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PHENOLIC GLYCERIDES FROM *LILIUM AURATUM*

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Abstract Phenolic glycerides have been isolated from fresh bulbs of *Lilium auratum*. By spectral and chemical means, they have been identified as the new components, 1,2-*O*-diferuloylglycerol, a mixture of 1-*O*-feruloyl-2-*O*-*p*-coumaroylglycerol and 1-*O*-*p*-coumaroyl-2-*O*-feruloylglycerol, 1-*O*-feruloylglycerol and the known compounds, 1,3-*O*-diferuloylglycerol, 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol and 1-*O*-*p*-coumaroylglycerol.

INTRODUCTION

During our search for bitter substances of natural origin, we have previously isolated bitter phenylpropanoid glycosides, 3,6'-diferuloylsucrose and its derivatives, from *Lilium speciosum* var. *rubrum* [1]. Glycerol glucosides, liliosides A–E, have been recently reported as the characteristic constituents of the genus *Lilium* [2–4].

The present communication deals with structure determination of the new phenolic glycerides, 1,2-*O*-diferuloylglycerol, a mixture of 1-*O*-feruloyl-2-*O*-*p*-coumaroylglycerol and 1-*O*-*p*-coumaroyl-2-*O*-feruloylglycerol, and 1-*O*-feruloylglycerol, isolated from the methanolic extract of *L. auratum*.

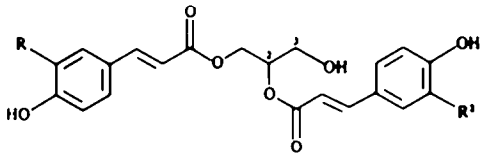
RESULTS AND DISCUSSION

The MeOH extract of the fresh bulbs of the plant was extracted with $CHCl_3$ and then with *n*-BuOH. From the $CHCl_3$ soluble fraction, phenolic diglycerides (**1**–**4**) were isolated, and from the *n*-BuOH soluble fraction phenolic monoglycerides (**5**, **6**) were isolated after repeated CC on silica gel and Sephadex LH-20.

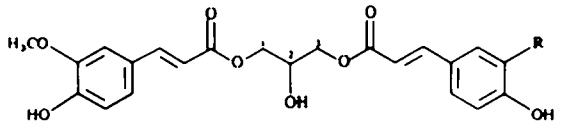
Compound **1**, $C_{23}H_{24}O_9$, was colourless and amorphous. The UV and IR spectra of **1** showed hydroxy groups (3300 cm^{-1}), aromatic rings (1590, 1515 cm^{-1}; λ_{max} 237, 327 nm) and carbonyl groups of an aromatic ester (1700 cm^{-1}). The EI mass spectrum and ^1H NMR of **1** indicated the presence of two feruloyl moieties (*m/z* 444 $[M]^+$, 194 (ferulic acid), 177 (feruloyl group); δ 7.65, 7.63, 6.35, 6.32 (each *d*, *J* = 16.0 Hz), 3.93 (6H, *s*)). Hydrolysis of **1** with 3% NaOMe/MeOH gave methyl ferulate and glycerol. In the ^1H NMR spectrum, the signals for the two OCH_2 groups of glycerol were observed at δ 4.50 (*d*, *J* = 6.0 Hz) and δ 3.87 (*m*), and the signal of an OCH group at δ 5.29 (*m*), which revealed that the feruloyl moieties were located at the asymmetrical positions on a glycerol residue, namely glycerol C-1 and C-2 hydroxyl positions. Thus, **1** was identified as 1,2-*O*-diferuloylglycerol.

Compound **2** was obtained as a mixture of two similar phenolic diglycerides (**2a** and **2b**); efforts to separate the two were unsuccessful. The EI mass spectrum of **2** gave one $[M]^+$ at *m/z* 414, and the highest fragment ions at *m/z* 177 and 147, corresponding to a feruloyl and a *p*-coumaroyl moiety, respectively. Hydrolysis of **2** with NaOMe/MeOH afforded methyl ferulate, methyl *p*-coumarate and glycerol. The ^1H NMR spectrum of **2** indicated that **2a** and **2b** were 1,2-disubstituted glycerols. Compound **2** was thus determined to be a mixture of 1-*O*-feruloyl-2-*O*-*p*-coumaroylglycerol (**2a**) and 1-*O*-*p*-coumaroyl-2-*O*-feruloylglycerol (**2b**). The aromatic methoxyl groups of the feruloyl moieties of the mixture were observed at δ 3.92 and 3.91 in the ^1H NMR spectrum in the approximate ratio of 1:1.

