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BITTER PHENYLPROPANOID GLYCOSIDES FROM *LILIUM SPECIOSUM* VAR. *RUBRUM*

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Key Word Index—*Lilium speciosum* var. *rubrum*; Liliaceae; bitter phenylpropanoid glycosides; ferulic acid esters; sucrose esters.

Abstract—Seven bitter ferulic acid esters of sucrose have been isolated from *Lilium speciosum* var. *rubrum*. These compounds were identified as 3,6′-diferuloylsucrose, 4-acetyl-3,6′-diferuloylsucrose, 6-acetyl-3,6′-diferuloylsucrose, 4′-acetyl-3,6′-diferuloylsucrose, 4,6-diacetyl-3,6′-diferuloylsucrose, 6,3′-diacetyl-3,6′-diferuloylsucrose and 4,6,3′-triacetyl-3,6′-diferuloylsucrose on the basis of spectroscopic studies.

INTRODUCTION

Bulbs of the genus *Lilium* (Liliaceae) are used in traditional Chinese medicine and some have a very bitter taste. However, there have been few reports on the phenolic compounds in bulbs of *Lilium* species [1].

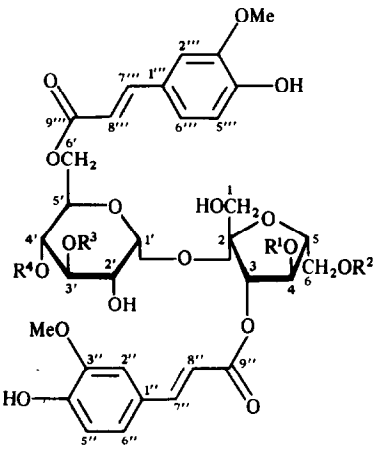
In the course of our search for the bitter substances, seven bitter phenylpropanoid glycosides, 3,6′-diferuloylsucrose and its derivatives, have been isolated from a methanolic bulb extract of *L. speciosum* Thumb. var. *rubrum* Masters. 3,6′-Diferuloylsucrose has already been detected in the anthers of many Liliaceae taxa [2, 3], but the six other derivatives are new compounds.

RESULTS AND DISCUSSION

The methanolic extract of fresh bulbs of *L. speciosum* var. *rubrum* was separated into a chloroform soluble part and an *n*-butanol soluble part. The latter was further fractionated by silica gel and Sephadex LH-20 column chromatography, giving seven compounds (**1**–**7**). By a combination of chemical and spectroscopic methods (Table 1 and Experimental), **1** was identified as 3,6′-diferuloylsucrose [2, 3].

Compounds **2**–**7** were amorphous white powders, and their IR, UV and ^{1}H NMR spectra were very similar to those of **1**. The IR, EI/MS and ^{1}H NMR spectra of **2** showed the presence of an aliphatic acetyl group attached to diferuloylsucrose. The positions of attachment of the acyl moieties were determined by the ^{1}H NMR spectral data. The signals attributed to H-3, H-4, H-6′a and H-6′b appeared *ca* 0.6–1.4 ppm downfield as compared with those of sucrose, which suggested a 3,4,6′-trisubstitution. Acetylation of **2** with Ac_2O–pyridine gave the hepta-acetate of **2**, whose IR, ^{1}H NMR and ^{13}C NMR, and TLC precisely agreed with those of the octaacetate of **1**. Consequently, two feruloyl moieties were present in the C-3, and C-6′ hydroxy positions as in **1** and an acetyl group in the C-4 hydroxy position. Thus, **2** was established as 4-acetyl-3,6′-diferuloylsucrose. In the same way, **3** and **4** were established as 6-acetyl-3,6′-diferuloylsucrose and 4′-acetyl-3,6′-diferuloylsucrose, respectively (Table 1 and Experimental).

The ^{1}H NMR spectrum of **5** showed the presence of two acetyl groups attached to diferuloylsucrose, and the signals attributed to H-3, H-4, H-6, H-6′a and H-6′b appeared *ca* 0.7–1.5 ppm downfield as compared with those of sucrose suggesting a 3,4,6,6′-tetrasubstitution. The IR, ^{1}H NMR and ^{13}C NMR spectra, and TLC of the peracetate of **5** also precisely agreed with those of the octaacetate of **1**. The structure of **5** was therefore established as 4,6-diacetyl-3,6′-diferuloylsucrose. In the same way, **6** was identified as 6,3′-diacetyl-3,6′-diferuloylsucrose.



