycopyranosyl carbon signals was observed (Table 2). These data suggested that compound **3** was a diphenylbutane-type lignan glucoside. Glucose was detected after hydrolysis of **3** followed by GLC analysis of the liberated sugar as its TMS derivative. The ^{13}C NMR signals of the aglycone moiety (in CD_3OD) corresponded closely with those reported for secoisolariciresinol (**3a** in $CDCl_3$) with a large shift of C-8′ and C-9′ (−2.1 and +9.9 ppm, respectively) [5]. The above data was reminiscent of (−)-secoisorariciresinol-9′-*O*-*β*-D-glucopyranoside with which compound **3** was identified by direct comparison with an authentic sample [6] by means of ^{1}H NMR, ^{13}C NMR and optical rotation.

Compound **4**, $C_{13}H_{18}O_8$ and **5**, $C_{13}H_{18}O_8$ were closely related compounds and showed similar behavior on TLC and silica gel column chromatography. Final separation was achieved by preparative reversed-phase HPLC. The ^{13}C NMR spectra of both compounds were very similar, and showed the presence of *β*-glucopyranosyl carbons, trisubstituted benzene ring carbons and a methoxyl carbon (Table 3). In addition, a phenolic hydroxyl proton, and 1,2,4-trisubstituted aromatic protons were observed by ^{1}H NMR. Acid hydrolysis of **4** and **5** afforded glucose, which was confirmed by the GC analysis of its TMS derivatives. They also afforded the same aglycone, methoxyhydroquinone, which was identified by HPLC with an authentic sample. This procedure also discriminated between the alternative

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Table 1. ^{13}C NMR data of compound 2 and related compounds (25 MHz, TMS as int. standard)

	2	2a	2b	2c	2c[3]
C	(CD_3OD)	(CD_3OD)	(CD_3OD)	(CD_3OD)	(C_5D_5N)
1	34.0 (*t*)	34.0 (*t*)	33.9 (*t*)	32.4 (*t*)	33.9 (*t*)
2	40.7 (*d*)	40.6 (*d*)	40.4 (*d*)	38.8 (*d*)	41.2 (*d*)
2α	66.0 (*t*)	66.0 (*t*)	65.9 (*t*)	65.5 (*t*)	66.2 (*t*)
3	46.9 (*d*)	46.8 (*d*)	46.7 (*d*)	45.8 (*d*)	46.6 (*d*)
3α	71.0 (*t*)	71.0 (*t*)	70.9 (*t*)	71.4 (*t*)	71.9 (*t*)
4	43.4 (*d*)	43.3 (*d*)	42.9 (*d*)	42.2 (*d*)	43.3 (*d*)
5	148.7 (*s*)	148.8 (*s*)	148.8 (*s*)	147.6 (*s*)	148.6 (*s*)
6	138.9 (*s*)	138.8 (*s*)	138.8 (*s*)	138.5 (*s*)	138.8 (*s*)
7	147.5 (*s*)	147.5 (*s*)	147.5 (*s*)	147.5 (*s*)	147.5 (*s*)
8	107.5 (*d*)	107.6 (*d*)	107.7 (*d*)	107.3 (*d*)	107.8 (*d*)
9	130.1 (*s*)	130.0 (*s*)	130.0 (*s*)	129.3 (*s*)	130.3 (*s*)
10	126.3 (*s*)	126.2 (*s*)	126.4 (*s*)	126.2 (*s*)	126.2 (*s*)
1′	139.6 (*s*)	139.5 (*s*)	139.3 (*s*)	138.9 (*s*)	139.5 (*s*)
2′	106.9 (*d*)	106.9 (*d*)	106.8 (*d*)	107.1 (*d*)	107.1 (*d*)
3′	148.9 (*s*)	148.8 (*s*)	148.8 (*s*)	148.6 (*s*)	148.9 (*s*)
4′	134.4 (*s*)	134.4 (*s*)	134.4 (*s*)	135.1 (*s*)	134.6 (*s*)
5′	148.9 (*s*)	148.8 (*s*)	148.8 (*s*)	148.6 (*s*)	148.9 (*s*)
6′	106.9 (*d*)	106.9 (*d*)	106.8 (*d*)	107.1 (*d*)	107.1 (*d*)
1″	105.0 (*d*)	104.9 (*d*)	105.4 (*d*)	104.5 (*d*)	104.2 (*d*)
2″	74.9 (*d*)	74.8 (*d*)	74.8 (*d*)	74.8 (*d*)	75.1 (*d*)
3″	78.0 (*d*)	77.9 (*d*)	77.9 (*d*)	78.1 (*d*)	77.9 (*d*)
4″	71.3 (*d*)	71.2 (*d*)	71.1 (*d*)	71.4 (*d*)	71.5 (*d*)
5″	67.1 (*t*)	67.0 (*t*)	66.9 (*t*)	78.1 (*d*)	78.2 (*d*)
6″	—	—	—	62.5 (*t*)	62.7 (*t*)
5-O-Me	59.9 (*q*)	59.8 (*q*)	60.0 (*q*)	59.6 (*q*)	60.1 (*q*)
-O-Me	56.6 (*q*)	56.5 (*q*)	56.5 (*q*)	56.1 (*q*)	56.6 (*q*)
-O-Me	56.8 (*q*)	56.7 (*q*)	56.8 (*q*)	56.5 (*q*)	56.9 (*q*)
-O-Me	56.8 (*q*)	56.7 (*q*)	56.8 (*q*)	56.5 (*q*)	56.9 (*q*)