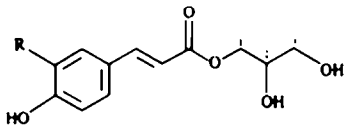
Compounds **3** and **4** were phenolic 1,3-disubstituted diglycerides whose structures were confirmed as 1,3-*O*-diferuloylglycerol and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol, respectively. These compounds have been isolated previously from the fruits of *Aegilops ovata* [5].



	R^1	R^2
1	OCH_3	OCH_3
2a	OCH_3	H
2b	H	OCH_3



	R
3	OCH_3
4	H



	R
5	OCH_3
6	H

Compounds **5** and **6** were phenolic monoglycerides. The EI mass spectrum, ^{1}H NMR and basic hydrolysis indicated that the aromatic acid constituting **5** was a ferulic acid and that the aromatic acid constituting **6** was a *p*-coumaric acid. In the ^{1}H NMR spectrum of **5**, the signals attributed to two OCH_2 groups of the glycerol moiety appeared at δ4.23 (*m*) and 3.60 (*d*, J = 5.5 Hz), showing that the ferulic acid was linked to one of the primary hydroxyl groups of glycerol. Thus, the structure of **5** was established as 1-*O*-feruloylglycerol. In the same way, **6** was identified as 1-*O*-*p*-coumaroylglycerol. Compound **6** has been detected in *Ananas comosus* var. *cayenne* [6].

Compounds **1**, **2**, **5** and **6** were obtained as racemates. In the case of **4**, no rotation was observed either, but it was not clear whether this was because **4** was a racemate or because the substituents of C-1 and C-3 hydroxy groups of glycerol had very similar structures.

Natural phenolic glycerides are known to occur in Gramineae [5, 7, 8], Bromeliaceae [6] and Salicaceae [8, 9]. In the known phenolic diglycerides, the aromatic acid moieties are located at positions C-1 and C-3 of glycerol. The present diglycerides (**1** and **2**), in which one of the aromatic acids is linked to the C-2 hydroxy group of glycerol, are new constituents, and there has been no previous report on the isolation of 1-*O*-feruloylglycerol (**5**) from a natural source.

EXPERIMENTAL

Extraction and isolation. Dormant fresh bulbs of *L. auratum* Lindle. (4.1 kg) purchased from Heiwaen Co., Japan, were exhaustively extracted with hot MeOH (9 l.). The MeOH extract was concd under red. press. The dark viscous concentrate was partitioned between H_2O and $CHCl_3$, and then between H_2O and *n*-BuOH. Each partition was repeated twice. To obtain **1**–**4**, the $CHCl_3$ sol. fraction was repeatedly subjected to CC on silica gel with various solvent systems and on Sephadex LH-20 with $CHCl_3$ or MeOH as eluent. From the MeOH sol. fraction, **5** and **6** were isolated by the same procedure.

Compound **1**. Amorphous white powder (58 mg), $[\alpha]_D^{15} \pm 0$ ($CHCl_3$; *c* 0.60). IR ν_{max}^{KBr} cm^{-1}: 3300, 1700, 1625, 1590, 1515; UV λ_{max}^{EtOH} nm (log ε): 237 (4.42), 301sh (4.47), 327 (4.63); EI/MS 70 eV, *m/z* (rel. int.): 444 [M]$^+$ (12), 194 (8), 177 (100), 145 (12), 101 (19); ^{1}H NMR (90 MHz, $CDCl_3$): δ7.65, 7.63, 6.35, 6.32 (each 1H, *d*, J = 16.0 Hz, *trans* alkene protons), 7.12–6.85 (6H, aromatic protons), 5.29 (1H, *m*, glycerol H-2), 4.50 (2H, *d*, J = 6.0 Hz, glycerol H-1), 3.93 (6H, *s*, OMe × 2), 3.87 (2H, *m*, glycerol H-3).

Compound **2**. Amorphous pale-yellow powder (20 mg), $[\alpha]_D^{20} \pm 0$ (CH_3COCH_3; *c* 1.00). IR ν_{max}^{KBr} cm^{-1}: 3350, 1690, 1625, 1600, 1515; UV λ_{max}^{EtOH} nm (log ε): 230 (4.56), 300sh (4.72), 317 (4.84); EI/MS 70 eV, *m/z* (rel. int.): 414 [M]$^+$ (17), 268 (6), 221 (8), 194 (17), 177 (100), 164 (12), 147 (100), 119 (22); ^{1}H NMR (400 MHz, acetone-d_6): δ7.70 7.60, 6.43 6.33 (*trans* alkene protons), 7.58 7.53, 6.92 6.84 (aromatic protons of *p*-coumaric moieties), 7.37 7.16, 7.16 7.13, 6.92–6.84 (aromatic protons of feruloyl moieties), 5.29–5.20 (glycerol H-2), 4.53 4.48, 4.42–4.35 (glycerol H-1), 3.92, 3.91 (each *s*, OMe), 3.84 3.77 (glycerol H-3).