	R¹	R²	R³	R⁴
1	H	H	H	H
2	Ac	H	H	H
3	H	Ac	H	H
4	H	H	H	Ac
5	Ac	Ac	H	H
6	H	Ac	Ac	H
7	Ac	Ac	Ac	H

Table 1. ^{1}H NMR spectral data (400 MHz) for 1–7 and sucrose

	1	2	3	4	5	6	7	Sucrose
H-1a	4.21 *br s*	4.22 *d J* = 12.4	4.16 *br s*	4.11 *br s*	4.21 *d J* = 12.0	4.09 *br s*	4.18 *d J* = 12.5	4.31 *d J* = 12.1
H-1b		4.14 *d J* = 12.4			4.15 *d J* = 12.0		4.14 *d J* = 12.5	4.27 *d J* = 12.1
H-3	6.34 *d J* = 8.0	6.38 *d J* = 6.4	6.30 *d J* = 8.2	6.17 *d J* = 7.3	6.40 *d J* = 6.8	6.32 *d J* = 8.4	6.45 *d J* = 7.6	4.94 *d J* = 7.9
H-4	5.27 *dd J* = 8.0, 8.0	6.17 *dd J* = 6.4, 6.4	5.21 *dd J* = 8.2, 8.2	5.06 *dd J* = 7.3, 7.3	6.05 *dd J* = 6.8, 6.8	5.13 *dd J* = 8.4, 8.4	6.08 *dd J* = 7.6, 7.6	4.98 *dd J* = 7.9, 7.9
H-5	4.67 *ddd J* = 8.0, 6.4, 4.0	4.62 *ddd J* = 6.4, 6.4, 5.2	4.71 *ddd J* = 8.2, 7.8, 3.0	4.54 *ddd J* = 7.3, 6.4, 4.1	4.63 *ddd J* = 7.0, 6.8, 4.1	4.62 *ddd J* = 8.4, 7.4, 3.3	4.64 *ddd J* = 7.6, 6.8, 4.8	4.47 *m*
H-6a	4.55 *dd J* = 12.0, 6.4	4.48 *dd J* = 12.5, 6.4	4.99 *dd J* = 11.6, 3.0	4.37 *dd J* = 12.9, 6.4	4.94 *dd J* = 12.1, 4.1	4.92 *dd J* = 11.9, 7.4	4.92 *dd J* = 12.0, 4.8	4.32 *dd J* = 12.1, 4.8
H-6b	4.44 *dd J* = 12.0, 4.0	4.38 *dd J* = 12.5, 5.2	4.97 *dd J* = 11.6, 7.8	4.31 *dd J* = 12.9, 4.1	4.92 *dd J* = 12.1, 7.0	4.87 *dd J* = 11.9, 3.3	4.88 *dd J* = 12.0, 6.8	4.26 *dd J* = 12.1, 3.0
H-1′	6.10 *d J* = 4.0	6.01 *d J* = 3.6	6.06 *d J* = 3.7	5.94 *d J* = 3.8	6.02 *d J* = 3.6	6.04 *d J* = 3.7	6.07 *d J* = 3.8	6.13 *d J* = 3.9
H-2′	4.06 *dd J* = 9.6, 4.0	4.06 *dd J* = 9.4, 3.6	4.06 *dd J* = 9.3, 3.7	3.95 *dd J* = 9.6, 3.8	4.09 *dd J* = 9.2, 3.6	4.11 *dd J* = 9.7, 3.7	4.21 *dd J* = 9.6, 3.8	4.11 *dd J* = 9.2, 3.9
H-3′	4.43 *dd J* = 9.6, 9.6	4.52 *dd J* = 9.4, 9.4	4.49 *dd J* = 9.3, 9.3	4.40 *dd J* = 9.6, 9.6	4.51 *dd J* = 9.2, 9.2	6.00 *dd J* = 9.7, 9.7	6.11 *dd J* = 9.6, 9.6	4.61 *dd J* = 9.2, 9.2
H-4′	4.01 *dd J* = 9.6, 9.6	3.99 *dd J* = 9.4, 9.4	3.92 *dd J* = 9.3, 9.3	5.31 *dd J* = 9.6, 9.6	3.98 *dd J* = 9.2, 9.2	4.00 *dd J* = 9.7, 9.7	4.11 *dd J* = 9.6, 9.6	4.16 *dd J* = 9.2, 9.2
H-5′	4.98 *ddd J* = 9.6, 7.2, 2.0	4.96 *ddd J* = 9.4, 6.7, 0.8	5.01 *ddd J* = 9.3, 7.6, 1.5	4.81 *ddd J* = 9.6, 6.5, 2.1	4.90 *m*	4.96 *ddd J* = 9.7, 6.9, 1.6	5.03 *ddd J* = 9.6, 6.0 1.3	4.71 *ddd J* = 9.2, 4.5, 2.0
H-6′a	5.19 *dd J* = 12.0, 2.0	5.19 *dd J* = 11.4, 0.8	5.27 *dd J* = 11.7, 1.5	4.67 *dd J* = 12.1, 2.1	5.25 *dd J* = 12.0, 1.1	5.20 *dd J* = 11.6, 1.6	5.27 *dd J* = 11.7, 1.3	4.46 *dd J* = 11.6, 2.0
H-6′b	4.82 *dd J* = 12.0, 7.2	4.87 *dd J* = 11.4, 6.7	4.72 *dd J* = 11.7, 7.6	4.47 *dd J* = 12.1, 6.5	4.83 *dd J* = 12.0, 6.7	4.70 *dd J* = 11.6, 6.9	4.87 *dd J* = 11.7, 6.0	4.30 *dd J* = 11.6, 4.5
Aromatic protons	7.40–7.00	7.40–7.00	7.45–7.05	7.35–6.95	7.40–7.05	7.40–7.05	7.40–7.10	
Trans alkene protons	8.00 *d J* = 15.8	8.03 *d J* = 15.8	8.01 *d J* = 15.8	7.88 *d J* = 15.8	8.05 *d J* = 15.8	7.99 *d J* = 15.8	8.09 *d J* = 15.8	
	7.92 *d J* = 15.8	7.91 *d J* = 15.8	7.94 *d J* = 15.8	7.87 *d J* = 15.8	7.92 *d J* = 15.8	7.91 *d J* = 15.8	7.95 *d J* = 15.8	
	6.70 *d J* = 15.8	6.86 *d J* = 15.8	6.85 *d J* = 15.8	6.74 *d J* = 15.8	6.79 *d J* = 15.8	6.79 *d J* = 15.8	6.81 *d J* = 15.8	
	6.60 *d J* = 15.8	6.63 *d J* = 15.8	6.63 *d J* = 15.8	6.58 *d J* = 15.8	6.66 *d J* = 15.8	6.64 *d J* = 15.8	6.72 *d J* = 15.8	
OMe	3.81 *s*	3.85 *s*	3.89 *s*	3.81 *s*	3.87 *s*	3.87 *s*	3.90 *s*	
	3.77 *s*	3.84 *s*	3.88 *s*	3.74 *s*	3.86 *s*	3.79 *s*	3.86 *s*	
Ac	—	2.05 *s*	1.98 *s*	1.96 *s*	2.01 *s*	1.92 *s*	2.03 *s*	
					1.96 *s*	1.86 *s*	1.99 *s*	
							1.93 *s*	

