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FIVE PHENYLPROPANOID GLYCOSIDES FROM *MUSSATIA*

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Key Word Index—*Mussatia* sp., Bignoniaceae; phenylpropanoid glycosides; isolation; mussatioside; 4-vanilloyl mussatioside; 4-*p*-coumaroyl mussatioside; 4-feruloyl mussatioside; 4- cinnamoyldesxylosyl mussatioside.

Abstract—Five new phenylpropanoid glycosides, mussatioside, 4-vanilloyl mussatioside, 4-*p*-coumaroyl mussiatoside, 4-feruloyl mussatioside, and 4-cinnamoyl desxylosyl mussatioside were isolated from the methanolic extract of the bark of a *Mussatia* species. These compounds are very closely related to mussatioside I (previously isolated as the major compound of the plant). The structures of the new compounds were determined by NMR spectral data comparison of these compounds to those of mussatioside I and by chemical evidence.

INTRODUCTION

The phenylpropanoid glycosides constitute a group of natural products the known numbers of which have increased in recent years [1–4].

In the preceding paper [5], we reported the isolation and structural determination of three new phenylpropanoid glycosides, named mussatioside I, mussatioside II and mussatioside III. These are the major constituents from the methanolic extract of the bark of a new *Mussatia* species [6]. As a continuation of our investigations on the bark composition of this plant, this paper deals with the isolation and structure elucidation of five additional new phenylpropanoid glycosides (**1**–**5**). All are closely related to mussatioside I (**6**), with the only differences being in the acidic moiety acylating the C-4 hydroxy group of rhamnose in compounds **1** to **4**, and the absence of xylose in compound **5**. In order to bring some order to the nomenclature, we have designated one of the new compounds (**1**) as mussatioside. All other compounds (**2**–**8**) have now been named as mussatioside derivatives.

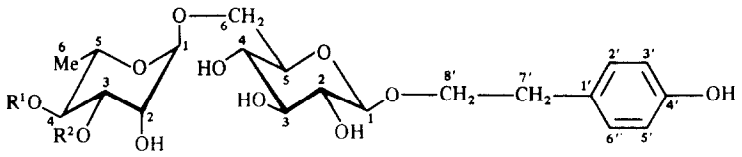
RESULTS AND DISCUSSION

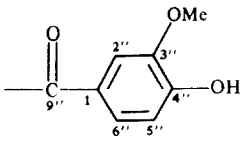
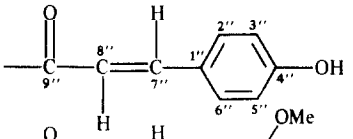
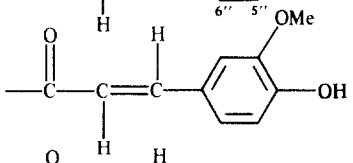
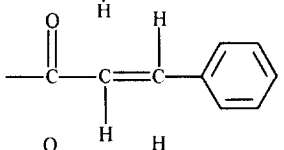
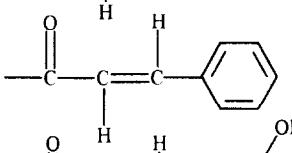
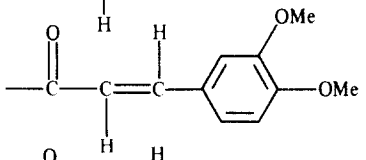
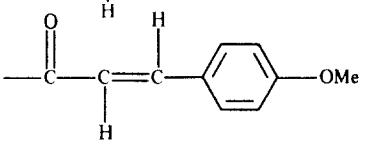
Mussatioside (**1**), was isolated as an amorphous yellow powder, $C_{25}H_{38}O_{15}$. The presence of glucose, rhamnose and xylose moieties in **1** was suggested as a result of acid hydrolysis with 4N HCl, with the sugars confirmed by PC and their ratio established as 1:1:1 by HPLC. This compound was shown to be identical with descinnamoyl mussatioside I (obtained previously [5] by alkaline hydrolysis of mussatioside I), by direct comparison of their IR, ^{1}H NMR, ^{13}C NMR, and 2D-homonuclear (COSY) spectra and by ^{13}C–^{1}H correlations.