candidates, 4-methoxyresorcinol and 4-methoxycatechol. Thus, **4** and **5** are regio-isomers of methoxyhydroquinone glycoside. One of them, methoxyhydroquinone-1-*O*-β-glucopyranoside (isotachioside) has been isolated from the liverwort, *Isotachis japonica* Steph [7]. The reported physicochemical properties of isotachioside are identical with those of **5**. From these evidences, the other isomeric glucoside (**4**) is assigned the structure of methoxyhydroquinone-4-*O*-β-glucopyranoside. Since this is a new compound, we propose to name it tachioside, rather than isoisotachioside. The structures of these compounds were consistent with the ^{13}C NMR substitution induced shift trends: β-Glucosylation shift value of arbutin [$\Delta\delta = \delta$ (arbutine) $-\delta$ (hydroquinone)] on the *ipso*, *ortho*, *meta* and *para* carbons were +0.5, +1.9, −0.3 and +2.3, respectively (in DMSO-d_6). These $\Delta\delta$ values were used to calculate the expected chemical shift of both glucosides of methoxyhydroquinone. On going from the methoxyhydroquinone (δ C(1-6) = 138.9, 148.1, 100.7, 150.3, 106.3 and 115.7, in DMSO-d_6 respectively), the calculated chemical shifts of all carbons of **4** and **5** were within 0.4 ppm from the observed value.

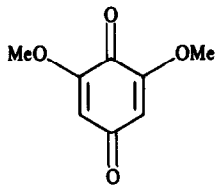
Compound **6**, $C_{15}H_{20}O_{10}$ was obtained as colourless crystals. Methanolysis of **6** followed by GC analysis of the TMS derivative showed the presence of glucose. The ^{13}C NMR spectrum of **6** showed the presence of 1,3,4,5-tetra-substituted symmetrical aromatic ring carbons, two equivalent methoxyl carbons, carbonyl carbon and one set of β-glucopyranosyl carbons. The chemical shift of anomeric carbon (δ96.4) was characteristic of esterified glucose. Acid hydrolysis of **6** afforded an aglycone, which was identified with syringic acid (**6a**) by means of ^{1}H NMR and ^{13}C NMR spectroscopy. Compound **6** could thus be designated as syringic acid β-D-glucopyranosyl ester. Although the isomeric glucoside, glucosyringic acid is a known compound, to our knowledge, **6** has not been reported in Nature (Table 4).

EXPERIMENTAL

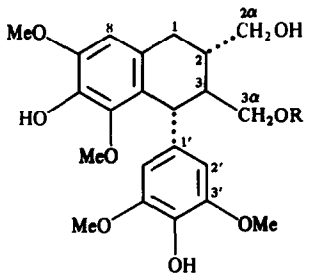
Mp: uncorr; ^{1}H NMR and ^{13}C NMR: 100 and 25 MHz, respectively; MS: 75 eV.

Plant material. Berchemia racemosa Sieb. et Zucc was collected in the vicinity of Taishaku-kyo, Hiroshima Prefecture, Japan. A specimen is deposited at the Herbarium of Experimental Station of Medicinal Plants, Hiroshima University School of Medicine.