Compound **3**. Amorphous white powder (55 mg), IR ν_{max}^{KBr} cm^{-1}: 3400, 1680, 1625, 1600, 1515; UV λ_{max}^{EtOH} nm (log ε): 235 (4.51), 299sh (4.56), 327 (4.73); EI/MS 70 eV, *m/z* (rel. int.): 444 [M]$^+$ (22), 224 (8), 194 (37), 177 (100), 145 (10), 99 (26); ^{1}H NMR (90 MHz, $CDCl_3$): δ7.60, 6.30 (each 2H, *d*, J = 16.0 Hz, *trans* alkene protons), 7.15 6.80 (6H, aromatic protons), 4.43 4.20 (5H, overlapping, glycerol H-1,2,3), 3.87 (3H, *s*, OMe).

Compound **4**. Amorphous pale-yellow powder (68 mg), $[\alpha]_D^{15} \pm 0$ ($CHCl_3$; *c* 1.75). IR ν_{max}^{KBr} cm^{-1}: 3300, 1690, 1625, 1595, 1515; UV λ_{max}^{EtOH} nm (log ε): 235sh (4.56), 301sh (4.72), 317 (4.78); EI/MS 70 eV, *m/z* (rel. int.): 414 [M]$^+$ (7), 268 (27), 238 (12), 194 (27), 177 (55), 164 (27), 147 (100), 119 (14); ^{1}H NMR (90 MHz, acetone-d_6): δ7.62 (2H, *d*, J = 16.0 Hz, *trans* alkene protons), 6.41, 6.38 (each 1H, *d*, J = 16.0 Hz, *trans* alkene protons), 7.52 6.75 (7H, aromatic protons), 4.35 4.11 (5H, overlapping, glycerol H-1,2,3), 3.90 (3H, *s*, OMe).

Compound **5**. Colourless syrup (43 mg), $[\alpha]_D^{15} \pm 0$ (MeOH; *c* 0.35). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1700, 1625, 1595, 1505; UV λ_{max}^{EtOH} nm (log ε): 235sh (4.05), 301sh (4.06), 326 (4.21); EI/MS 70 eV, *m/z* (rel. int.): 268 [M]$^+$ (68), 194 (60), 177 (100), 145 (25), 117 (10); ^{1}H NMR (90 MHz, CD_3OD): δ7.65, 6.37 (each 1H, *d*, J = 16.0 Hz, *trans* alkene protons), 7.15 6.75 (3H, aromatic protons), 4.23 (2H, *m*, glycerol H-1), 3.85 (3H, *s*, OMe), 3.80 (1H, *m*, glycerol H-2), 3.60 (2H, *d*, J = 5.5 Hz, glycerol H-3).

Compound **6**. Amorphous white powder (19 mg), $[\alpha]_D^{15} \pm 0$ (MeOH; *c* 0.40); IR ν_{max}^{KBr} cm^{-1}: 3350, 1700, 1625, 1590, 1510; UV λ_{max}^{MeOH} nm (log ε): 228 (4.14), 302sh (4.32), 313 (4.36); EI/MS 70 eV, *m/z* (rel. int.): 238 [M]$^+$ (18), 164 (38), 147 (100), 119 (15); ^{1}H NMR (90 MHz, CD_3OD): δ7.67, 6.38 (each 1H, *d*, J = 16.0 Hz, *trans* alkene protons), 7.48, 6.83 (each 2H, *d*, J = 9.0 Hz, aromatic protons), 4.25 (2H, *m*, glycerol H-1), 3.87 (1H, *m*, glycerol H-2), 3.63 (2H, *d*, J = 5.5 Hz, glycerol H-3).

Basic hydrolysis of **1**–**6**. Glycerides (**1**–**6**) were treated with 3% NaOMe/MeOH for 2 hr at room temp. Each gave cinnamic acid derivatives and glycerol. The cinnamic acid derivatives were identified by TLC on silica gel with $CHCl_3$–MeOH; detection, UV light (254 nm) and 10% H_2SO_4 followed by heating. Glycerol was identified as its TMSi ether by GC (OV-17 SCOT, 20 m, 100°, N_2, FID) comparison with an authentic sample.

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