4-Vanilloyl mussatioside (**2**) was isolated as an amorphous white powder, $C_{33}H_{44}O_{18}$. Upon acid hydrolysis, **2** gave glucose, rhamnose and xylose which were identified by PC and HPLC. The characteristic feature of this compound is the presence of a vanillyl group acylating the C-4 rhamnose hydroxyl instead of the cinnamic derivative residue which is present in the other glycosides [1–4]. The assignments of the chemical shifts for the OMe group and aromatic protons were established by 2D-homonuclear COSY and irradiation experiments. The presence of an NOE between the methoxy group and the multiplet centred at δ7.52 (2H, *m*, H-2″ and H-6″) corroborated the position of the OMe in the aromatic ring of the vanillyl group (see Fig. 1). All other ^{1}H and ^{13}C NMR spectral data are very similar to those of mussatioside I (**6**).

4-*p*-Coumaroyl mussatioside (**3**) was isolated as an amorphous white powder, $C_{34}H_{44}O_{17}$, which gave glucose, xylose and rhamnose on acid hydrolysis. The ^{1}H and ^{13}C NMR spectral data of **3** were very similar to those of mussatioside III (**8**), except for the lack of a methoxy resonance. In the downfield portion of the ^{1}H NMR spectrum of **3**, three AB systems appear. Two belong to the *p*-coumaric acid moiety, one at δ7.42 and 6.78 (each 2H, *d*, J = 8.6 Hz) for the aromatic protons, and the other at δ7.60 and 6.30 (each 1H, *d*, J = 15.9 Hz) for the *trans*-olefinic protons. The third AB system results from the *p*-hydroxyphenyl-ethyl moiety and appears at δ7.05 and 6.68 (each 2H, *d*, J = 8.5 Hz). The chemical shifts of the anomeric protons of Glu, Rham, and Xyl, that of H-4 Rham α to the ester function and that of H-3 Rham α to Xyl are essentially the same as those of mussatioside III. In the ^{13}C NMR spectrum of **3**, except for the signals corresponding to the *p*-coumaroyl moiety, the values were assigned by comparison with the ^{13}C NMR spectrum of mussatioside III (**8**).

4-Feruloyl mussatioside (**4**) was isolated as an amorphous yellow powder, $C_{35}H_{46}O_{18}$. It afforded glucose, rhamnose and xylose on complete acid hydrolysis, as determined by PC and HPLC. In this case, the ester linkage in the C-4 Rham position was formed from ferulic acid as was evident in the ^{1}H NMR spectrum of **4**, where three protons appear downfield: δ7.12 (1H, *br s*), 7.02 (1H, *d*, J = 8.1 Hz) and 6.76 (1H, *d*, J = 8.1 Hz). The position of the OMe in the aromatic ring of the ferulic acid was deduced by an NOE observed between the methoxy aromatic group and the broad singlet at δ7.12 (see Fig. 1). The rest of the signals, both in the ^{1}H and ^{13}C NMR spectra, were very close to those of mussatioside I (**6**).



		R^1	R^2
Mussatioside	**1**	H	β-D-xylose
4-Vanilloyl mussatioside	**2**		β-D-xylose
4-*p*-Coumaroyl Mussatioside	**3**		β-D-xylose
4-Feruloyl mussatioside	**4**		β-D-xylose
4-Cinnamoyl desxylosyl mussatioside	**5**		H
Mussatioside I (4-cinnamoyl mussatioside)	**6**		β-D-xylose
Mussatioside II (4-dimethylcaffeoyl mussatioside)	**7**		β-D-xylose
Mussatioside III (4-*p*-methoxycinnamoyl mussatioside)	**8**		β-D-xylose

4-Cinnamoyl desxylosylmussatioside (**5**) was isolated as an amorphous white powder, $C_{29}H_{36}O_{12}$. Acid hydrolysis of **5** with 4 N HCl gave rhamnose and glucose as the only sugars detected by PC and HPLC. The spectral data (^1H and ^{13}C NMR and 2D-homonuclear (COSY)) of **5**, as well as the behaviour by TLC, were identical to the compound without the xylose residue which was obtained previously [5] by milder acid hydrolysis of mussatioside I (**6**).

