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HYDROXYCINNAMIC ACID ESTERS FROM *POLYGALA CHAMAEBUXUS*

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Key Word Index—*Polygala chamaebuxus*; Polygalaceae; ferulic acid ester; sinapic acid ester; sucrose ester.

Abstract—Three new glycosides have been isolated from the aerial parts of *Polygala chamaebuxus* by preparative liquid chromatography on an axially-compressed silica column. The compounds were identified as 1,3-diesters of β-D-fructofuranosyl-α-D-glucopyranoside with sinapoyl, feruloyl and acetyl ester moieties on the furanose ring. The structures were elucidated by a combination of chemical and spectroscopic methods (D/CI-MS, ^{1}H and ^{13}C NMR).

INTRODUCTION

Plants of the genus *Polygala* have to be considered as a potential source of pharmacologically-active compounds, since various xanthones [1], lignans [2, 3], saponins [4–6], flavonoids [7] and coumarins [8, 9] have been isolated from American and Asian species. In contrast, very little is known about the constituents of European *Polygala* species. In our search for natural products with biological activities, we therefore investigated *P. chamaebuxus*. This perennial, creeping plant is widely distributed in the European Alps. Only the presence of the triterpene presenegenin has been reported previously from this species [10].

A preliminary TLC investigation of the methanolic extract of the aerial parts revealed, apart from numerous saponins, a complex pattern of spots showing blue fluorescence under UV 366 light. In this paper we report the isolation and structure elucidation of three of these UV-active compounds.

RESULTS AND DISCUSSION

The methanolic extract of the aerial parts of *P. chamaebuxus* was separated into eight fractions by preparative liquid chromatography on an axially-compressed silica column with $CHCl_3$–MeOH–H_2O (70:30:5). Further purification by the same technique, using EtOAc–MeOH–H_2O (100:14:7) as eluent gave seven fractions (A–G). Fraction C consisted of pure compound **1**. Fraction D, upon preparative liquid chromatography with CH_2Cl_2–MeOH–H_2O (40:10:1), yielded pure compounds **2** and **3**.

Acid hydrolysis of **1–3** destroyed the aglycones, but glucose and fructose were detected by TLC, as well as by GC of the per-trimethylsilyl derivatives. After mild basic hydrolysis of the glycosides, both ferulic and sinapic acids in the case of compound **1**, sinapic and ferulic acids for **2** and **3**, respectively, were identified by TLC. A disaccharide, identical to sucrose with regard to chromatographic behaviour and staining, was found in all three cases.

The desorption/chemical ionization (D/CI) [11] mass spectrum of compound **2** showed quasimolecular ions at *m/z* 772 $[M+NH_4]^+$ and 755 $[M+H]^+$. The successive elimination of two sinapoyl moieties was indicated by fragment ions at *m/z* 566 $[M+NH_4-206]^+$ and 360 $[M+NH_4-412]^+$. The peaks appearing at *m/z* 592 $[M+NH_4-180]^+$ and 575 $[M+H-180]^+$ were due to the loss of one hexose unit. Both sinapoyl residues were therefore attached to the other sugar unit. The positions of attachment of the acyl moieties were determined by the ^{1}H NMR spectral data of **2** and of its peracetate **2b**. The assignment of sugar protons was based on decoupling experiments, and on the 2D-homonuclear (COSY) spectrum of **2** (Fig. 1 and Table 1). Chemical shifts and