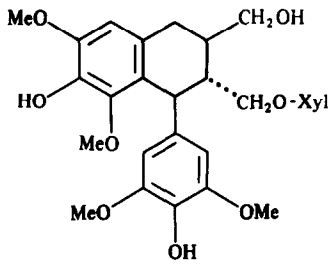
Extraction and separation of the constituent of B. racemosa. Dried stems of the plants (2.0 kg) were crushed and extracted with *n*-hexane and MeOH successively. The MeOH extract was suspended in H_2O and extracted with *n*-hexane, Et_2O, EtOAc, BuOH and H_2O successively. From the EtOAc fraction, **1** was obtained [1]. The BuOH-soluble fraction (20.2 g) was chromatographed on the highly porous polymer, Diaion-HP-20, H_2O



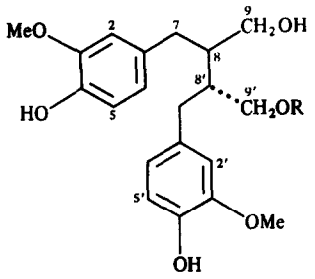
1



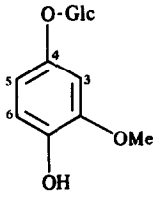
2 ≡ 2a R = Xyl
2c R = Glc



2b



3 R = Glc
3a R = H



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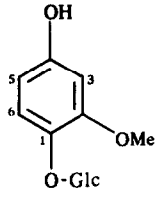

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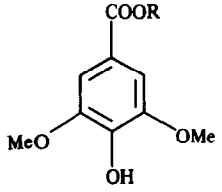

6 R = Glc
6a R = H

Xyl β-D-Xylopyranosyl
Glc β-D-Glucopyranosyl

Table 2. ^{13}C NMR data of compounds 3 and 3a (25 MHz, TMS as int. standard)

	3		3a
C	(CD_3OD)	(C_5D_5N)	($CDCl_3$)
1	134.0	133.2	132.4
2	113.4[a]	113.5[a]	111.7
3	148.8	148.5	146.6
4	145.4	146.1	143.7
5	115.7	116.2	114.3
6	122.7	122.5	121.5
7	35.5	35.0	35.8
8	44.0	43.8	43.7
9	62.8	61.7[c]	60.5
1′	134.0	132.9	132.4
2′	113.6[a]	113.7[a]	111.7
3′	148.8	148.5	146.6
4′	145.4	146.1	143.7
5′	115.7	116.2	114.3
6′	122.7	122.5	121.5
7′	35.5	35.0	35.8
8′	41.6	41.5	43.7
9′	70.4	70.4	60.5
1″	104.6	105.3	—
2″	75.2	75.4	—
3″	78.0[b]	78.5[b]	—
4″	71.7	71.7	—
5″	78.2[b]	78.6[b]	—
6″	62.8	62.8[c]	—
–OMe	56.3 × 2	55.9 × 2	55.7 × 2

[a, b, c]Assignments may be interchanged between the same superscripts.

with 10, 20, 30, . . . 90% MeOH and 100% MeOH). The 20% MeOH eluent was chromatographed again on Diaion HP-20 (H_2O–MeOH), then subjected to silica gel CC, Sephadex LH-20 CC (MeOH) and prep. HPLC (TSK gel ODS 120T, H_2O–MeOH–MeCN) to afford compound 4 (7 mg) and 5 (6 mg) along with 1 (6 mg).

The 50% MeOH eluent from the first Diaion column was subjected to CC (silica gel, $CHCl_3$–MeOH–H_2O), DCC ($CHCl_3$–MeOH–H_2O, 5:6:4) and DCC again ($CHCl_3$–MeOH–H_2O-propan-1-ol, 5:6:4:1) to give compound 6 (21 mg).

The 60% MeOH eluent from the first Diaion column was subjected to silica gel CC ($CHCl_3$–MeOH–H_2O), DCC ($CHCl_3$–MeOH–H_2O), silica-gel CC (solvent:

Table 3. ^{13}C NMR data of compounds 4 and 5 (25 MHz, DMSO-d_6, TMS as int. standard)

C	4	5
1	141.2 (*s*)	139.3 (*s*)
2	147.7 (*s*)	149.8 (*s*)
3	102.4 (*d*)	100.8 (*d*)
4	150.6 (*s*)	152.6 (*s*)
5	107.9 (*d*)	105.9 (*d*)
6	115.1 (*d*)	117.2 (*d*)
1′	101.6 (*d*)	101.4 (*d*)
2′	73.2 (*d*)	73.2 (*d*)
3′	76.9 (*d*)	76.8 (*d*)
4′	69.9 (*d*)	69.7 (*d*)
5′	76.6 (*d*)	76.7 (*d*)
6′	60.8 (*t*)	60.7 (*t*)
–OMe	55.4 (*q*)	55.5 (*q*)

Table 4. ^{13}C NMR data of compounds 6 and 6a (25 MHz, C_5D_5N, TMS as int. standard)