All assignments were confirmed by double resonance experiments.
In C_5D_5N–CD_3OD = 4:1.
J values in Hz.

Compound 7 was shown to be the triacetyl derivative of 1, and its structure established as 4,6,3′-triacetyl-3,6′-diferuloylsucrose by the same methods as above.

The seven ferulic acid esters of sucrose have a bitter taste. There have been a few reports on the esters of cinnamic acid derivatives with sucrose [2–6]. These derivatives also would expected to be bitter.

EXPERIMENTAL

Plant material. Dormant bulbs of *L. speciosum* var. *rubrum* were purchased from Sakata-shubyoo Co., Ltd. in Kanagawa Prefecture.

Extraction and isolation. The fresh bulbs (7.2 kg) were cut into pieces and extracted twice with MeOH under reflux. The extract was concd under red. press., and the residue suspended in H_2O. This suspension was extracted with $CHCl_3$ and *n*-BuOH, successively. The *n*-BuOH soluble part was repeatedly subjected to CC on silica gel and on Sephadex LH-20, giving seven compounds (1–7).

Compound 1. Amorphous white powder (3.9 g), $[\alpha]_D^{25}$ −80.2° (EtOH; *c* = 1.00). IR ν_{max}^{KBr} cm^{-1}: 3350, 1690, 1620, 1590, 1510; UV λ_{max}^{EtOH} nm (log ε): 237 (4.21), 300sh (4.40), 327 (4.58); EI/MS 70 eV, *m/z*: 338, 194, 177, 150, 135, 107; ^{1}H NMR: see Table 1.

Basic hydrolysis of 1. Compound 1 was treated with 3% NaOMe–MeOH for 2 hr at room temp., and methyl ferulate and sucrose were obtained. Methyl ferulate was identified by comparison with an authentic sample (IR, ^{1}H NMR and TLC) and sucrose by direct GC (OV-17 G-SCOT 20 m; 200°; N_2; FID) comparison with an authentic sample of the TMS–ether.