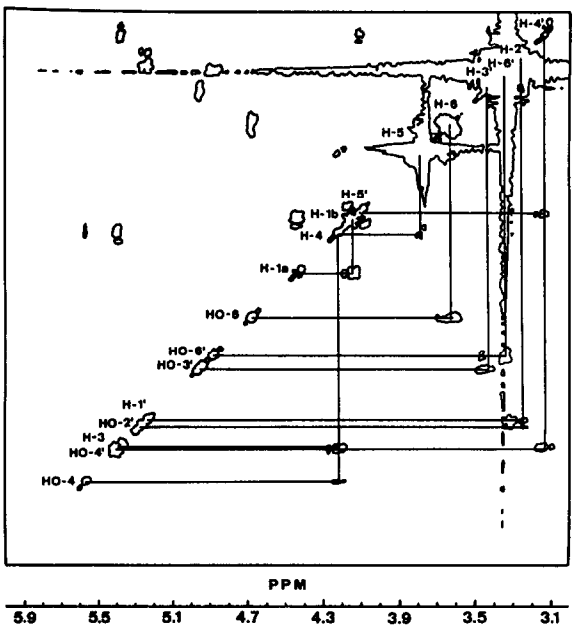
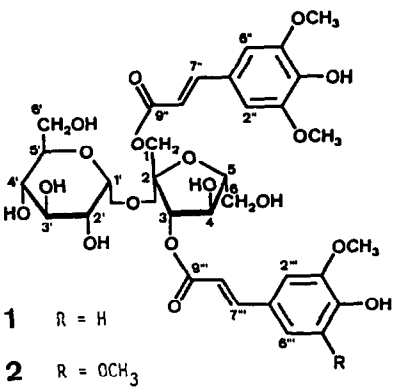


Fig. 1. 2-D Homonuclear ^{1}H NMR spectrum (COSY) of compound **2** (300 MHz, DMSO-d_6). The contour plot shows the region of the sugar protons. Correlations are indicated by the lines H 1,2 . . . = protons of fructose; H 1′,2′ . . . = protons of glucose.

Table 1. ^{1}H NMR spectral data of compounds **1**, **1c**, **2**, **3**, **3c**, (DMSO-d_6–D_2O), **1b**, **2b** and **3b** ($CDCl_3$)