C	6	6a
1	119.6 (*s*)	122.0 (*s*)
2	108.5 (*d*)	108.3 (*d*)
3	148.6 (*s*)	148.7 (*s*)
4	143.2 (*s*)	142.2 (*s*)
5	148.6 (*s*)	148.7 (*s*)
6	108.5 (*d*)	108.3 (*d*)
–COOH	166.0 (*s*)	169.2 (*s*)
1′	96.4 (*d*)	—
2′	74.1 (*d*)	—
3′	79.4 (*d*)	—
4′	71.0 (*d*)	—
5′	78.3 (*d*)	—
6′	62.1 (*t*)	—
2 × –OMe	56.3 (*q*)	56.3 (*q*)

$CHCl_3$–MeOH–H_2O), Sephadex LH-20 CC (MeOH), low pressure LC (Lichroprep RP-8: H_2O–MeOH), prep HPLC (TSK gel ODS 120T, H_2O–MeOH) and silica gel CC ($CHCl_3$–MeOH–H_2O) to afford compound 2 (15 mg).

From the other fraction recovered from DCC of the 60% MeOH eluent, compound 3 (11 mg) was obtained by Sephadex LH-20 CC (MeOH), silica gel CC ($CHCl_3$–MeOH–H_2O) and Lichroprep RP-8 (H_2O–MeOH).

Nudiposide (2). Colourless needles from benzene–Me_2CO, mp 169–172°, $[\alpha]_D$ −66.3° (MeOH; *c* 0.48), lit [4] mp 175–178°, $[\alpha]_D$ −68.9° (MeOH; *c* 0.65). IR ν_{max}^{KBr} cm^{-1}: 3360, 2900, 1610, 1515, 1500, 1315, 1212, 1110; UV λ_{max}^{EtOH} nm (logε): 230 inf. (4.27), 280 (3.60); ^{1}H NMR (CD_3OD): δ 1.80–2.20 (2H, *m*), 2.69 (2H, *d*, *J* = 8 Hz), 3.62 (2H, *d*, *J* = 5 Hz), 3.74 (9H, *s*, –OMe), 3.84 (3H, *s*, –OMe), 4.09 (1H, *d*, *J* = 7 Hz, anomeric H), 4.22 (1H, *d*, *J* = 7 Hz), 6.41 (2H, *s*), 6.56 (1H, *s*); ^{13}C NMR (CD_3OD): see Table 1. Identified by comparison with an authentic sample (^{1}H NMR, ^{13}C NMR, IR, UV, $[\alpha]_D$, mmp, TLC).

(−)-*Secoisolariciresinol-9′-O-β-D-glucopyranoside* (3). Amorphous powder, $[\alpha]_D$ −22.9° (EtOH, *c* 0.50), lit [5] $[\alpha]_D$ −20.5° (MeOH, *c* 3.2). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1600, 1512, 1450, 1370, 1270, 1028, UV λ_{max}^{EtOH} nm (logε): 223 sh (4.26), 282 (3.88); ^{1}H NMR (CD_3OD): δ 1.80–2.30 (2H, *m*), 2.45–2.80 (4H, *m*), 3.61 (2H, *br d*), 3.75 (6H, *s*, –OMe), 4.20 (1H, *d*, *J* = 7 Hz, anomeric H), 6.45–6.80 (6H, *m*); ^{13}C NMR (CD_3OD): see table 2. Identified by comparison with an authentic sample (^{1}H NMR, ^{13}C NMR, $[\alpha]_D$, TLC).

Tachioside (*Methoxyhydroquinone-4-β-D-glucopyranoside*, (4). Mp 211–213° (aq. MeOH, colourless needles, $[\alpha]_D$ −55.4° (MeOH *c* 0.21); EIMS *m/z* (rel. int): 302.1001 $[M]^+$ (calc. 302.1001, $C_{13}H_{18}O_8$, 15), 140.0482 (calc. 140.0473, $C_7H_8O_3$, 100), 125.0279 (calcd 125.0239, $C_6H_5O_3$, 15); IR ν_{max}^{KBr} cm^{-1}: 3600–3000, 1610, 1510, 1445, 1370, 1295, 1245, 1220, 1195, 1168, 1081, 1042, 995, 941, 840, 805; UV λ_{max}^{MeOH} nm (logε): 206 (4.21), 220 sh (3.85), 227 sh (3.84), 285 (3.60); ^{1}H NMR (C_5D_5N, 270 MHz): δ 7.16 (1H, *d*, *J* = 2.5 Hz, H-3), 7.15 (1H, *d*, *J* = 8 Hz, H-5), 7.05 (1H, *dd*, *J* = 2.5, 8 Hz, H-5), 5.55 (1H, *d*, *J* = 7 Hz, H-1′), 4.59 (1H, *br*, *d*, *J* = 10 Hz, H-6′), 4.40 (1H, *dd*, *J* = 5, 10 Hz, H-6′), 4.45–4.29 (3H, *m*, H-2′, 3′, 4′), 4.12 (1H, *br*, *s*, H-5′), 3.71 (3H, *s*, –OMe), 8.55 (1 H, OH); ^{13}C NMR: see Table 3.