EXPERIMENTAL

NMR: 250 (^1H NMR) and 62.83 MHz (^{13}C NMR) $CDCl_3$ and CD_3OD, TMS as internal standard; MS: 70 eV; HRMS (FAB) were performed by the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, U.S.A.; IR: KBr. Rotation locular counter-current chromatography (RLCC) was performed on a Tokyo Rikakikai Co. RLCC-A apparatus. HPLC separation of the phenylpropanoid glycosides on a μ-Bondapack C_{18} column were performed using a Waters Associates Model 590 chromatograph, equipped with a UV detector operated at 254 nm and a R401 differential refractometer. Neutral alumina (Woelm N, Act. 1) was used for column chromatography. Precoated RP-8F_{254}s plates (Merck) were used for TLC. Spots were detected by UV fluorescence and spraying with Liebermann's reagent, followed by heating at 100° for 5–10 min. The conditions for GC were as follows: column GP 3% SP-2330, 2 mm i.d./2 m; column temp., 230°; carrier gas, N_2(30 ml/min). Paper chromatograms (PC) were done on Whatman No. 1 paper.

Plant materials. The major extraction and isolation was carried out on bark of *Mussatia* sp. nov. supplied by E. Wade Davis, (Botanical Museum of Harvard University). This was collected on the upper Apurimac River (Peru), a voucher deposited (EWD No. 1322) at Harvard University and identified by A. Gentry as a new species of *Mussatia*, related to *M. hyacinthia* (Standl.) Sandw. A specific taxonomic classification is awaiting additional botanical collections.

Extraction and isolation. The bark (290 g) of *Mussatia* sp. nov. was defatted with hexane and the residue extracted with MeOH and then lyophilized to give 72 g. This extract (45 g) was dissolved in a minimal amount of MeOH and the soln dropped

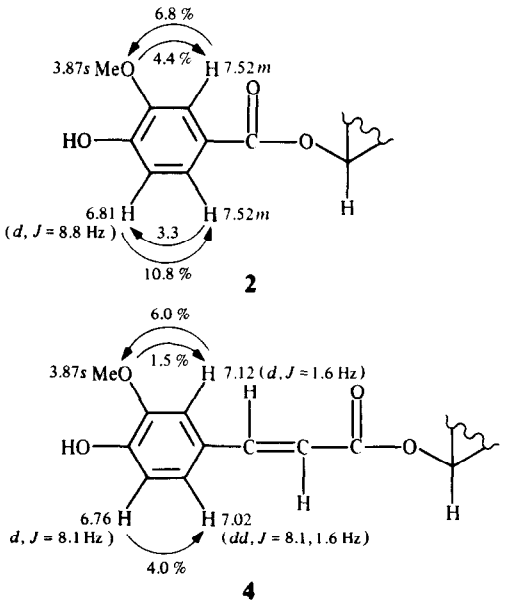


Fig. 1. NOE between the OMe group and aromatic protons in compounds **2** and **4**