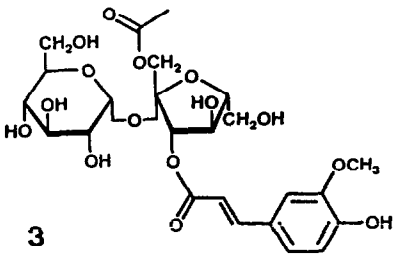
	1*	**1b***	**1c***	**2†**	**2b†‡**	**3***	**3b***	**3c***
H-1a	4.45 $J_{1a,1b}=11$§	4.20–4.42	4.33 $J_{1a,1b}=11$	4.44 $J_{1a,1b}=11$	4.20–4.40	4.37 $J_{1a,1b}=10$	4.10–4.42	3.70
H-1b	4.15		4.15–4.25	4.12		4.00		3.50
H-3	5.43 $J_{3,4}=9$	5.63 $J_{3,4}=6$	3.95 $J_{3,4}=9$	5.37 $J_{3,4}=8$	5.61 $J_{3,4}=6$	5.37 $J_{3,4}=8$	5.63 $J_{3,4}=6.5$	5.37 $J_{3,4}=8$
H-4	4.25 $J_{4,5}=9$	5.48 $J_{4,5}=6$	4.20	4.22 $J_{4,5}=8$	5.46 $J_{4,5}=6.5$	4.07 $J_{4,5}=8$	5.52 $J_{4,5}=6.5$	4.13 $J_{4,5}=8$
H-5	3.82	4.20–4.42	3.90	3.70	4.26	3.77	4.10–4.42	3.78
H-6a	3.65	4.20–4.42	3.63	3.60	4.30–4.45	3.62	4.10–4.42	3.62
H-6b								
H-1′	5.30 $J_{1',2'}=4$	5.73 $J_{1',2'}=4$	5.25 $J_{1',2'}=4$	5.26 $J_{1',2}=3.5$	5.73 $J_{1',2'}=3.5$	5.25 $J_{1',2'}=4$	5.72 $J_{1',2'}=4$	5.22 $J_{1',2'}=4$
H-2′	3.32 $J_{2',3'}=9$	4.95 $J_{2',3'}=10$	3.27 $J_{2',3'}=10$	3.27 $J_{2',3'}=10$	4.95 $J_{2',3'}=10.5$	3.27 $J_{2',3'}=9$	4.95 $J_{2',3'}=10$	3.22 $J_{2',3'}=9$
H-3′	3.47 $J_{3',4'}=9$	5.48 $J_{3',4'}=10$	3.50 $J_{3',4'}=10$	3.44 $J_{3',4'}=9.5$	5.47 $J_{3',4'}=10$	3.42 $J_{3',4'}=9$	5.48 $J_{3',4'}=10$	3.44 $J_{3',4'}=9$
H-4′	3.17 $J_{4',5'}=9$	5.08 $J_{4',5'}=10$	3.10 $J_{4',5'}=10$	3.13 $J_{4',5'}=9.5$	5.07 $J_{4',5'}=10$	3.08 $J_{4',5'}=9$	5.07 $J_{4',5'}=10$	3.20 $J_{4',5'}=9$
H-5′	4.13	4.20–4.42	4.05	4.10	4.26	4.00	4.10–4.42	3.92
H-6a′	3.37	4.20–4.42	3.38	3.35	4.20–4.30	3.35	4.10–4.42	3.42
H-6b′								
H-2″	7.05	6.78	7.08	7.10	6.80			
H-3″	—	—	—	—	—			
H-6″	7.05	6.78	7.08	7.10	6.80			
H-7″	7.58 $J_{7'',8''}=6$	7.60 $J_{7'',8''}=16$	7.58 $J_{7'',8''}=16$	7.64 $J_{7'',8''}=16$	7.59 $J_{7'',8''}=16$			
H-8″	6.55	6.51	6.58	6.57	6.50			
MeO-3″	3.80	3.85	3.80	3.90	3.87			
MeO-5″								
H-2‴	7.30	7.30 $J_{2''',6'''}=2$		7.10	6.90	7.30	7.32 $J_{2''',6'''}=2$	7.33
H-5‴	6.83 $J_{5''',6'''}=8$	7.05 $J_{5''',6'''}=8$		—	—	6.81 $J_{5''',6'''}=8$	7.07 $J_{5''',6'''}=8$	6.82 $J_{5''',6'''}=8$
H-6‴	7.18	7.18		7.10	6.90	7.18	7.22	7.15
H-7‴	7.65 $J_{7''',8'''}=16$	7.72 $J_{7''',8'''}=16$		7.73 $J_{7''',8'''}=16$	7.67 $J_{7''',8'''}=16$	7.62 $J_{7''',8'''}=16$	7.75 $J_{7''',8'''}=16$	7.63 $J_{7''',8'''}=16$
H-8‴	6.45	6.48		6.64	6.46	6.44	6.50	6.45
MeO-3‴	3.83	3.90				3.82	3.92	3.85
MeO-5‴	—	—		3.95	3.88	—	—	—
AcO-1						2.03		
AcO		1.88, 1.96			1.89, 1.97		1.88, 1.98	
		2.07, 2.09			2.08, 2.10		2.07, 2.09	
		2.10 (2x)			2.11 (2x)		2.12, 2.14 (2x)	
		2.30, 2.33			2.34 (2x)		2.32	

*200 MHz.
†250 MHz.
‡The values of the sinapoyl moieties are interchangeable.
§Coupling constants (J) in Hz.



1 R = H

2 R = OCH_3



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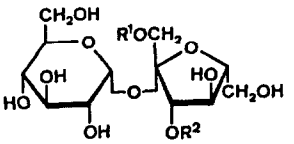

1c R^1 = sinapoyl, R^2 = H

3c R^1 = H, R^2 = feruloyl

Table 2. ^{13}C NMR chemical shifts of compounds 1, 2 and 3 (90.25 MHz, DMSO-d_6)