Acetylation of 1. Treatment of 1 with Ac_2O–pyridine overnight at room temp. gave the octaacetate of 1 as an amorphous white powder, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1640, 1600, 1510; EI/MS 70 eV, *m/z*: 507, 465 219, 177; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71, 7.62, 6.50, 6.45 (each 1H, *d*, *J* = 16.0 Hz, *trans* alkene protons), 7.30–7.00 (6H, aromatic protons), 5.71 (1H, *d*, *J* = 3.6 Hz, H-1′), 5.60 (1H, *d*, *J* = 6.1 Hz, H-3), 5.47 (1H, *dd*, *J* = 6.1, 6.1 Hz, H-4), 5.46 (1H, *dd*, *J* = 9.5, 9.5 Hz, H-3′), 5.06 (1H, *dd*, *J* = 9.5, 9.5 Hz, H-4′), 4.94 (1H, *dd*, *J* = 9.5, 3.6 Hz, H-2′), 4.45–4.15 (8H, overlapping, H-1, 5, 6, 5′, 6′), 3.90, 3.87 (each 3H, *s*, OMe), 2.31–1.88 (3H × 8, each *s*, OAc); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.6, 170.3, 170.0, 169.9, 169.8, 169.6, 168.7, 168.6 (MeCO), 166.4, 165.5 (C-9″, 9‴), 151.6 × 2 (C-3″, 3‴), 146.4, 145.0 (C-7″, 7‴), 142.0, 141.6 (C-4″, 4‴), 133.3, 133.0 (C-1″, 1‴), 123.3, 123.2 (C-6″, 6‴), 122.0, 121.7 (C-5″, 5‴), 117.6, 116.5 (C-8″, 8‴), 111.6, 111.5 (C-2″, 2‴), 104.0 (C-2), 90.2 (C-1′), 79.1 (C-5), 76.3 (C-3), 75.0 (C-4), 70.2, 69.7, 68.7 × 2 (C-2′, 3′, 4′, 5′ interchangeable), 63.8 × 2 (C-1, 6), 62.2 (C-6′), 56.2 × 2 (OMe × 2), 20.7, 20.6, 20.4 (MeCO).

Compound 2. Amorphous white powder (420 mg), $[\alpha]_D^{25}$ −75.7° (EtOH; *c* = 0.30). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1635, 1600, 1520; UV λ_{max}^{EtOH} nm (log ε): 237 (4.45), 300sh (4.45), 328 (4.62); EI/MS 70 eV, *m/z*: 380, 338, 194, 177, 150, 135; ^{1}H NMR: see Table 1.

Compound 3. Amorphous white powder (390 mg), $[\alpha]_D^{25}$ −71.6° (EtOH; *c* = 0.35). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1640, 1600, 1520; UV λ_{max}^{EtOH} nm (log ε): 235 (4.27), 300sh (4.33), 327 (4.50); EI/MS 70 eV, *m/z*: 380, 338, 194, 177, 150, 135; ^{1}H NMR: see Table 1.

Compound 4. Amorphous white powder (720 mg), $[\alpha]_D^{25}$ −83.3° (EtOH; *c* = 0.90). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1630, 1600, 1520; UV λ_{max}^{EtOH} nm (log ε): 237 (4.37), 300sh (4.40), 328 (4.59); EI/MS 70 eV, *m/z*: 380, 338, 194, 177, 150, 135; ^{1}H NMR: see Table 1.

Compound 5. Amorphous white powder (800 mg), $[\alpha]_D^{25}$ −76.4° (EtOH; *c* = 0.45). IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1640, 1600, 1520; UV λ_{max}^{EtOH} nm (log ε): 235 (4.35), 300sh (4.58), 327 (4.54); EI/MS 70 eV, *m/z*: 380, 338, 194, 177, 150, 135; ^{1}H NMR: see Table 1.

Compound 6. Amorphous white powder (162 mg), $[\alpha]_D^{18}$ −40.8° (EtOH; *c* = 0.78). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1630, 1600, 1515; UV λ_{max}^{EtOH} nm (log ε): 234 (4.57), 300sh (4.65), 327 (4.81); EI/MS 70 eV, *m/z*: 380, 338, 247, 194, 177, 150; ^{1}H NMR: see Table 1.

Compound 7. Amorphous white powder (82 mg), $[\alpha]_D^{18}$ −44.4° (EtOH; *c* = 0.50). IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1630, 1600, 1520; UV λ_{max}^{EtOH} nm (log ε), 234 (4.44), 300sh (4.52), 327 (4.67); EI/MS 70 eV, *m/z*: 422, 380, 338, 247, 194, 177; ^{1}H NMR: see Table 1.

Acetylation of 2–7. Treatment of 2–7 with Ac_2O–pyridine overnight at room temp. gave the heptaacetates of 2–4, the hexaacetates of 5–6 and the pentaacetate of 7, respectively. The IR, ^{1}H NMR and ^{13}C NMR, and TLC of the peracetates of 2–7 precisely agreed with those of the peracetate of 1.

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