into Me_2CO and centrifuged. The ppt. was filtered off and the filtrate concd and partitioned between H_2O and H_2O-satd *n*-BuOH. The aqs layer was concd under red. pres. (5.3 g), and 1 g of this extract was fractionated by RLCC, using a $CHCl_3$–MeOH–H_2O (7:13:8) solvent system (the upper layer as the mobile phase, the lower layer as the stationary phase, a flow of 0.8 ml/min and 80 r.p.m. of rotation), to give 94 mg of a compound which was purified by reversed phase HPLC with MeOH–H_2O (7:13) and 3 ml/min of flow to finally yield compound **1** (R_t 15 min, 40 mg). The *n*-BuOH extract was concd (24.8 g), loaded on a column of neutral Al_2O_3 (260 g) and rapidly eluted with *n*-BuOH–H_2O–MeOH (7:3:1) to give 17 g of a residue after concentration. 8 g of this residue was fractionated by RLCC (conditions as before) to give three fractions. The first fraction eluted from the RLCC (506 mg) was separated by reverse phase HPLC with MeOH–H_2O (29:21) as solvent and 3.5 ml/min of flow togve crude **1** and a mixture of three phenylpropanoid glycosides. Compound **1** was purified by reversed phase HPLC with MeOH–H_2O (2:3) (flow = 3 ml/min, P = 1375 p.s.i.) to give **1** (R_t 13.5 min, 150 mg). The mixture was separated by HPLC (reversed phase, MeOH–H_2O (21:29), flow = 3 ml/min, P = 869 p.s.i.) to give mainly compounds **2** (R_t 48 min, 75 mg) **3** (R_t 96 min, 15 mg) and **4** (R_t 111 min, 40 mg). The second fraction contained the three major phenylpropanoid glycosides (**6–8**) which were reported previously. The third fraction, the last eluted from the RLCC (123 mg), was purified by HPLC (reversed phase, MeOH–H_2O (29:21), flow = 3.5 ml/min) to give the compound **5** (R_t 30 min, 37 mg).

Mussatioside (*β-(4′-hydroxyphenyl)-ethyl-*O*-β-*D*-xylopyranosyl* (1→3)-O-α-L-*rhamnopyranosyl* (1→6)-O-β-D-*glucopyranoside*) (**1**). Amorphous yellow powder, $[\alpha]_D$ −36.4 (MeOH; *c* 0.22); IR ν_{max}^{KBr} cm^{-1} 3400, 1510, 1020; ^1H NMR (CD_3OD): aglycone moiety: δ2.85 (2H, *t*-like, *J* = 7.3 Hz, H-7′), 3.66 (1H, *m*, H-8′), 3.87 (1H, *m*, H-8′), 6.73 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.09 (2H, *d*, *J* = 8.5 Hz, H-2′ and H-6′); glucose moiety: δ4.31 (1H, *d*, *J* = 7.7 Hz, H-1), 3.20 (1H, *t*, *J* = 7.7, 9.0 Hz, H-2), 3.35 (1H, *t*, *J* = 9.0 Hz, H-3), 3.33 (1H, *t*, *J* = 9.0 Hz, H-4), 3.40 (1H, *m*, H-5), 3.95 and 3.66 (2H, *m*, H-6); rhamnose moiety: δ4.78 (1H, *br s*, H-1), 4.05 (1H, *d*, *J* = 3.0 Hz, H-2), 3.76 (1H, *dd*, *J* = 9.7, 3.0 Hz, H-3), 3.59 (1H, *t*, *J* = 9.7 Hz, H-4), 3.77 (1H, *m*, H-5), 1.28 (3H, *d*, *J* = 6.1 Hz, Me-5); xylose moiety: δ4.48 (1H, *d*, *J* = 7.0 Hz, H-1), 3.30 (1H, *dd*, *J* = 7.0, 9.0 Hz, H-2), 3.35 (1H, *t*, *J* = 9.0 Hz, H-3), 3.48 (1H, H-4), 3.77 and 3.16 (2H, *m*, H-5). ^{13}C NMR (CD_3OD): aglycone moiety δ130.83 (C-1′), 116.28 (C-2′ and C-6′), 130.97 (C-3′ and C-5′), 156.76 (C-4′), 36.39 (C-7′), 72.70 (C-8′); glucose, rhamnose and xylose moieties: see Table 1; FABMS *m/z* (rel. int.):

Table 1. ^{13}C NMR data for the sugar moieties of **1–6** (CD_3OD, TMS as internal standard)