	1	2*	3
C-1	64.14 *t*	64.17 *t*	64.14 *t*
C-2	103.08 *s*	103.12 *s*	103.17 *s*
C-3	77.31 *d*	77.34 *d*	77.56 *d*
C-4	70.57 *d*	70.61 *d*	70.73 *d*
C-5	82.91 *d*	82.96 *d*	82.92 *d*
C-6	63.60 *t*†	63.65 *t*†	63.66 *t*†
C-1′	90.97 *d*	90.95 *d*	91.21 *d*
C-2′	71.38 *d*	71.42 *d*	71.46 *d*
C-3′	73.09 *d*	73.12 *d*	73.17 *d*
C-4′	70.15 *d*	70.14 *d*	70.24 *d*
C-5′	72.59 *d*	72.64 *d*	72.92 *d*
C-6′	62.23 *t*†	62.20 *t*†	62.19 *t*†
C-1″	124.45 *s*	124.46 *s*	
C-2″	106.28 *d*	106.31 *d*	
C-3″	148.08 *s*	148.10 *s*	
C-4″	138.39 *s*	138.47 *s*	
C-5″	148.08 *s*	148.10 *s*	
C-6″	106.28 *d*	106.31 *d*	
C-7″	145.28 *d*	145.27 *d*	
C-8″	114.88 *d*	114.89 *d*	
C-9″	166.67 *s*	166.67 *s*	
MeO-3″	56.07 *q*	56.11 *q*	
MeO-5″			
C-1‴	125.55 *s*	124.38 *s*	125.60 *s*
C-2‴	111.68 *d*	106.32 *d*	111.91 *d*
C-3‴	149.41 *s*	148.11 *s*	149.53 *s*
C-4‴	147.95 *s*	138.47 *s*	148.18 *s*
C-5‴	114.30 *d*	148.14 *s*	114.39 *d*
C-6‴	122.74 *d*	106.32 *d*	122.72 *d*
C-7‴	145.46 *d*	145.74 *d*	145.60 *d*
C-8‴	115.63 *d*	114.76 *d*	115.59 *d*
C-9‴	165.62 *s*	165.53 *s*	165.64 *s*
MeO-3‴	55.70 *q*	56.14 *q*	55.82 *q*
MeO-5‴			
MeCOO-1			20.53 *q*
MeCOO-1			170.50 *s*

*The values of the sinapoyl moieties are interchangeable.

†Values are interchangeable.

coupling constants were in good agreement with values reported for sucrose [12]. However, the signals attributed to H-1a, H-1b and H-3 of fructose appeared 0.5–1 ppm downfield, and the presence of free hydroxyl groups at C-2′, C-3′, C-4′ and C-6′ of glucose and at C-4 and C-6 of the fructose unit suggested a 1,3-disubstitution of the fructofuranosyl ring. In the ^1H NMR spectrum of the octaacetate **2b**, the chemical shifts of the protons H-1a, H-1b and H-3 remained virtually unchanged, when compared with **2**, whereas the signals of H-4, H-6, H-2′, H-3′, H-4′ and H-6′ underwent a significant downfield shift of 0.7–2.0 ppm. The data for the sugar protons of peracetate **2b** were almost identical with values published for sucrose octaacetate [13] and hydropiperoside octaacetate [14]. Compound **2** was therefore identified as β-D-(1,3-disinapoyl)-fructofuranosyl-α-D-glucopyranoside. The ^{13}C NMR spectral data (Table 2) confirmed the nature of the acyl moieties. The signals of the sugar carbon atoms were attributed on the basis of off-resonance decoupling, comparison with reported data of sucrose [15] and hydropiperoside [14], and by application of acetylation shifts [16].

In the D/CI mass spectrum of the mixed ester **1**, quasimolecular ions appeared at *m/z* 742 $[M+NH_4]^+$ and 725 $[M+H]^+$. The important fragment ions at *m/z* 566 $[M+NH_4-176]^+$ and 536 $[M+NH_4-206]^+$ were due to the elimination of a feruloyl and a sinapoyl residue, respectively. The independent cleavage of a hexose unit was indicated by the peak at *m/z* 545 $[M+H-180]^+$. Thus, ferulic and sinapic acid must be attached to the same sugar unit. The fragment ions at *m/z* 404, 387, 369, 360 and 339 resulted from further cleavage of acyl or hexose moieties. The ^{13}C and ^1H NMR spectra (Tables 1 and 2) confirmed the presence of ne sinapoyl and one feruloyl group. The data for the disaccharide moiety of **1** and octaacetate **1b** were almost identical with the values measured for **2** and **2b**, proving the 1,3-substitution of the fructofuranosyl ring. The exact positions of esterification of the two different acids was established by partial hydrolysis. Mild treatment of diester **1** with 10% NH_3 in