Isotachioside (*methoxyhydroquinone-1-β-D-glucopyranoside*, (5). Mp 195–197° (aq. MeOH), colourless needles, $[\alpha]_D$ −54.5° (MeOH *c* 0.15), EIMS *m/z* (rel. int.): 302 $[M]^+$ (<1), 140.0461 (calc. 140.0473, $C_7H_8O_3$, 100), 125.0211 (calc. 125.0239, $C_6H_5O_3$, 100); IR ν_{max}^{KBr} cm^{-1}: 3600–3000, 1610, 1510, 1460, 1360, 1305, 1285, 1260, 1220, 1200, 1160, 1130, 1081, 1030, 995, 955, 840, 805; UV λ_{max}^{MeOH} nm (logε): 206 (4.30), 223 (3.95), 231 inf (3.88), 285 (3.56); ^{1}H NMR (C_5D_5N, 270 MHz): δ 7.55 (1H, *d*, *J* = 9 Hz, H-6), 6.92 (1H, *d*, *J* = 3 Hz, H-3), 6.71 (1H, *dd*, *J* = 3, 8 Hz, H-5), 5.56 (1H, *d*, *J* = 7 Hz, H-1′), 4.54 (1H, *br*, *d*, *J* = 10 Hz, H-6′), 4.42 (1H, *dd*, *J* = 5, 10 Hz, H-6′), 4.48–4.27 (3H, *m*, H-2′, 3′, 4′), 4.07 (1H, *br*, *s*, H-5′), 3.70 (3H, *s*, –OMe), 9.08 (1H, OH). (Identical with the reported ones [7].) ^{13}C NMR: see Table 3.

HPLC analysis of aglycones of 4 and 5. Methoxyhydroquinone was purchased from Tokyo–Kasei Co. Ltd (Tokyo). Authentic 4-methoxyresorcinol (mp 72–74°, δ *c* (1–6) = 140.6, 147.4, 103.7, 151.8, 104.8 and 114.1, respectively) was synthesized from isovanillin by Baeyer–Villiger oxidation and then alkaline hydrolysis of the formate. [8, 9]. Selective methylation of 1,2,4-hydroxybenzene gave 4-methoxycatechol [10], colourless oil, δ *c* (1–6) = 139.1, 145.8, 102.5, 152.6, 103.3 and 115.6, respectively. About 1 mg of 4 and 5 was hydrolysed with 1 M H_2SO_4 at 100° for 30 min and the aglycones thus liberated, was taken up in Et_2O. The soln was evapd to dryness and subjected to HPLC analysis (column: Toyo–Soda ODS-120A (10 μm) 4 × 150 mm; MeOH–H_2O 1:9, at 25°, 1.5 ml/min; detection: UV at 290 nm). R_t (min) of authentic methoxyhydroquinone, 4-methoxyresorcinol and 4-methoxycatechol were 4.00, 6.05 and 8.00. The aglycone from the hydrolysates of 4 and 5 was eluted at the same R_t as methoxyhydroquinone (4.00 min).

Syringic acid β-D-glucopyranosyl ester (6). Mp 122–126° (benzene–MeOH), colourless needles, $[\alpha]_D$ −19.5° (pyridine; *c* 0.44); found: C, 46.05; H, 6.11. $C_{15}H_{20}O_{10} \cdot 3/2H_2O$ requires: C, 46.51; H, 5.99%). IR ν_{max}^{KBr} cm^{-1}: 3600–3000 (–OH), 1702 (C=O), 1606, 1515, 1460, 1425, 1335, 1220, 1115, 1100, 1080, 1040, 1030, 1015, 765. UV λ_{max}^{EtOH} nm (logε): 222 (4.36), 281 (4.11); ^{1}H NMR (C_5D_5N) 7.72 (2H, *s*, H-2, 6), 3.76 (6H, *s*, –OMe), 4.70–4.00 (sugar moiety), 6.64 (1 H, *br*, *s*, H-1′), ^{13}C NMR: see Table 4.

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