	1	**2**	**3**	**4**	**5**	**6**
Glucose moiety						
1	104.46	104.45	104.54	104.40	104.56	104.46
2	75.06	75.11	75.17	75.06	75.19	75.11
3	78.05	78.00	78.11	77.98	78.11	78.04
4	71.70	71.58	71.68	71.58	71.59	71.60
5	76.79	76.61	76.71	76.57	76.69	76.63
6	68.28	68.27	68.38	68.29	68.07	68.33
Rhamnose moiety						
1	102.07	102.00	102.10	102.00	102.18	102.04
2	71.82	72.24	72.29	72.20	72.38	72.22
3	82.36	78.47	78.88	78.85	70.51	78.92
4	72.89	74.41	74.10	74.02	75.82	74.28
5	69.57	67.86	67.93	67.85	67.76	67.84
Me-5	18.01	17.99	17.89	17.87	17.93	17.88
Xylose moiety						
1	106.48	106.18	106.33	106.26	—	106.38
2	75.23	74.55	74.60	74.50	—	74.52
3	77.55	77.08	77.20	77.12	—	77.24
4	71.04	70.92	71.06	70.96	—	70.99
5	66.86	66.72	66.73	66.64	—	66.69

601 $[C_{25}H_{38}O_{15}(M)+Na]^+$ (52).

4-*Vanilloyl mussatioside* (*β-(4′-hydroxyphenyl)-ethyl-O-β-*D-*xylopyranosyl* (1→3)-O-(4-O-*vanilloyl-α-*L-*rhamnopyranosyl*) (1→6)-O-*β-*D-*glucopyranoside*) (**2**). Amorphous white powder, $[\alpha]_D$ −21.3 (MeOH; *c* 0.15); IR ν_{max}^{KBr} cm^{-1} 3400, 1700, 1600, 1510; ^1H NMR (CD_3OD): aglycone moiety: δ2.80 (2H, *t*-like, *J* = 7.3 Hz, H-7′), 3.60 (1H, *m*, H-8′), 3.95 (1H, *m*, H-8′), 6.65 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.00 (2H, *d*, *J* = 8.5 Hz, H-2′ and H-6′); glucose moiety; δ4.29 (1H, *d*, *J* = 7.8 Hz, H-1), 3.20 (1H, *dd*, *J* = 7.8, 9.0 Hz, H-2); rhamnose moiety: δ4.79 (1H, *br s*, H-1), 5.27 (1H, *t*, *J* = 9.7 Hz, H-4, 1.13 (3H, *d*, *J* = 6.3 Hz, Me-5); xylose moiety: δ4.30 (1H, *d*, *J* = 7.0 Hz, H-1), 3.10 (1H, *dd*, *J* = 7.0, 9.0 Hz, H-2); vanilloyl moiety; δ3.87 (3H, *s*, OMe), 6.81 (1H, *d*, *J* = 8.8 Hz, H-5″), 7.52 (2H, *m*, H-2″ and H-6″). ^{13}C NMR (CD_3OD): aglycone moiety: δ130.72 (C-1′), 116.25 (C-2′ and C-6′), 130.94 (C-3′ and C-5′), 156.76 (C-4′), 36.55 (C-7′), 72.34 (C-8′); glucose, rhamnose and xylose moieties: see Table 1; vanilloyl moiety: see Table 2; FABMS *m/z* (rel. int): 751 $[C_{33}H_{44}O_{18}(M)+Na]^+$ (0.11).