MeOH–H_2O (2:1) at room temperature yielded compound **1c**. The D/CI mass spectrum and the ^1H NMR data identified **1c** as sinapoylsucrose. The signals of the sugar protons were unchanged in comparison to **1**, except for the doublet attributable to H-3, which was significantly shifted upfield by 1.5 ppm, appearing at δ3.95. The sinapic acid was therefore esterified at C-1, establishing compound **1** as β-D-(1-sinapoyl-3-feruloyl)-α-D-glucopyranoside.

The D/CI mass spectrum of compound **3** showed quasimolecular ions at *m/z* 578 $[M+NH_4]^+$ and 561 $[M+H]^+$. The elimination of acetyl and feruloyl moieties was indicated by ions at *m/z* 536 $[M+NH_4-42]^+$ and 402 $[M+NH_4-176]^+$. As with **1** and **2**, elimination of a hexose unit occurred, resulting in a fragment peak at *m/z* 381 $[M+H-180]^+$. The signals appearing at *m/z* 662, 645, 620 and 603, as well as the fragment ions at *m/z* 486 and 444 were artefacts, due to migration of acetyl groups during the desorption process. The ^{13}C and ^1H NMR spectra of **3** (Table 1 and 2) confirmed the presence of one acetyl and one feruloyl moiety. The ^1H NMR data of **3** and peracetate **3b** confirmed the 1,3-substitution pattern of the fructofuranosyl ring. Mild hydrolysis of **3** with 10% NH_3 in MeOH–H_2O (2:1) gave exclusively the feruloylsucrose ester **3c**. In the ^1H NMR spectrum of **3c**, the AB quartet of H-1a and H-1b appeared at 0.5 ppm higher field than in **3**, whereas the signals of the other sugar protons were not affected. Thus, the structure of **3** could be established as β-D-(1-acetyl-3-feruloyl)-fructofuranosyl-α-D-gluco-pyranoside.

Hydroxycinnamic acids are known to occur in the genus *Polygala* as free acids or esterified with saponins [4–6]. Furthermore, the presence of some complex esters with glucose has been reported from *P. senega*, although the structures were not elucidated completely [17]. Esters of hydroxycinnamic acids with sucrose have now been found for the first time in the family Polygalaceae. Very few analogous compounds have been described from plants [14, 18, 19], in spite of the widespread occurrence of the phenylpropanoic acids and of sucrose. The three isolated compounds are new natural products; **1** and **3** represent, to our knowledge, the first mixed esters of this type.

EXPERIMENTAL

General. Mps are uncorr. D/CIMS were measured on a quadrupole instrument. ^1H NMR data were determined with 300, 250 and 200 MHz instruments. ^{13}C NMR spectra were obtained at 90.25 MHz.

Plant material. P. chamaebuxus L. was collected near Champex VS. A voucher specimen has been deposited at the Institute of Pharmacognosy, University of Lausanne.

Extraction and isolation. Isolation of compounds **1–3** was carried out with a prep. LC (column id 40 × 500 mm). The column was packed with a slurry of 180 g silica gel (15 μm) (Merck). For the final purification of compounds **1–3** and their derivatives, a Sephadex LH 20 column (MeOH) was used. TLC were carried out on silica gel precoated Al sheets (Merck). Aerial parts of *P. chamaebuxus* (150 g) were extracted at room temp with petrol, $CHCl_3$ and MeOH. The MeOH extract (30 g) was subjected to prep. LC on silica gel in 3 portions of 10 g each. Eight fractions were collected. Further separation of fraction 3 (3 53 g) with EtOAc–MeOH–H_2O (100:14:7) yielded seven fractions (A–G). Fraction C consisted of pure compound **1** (184 mg). Compounds **2** (97 mg) and **3** (35 mg) were obtained after chromatography of fraction D (986 mg) with CH_2Cl_2–MeOH–H_2O (40:10:1).