4-p-*Coumaroyl mussatioside* (*β-(4′-hydroxyphenyl)-ethyl-O-β-*D-*xylopyranosyl* (1→3)-O-(4-O-p-*coumaroyl-α-*L-*rhamnopyranosyl*) (1→6)-O-*β-*D-*glucopyranoside* (**3**). Amorphous white powder, $[\alpha]_D$ −35.3 (MeOH; *c* 0.27); IR ν_{max}^{KBr} cm^{-1} 3400, 1700, 1600, 1510, 1160; ^1H NMR (CD_3OD): aglycone moiety: δ2.84 (2H, *t*-like, *J* = 7.2 Hz, H-7′), 3.70 (1H, *m*, H-8′), 3.95 (1H, *m*, H-8′), 6.68 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.05 (2H, *d*, *J* = 8.5 Hz, H-2′ and H-6′); glucose moiety: δ4.30 (1H, *d*, *J* = 7.7 Hz, H-1), 3.15 (1H, *t*, *J* = 7.7, 9.0 Hz, H-2); rhamnose moiety: δ4.78 (1H, *br s*, H-1), 4.05 (1H, *d*, *J* = 3.0 Hz, H-2), 5.17 (1H, *t*, *J* = 9.7 Hz, H-4), 1.14 (3H, *d*, *J* = 6.3 Hz, Me-5); xylose moiety: δ4.34 (1H, *d*, *J* = 7.0 Hz, H-1), 3.20 (1H, *t*, *J* = 7.0, 9.0 Hz, H-2); *p*-coumaroyl moiety: δ6.30 (1H, *d*, *J* = 15.9 Hz, H-8″), 6.78 (2H, *d*, *J* = 8.6 Hz, H-3″ and H-5″), 7.42 (2H, *d*, *J* = 8.6 Hz, H-2″ and H-6″), 7.60 (1H, *d*, *J* = 15.9 Hz, H-7″). ^{13}C NMR (CD_3OD): aglycone moiety: δ130.84 (C-1′), 116.33 (C-2′ and C-6′), 131.38 (C-3′ and C-5′), 156.90 (C-4′), 36.56 (C-7′), 72.16 (C-8′); glucose, rhamnose and xylose moieties: see Table 1; *p*-coumaroyl moiety: see Table 2. FABMS *m/z* (rel. int.): 724 $[C_{34}H_{44}O_{17}(M)]^+$ (14.3).

4-*Feruloyl mussatioside* (*β-(4′-hydroxyphenyl)-ethyl-O-β-*D-*xylopyranosyl* (1→3)-O-(4-O-*feruloyl-α-*L-*rhamnopyranosyl*) (1→6)-O-*β-*D-*glucopyranoside*) (**4**). Amorphous yellow powder, $[\alpha]_D$ −30.5 (MeOH; *c* 0.20); IR ν_{max}^{KBr} cm^{-1} 3400, 1700, 1630, 1600, 1515; ^1H NMR (CD_3OD): aglycone moiety: δ2.81 (2H, *t*-like, *J* = 7.3 Hz, H-7′), 6.65(2H, *d*, *J* = 8.4 Hz, H-3′ and H-5′), 7.02 (2H, *d*, *J* = 8.4 Hz, H-2′ and H-6′); glucose moiety: δ4.27 (1H, *d*, *J* = 7.7 Hz, H-1); rhamnose moiety: δ4.77 (1H, *br s*, H-1), 5.16 (1H, *t*, *J* = 9.6 Hz, H-4), 1.12 (3H, *d*, *J* = 6.2 Hz, Me-5); xylose moiety: δ4.32 (1H, *d*, *J* = 6.9 Hz, H-1); feruloyl moiety: δ6.32 (1H, *d*, *J* = 15.9 Hz, H-8″), 6.76 (1H, *d*, *J* = 8.1 Hz, H-5″), 7.02 (1H, *dd*, *J* = 8.1, 1.6 Hz, H-6″), 7.12 (1H, *d*, *J* = 1.6 Hz, H-2″), 7.58 (1H, *d*, *J* = 15.9 Hz, H-7″), 3.81 (3H, *s*, OMe). ^{13}C NMR (CD_3OD): aglycone moiety: δ130.75 (C-1′), 116.29 (C-2′ and C-6′), 131.28 (C-3′ and C-5′), 156.76 (C-4′), 36.44 (C-7′), 72.08 (C-8′); glucose, rhamnose and xylose moieties: see Table 1; feruloyl moiety: see Table 2. FABMS-HR *m/z* (rel. int.): 755.2781 $[C_{35}H_{46}O_{18}(M)+H]^+$ (0.5).