Acetylation of **1–3**. To a pyridine (1 ml) soln of compound (20 mg), Ac_2O (1 ml) was added. The mixture was kept at room temp for 36 hr. The soln was poured into ice-H_2O and the crude peracetate was purified on Sephadex LH 20 with MeOH.

Acidic hydrolysis. The ester (1 mg) was refluxed in 4 ml 1 N HCl for 1 hr. The soln was extracted with Et_2O. The aq. layer was adjusted to pH 6 with $NaHCO_3$. After evapn to dryness, the residue was extracted with pyridine. Glucose and fructose were identified by TLC on silica gel with EtOAc–MeOH–H_2O–HOAc (13:3:3:4) (detection with naphthoresorcine) and by GC according to ref. [20].

Basic hydrolysis. Compound (1 mg) was stirred overnight in 5 ml 2% NaOH at room temp. The cinnamic acids were extracted with Et_2O and identified by TLC on silica gel with C_6H_6–dioxane–MeOH–HOAc (90:25:5:4); detection with UV 366 and $FeCl_3$. The aq. phase was treated as described above and sucrose was identified by TLC.

β-D-(1-Sinapoyl-3-feruloyl)fructofuranosyl-α-D-glucopyranoside (**1**). Amorphous powder; mp 131–136°; TLC (silica gel, CH_2Cl_2–MeOH–H_2O, 40:10:1): R_f 0.38, (silica gel, EtOAc–MeOH–H_2O, 100:14:7): R_f 0.54; UV λ_{max}^{MeOH} nm (ε): 220 (24 100), 238 (25 800), 329 (34 800); ^1H NMR (200 MHz, DMSO-d_6–D_2O): see Table 1; ^{13}C NMR (90.25 MHz, DMSO-d_6): see Table 2; D/CIMS (NH_3, positive ions) *m/z*: 742 $[M+NH_4]^+$, 725 $[M+H]^+$, 566 $[M+NH_4-176]^+$, 545 $[M+H-180]^+$, 536 $[M+H-206]^+$, 404 $[M+NH_4-338]^+$, 387 $[M+H-338]^+$, 369 $[M+H-356]^+$, 360 $[M+NH_4-412]^+$, 339 $[M+H-386]^+$. (Found C, 52.80; H, 5.50; O, 41.70. $C_{33}H_{40}O_{18}\cdot 1\frac{1}{2}H_2O$ requires C, 52.73; H, 5.77; O, 41.50%.)

Octaacetate of **1** (**1b**). Acetylation of **1** (20 mg) yielded **1b** (15 mg) as an amorphous, white powder; mp 93–98°; UV λ_{max}^{MeOH} nm: 216 sh, 222, 288; ^1H NMR (200 MHz, $CDCl_3$): see Table 1.

β-D-(1-Sinapoyl)fructofuranosyl-α-D-glucopyranoside (**1c**). Compound **1** (70 mg) in 10% NH_3 in MeOH–H_2O (2:1, 10 ml) were kept at room temp for 7 hr. NH_3 and MeOH were removed under red. pres. and the aq. soln lyophilized. Monoester **1c** (11 mg) was isolated from the reaction mixture by chromatography on a Lobar LichroPrep silica gel 60 (40–60 μm) size A column (Merck) with EtOAc–MeOH–H_2O (20:2:1). Amorphous powder; mp 118–123°; UV λ_{max}^{MeOH} nm: 223, 238, 329; ^1H NMR (200 MHz, DMSO-d_6–D_2O). see Table 1; D/CIMS (NH_3, positive ions) *m/z*: 566 $[M+NH_4]^+$, 387 $[M+H-162]^+$, 369 $[M+H-180]^+$, 360 $[M+NH_4-206]^+$

β-D-(1,3-Disinapoyl)fructofuranosyl-α-D-glucopyranoside (**2**). Amorphous powder; mp 136–141°; TLC (silica gel, CH_2Cl_2–MeOH–H_2O, 40:10:1): R_f 0.39; (silica gel, EtOAc–MeOH–H_2O, 100:14:7): R_f 0.50; UV λ_{max}^{MeOH} nm: (ε): 229 (27 000), 240 (30 500), 330 (36 500); ^1H NMR (250 MHz, DMSO-d_6–D_2O): see Table 1; ^{13}C NMR (90.25 MHz, DMSO-d_6): see Table 2, D/CIMS (NH_3, positive ions) *m/z*: 772 $[M+NH_4]^+$, 755 $[M+H]^+$, 575 $[M+H-180]^+$, 566 $[M+NH_4-206]^+$, 404 $[M+NH_4-368]^+$, 387 $[M+H-368]^+$, 369 $[M+H-386]^+$, 360 $[M+NH_4-412]^+$). (Found C, 52.28; H, 6.00; O, 41 72. $C_{34}H_{42}O_{19}\cdot 1\frac{1}{2}H_2O$ requires C, 52.24; H, 5.80; O, 41.95%.)

Octaacetate of **2** (**2b**). Acetylation of compound **2** (20 mg) gave **2b** (21 mg) as an amorphous, white powder; mp 101–105°; UV λ_{max}^{MeOH} nm: 225, 297; ^1H NMR (250 MHz, $CDCl_3$): see Table 1

*β-D-(1-acetyl-3-feruloyl)fructofuranosyl-α-D-*glucopyranoside (**3**). Amorphous powder; mp 97–103°; TLC (silica gel, CH_2Cl_2–MeOH–H_2O, 40:10:1): R_f 0.29; (silica gel, EtOAc–MeOH–H_2O, 100:14:7): R_f 0.51; UV λ_{max}^{MeOH} nm (ε): 219

(14 200), 236 (13 000), 302 sh, 327 (22 300); ^{1}H NMR (200 MHz, DMSO-d_6–D_2O): see Table 1; ^{13}C NMR (90.25 MHz, DMSO-d_6): see Table 2; D/CIMS (NH_3, positive ions) m/z: 578 $[M+NH_4]^+$, 561 $[M+H]^+$, 536 $[M+NH_4-42]^+$, 402 $[M+NH_4-176]^+$, 381 $[M+H-180]^+$, 360 ($[M+NH_4-218]^+$), 339 $[M+H-222]^+$. (Found C, 50.03; H, 6.05; O, 43.92. $C_{24}H_{32}O_{15}\cdot H_2O$ requires C, 49.83; H, 5.92; O, 44.25%.)

Octaacetate of **3** (**3b**). Upon acetylation of **3** (20 mg), 23 mg of the octaacetate **3b** were obtained. Amorphous, white powder; mp 60–64°; UV λ_{max}^{MeOH} nm: 212, 230 sh, 281, 310 sh; ^{1}H NMR (200 MHz, $CDCl_3$): see Table 1.

β-D-(3-feruloyl)fructofuranosyl-α-D-glucopyranoside (**3c**). Compound **3** (20 mg) was dissolved in 10% NH_3 in MeOH–H_2O (2:1) and kept at room temp for 60 min. NH_3 and MeOH were removed under red. pres. and the remaining soln lyophilized. The residue was purified on Sephadex LH 20 to yield 16 mg of ester **3c**. Amorphous powder; mp 105–111°; UV λ_{max}^{MeOH} nm: 217, 234, 299 sh, 327; ^{1}H NMR (200 MHz, DMSO-d_6–D_2O): see Table 1; D/CIMS (NH_3, positive ions) m/z: 536 $[M+NH_4]^+$, 519 $[M+H]^+$, 360 $[M+NH_4-176]^+$, 339 $[M+H-180]^+$.

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