4-*Cinnamoyl desxylosyl mussatioside* (*β-4′-hydroxyphenyl)-ethyl-*O-(4-O-*cinnamoyl-α-*L-*rhamnopyranosyl*) (1→6)-O-*β-*D-*glucopyranoside* (**5**). Amorphous white powder $[\alpha]_D$ −25.2 (Me_2CO; *c* 0.32); IR ν_{max}^{KBr} cm^{-1} 3400, 1700, 1630, 1510, 1180; ^1H NMR (CD_3OD): aglycone moiety: δ2.85 (2H, *t*-like, H-7′), 3.75 (1H, *m*, H-8′), 3.95 (1H, *m*, H-8′), 6.68 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.06 (2H, *d*, *J* = 8.5 Hz, H-2′ and H-6′); glucose moiety: δ4.31 (1H, *d*, *J* = 7.7 Hz, H-1), 3.20 (1H, *t*, *J* = 7.7, 9.0 Hz, H-2); rhamnose moiety: δ4.81 (1H, *br s*, H-1), 3.91 (1H, *d*, *J* = 3.0 Hz, H-2), 3.97 (1H, *dd*, *J* = 9.4, 3.0 Hz, H-3), 5.06 (1H, *t*, *J* = 9.4 Hz, H-4), 3.90 (1H, *m*, H-5), 1.16 (3H, *d*, *J* = 6.3 Hz, Me-5); cinnamoyl moiety: δ6.52 (1H, *d*, *J* = 16.0 Hz, H-8″), 7.39 (3H, *m*, H-3″, H-4″, and H-5″), 7.57 (2H, *m*, H-2″ and H-6″), 7.70 (1H, *d*, *J* = 16.0 Hz, H-7″). ^{13}C NMR (CD_3OD): aglycone moiety: δ130.10 (C-1′), 116.28 (C-2′ and C-6′), 131.61 (C-3′ and C-5′), 156.94 (C-4′), 36.58 (C-7′), 72.15 (C-8′); glucose, rhamnose and xylose moieties: see Table 1; cinnamoyl moiety: see Table 2. FABMS *m/z* (rel. int.): 577 $[C_{29}H_{36}O_{12}(M)+H]^+$ (9).

General procedure for acid hydrolysis of compounds **1**–**5**. A soln of the compound in 4 M HCl (2 ml) was refluxed for 1 hr. Then H_2O was added and the mixture was extracted with $CHCl_3$. The aq. layer was neutralized with Ag_2CO_3, the ppt. filtered off and the filtrate evapd *in vacuo* giving a residue which was identified by comparison with authentic samples of D-glucose, D-xylose and L-rhamnose by PC (*n*-BuOH–C_6H_6–pyridine–H_2O 10:2:6:3) and HPLC (Biorad HPX 87 H^+ column, using H_2O as solvent and a flow of 0.7 ml/min, *P* = 800 p.s.i.; glucose R_t 8.15 min, xylose R_t 8.74 min and rhamnose R_t 9.19 min).

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Table 2. ^{13}C NMR data of acid groups linked to C-4 of the rhamnose moiety in compounds **2**–**5** (CD_3OD, TMS as internal standard)

C	Vanillic group in **2**	*p*-Coumaric group in **3**	Ferulic group in **4**	Cinnamic group in **5**
1″	122.69	127.33	127.61	135.84
2″	114.10	116.89	111.94	130.99
3″	153.13	131.00	150.93	129.37
4″	148.90	161.38	149.43	130.10
5″	116.08	131.00	116.60	129.37
6″	125.40	116.89	124.35	130.99
7″		147.15	147.47	146.72
8″		115.25	115.32	118.98
9″	168.03	169.04	169.01	168.52
OMe	56.60		56.49	

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