(above) produced an isomeric pair dominated by **1**. ^{1}H NMR data (δ): 8.07 *d*, J = 8.6 Hz, H-2′6′; 6.91 *d*, J = *ca* 8.6 Hz, H-3′5′; 6.92 *s*, H-3; 4.64 *d*, J = 9.8 Hz, glucose H-1; 3.83 *s*, 3.90 *s*, OMe.

Acknowledgements—The authors are grateful to Dr K Morgan and particularly to Dr H Wong of Chemistry Division, DSIR, for the running of numerous NMR spectra.

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Phytochemistry, Vol. 28, No. 1, pp. 301 303, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00
Pergamon Press plc.

FLAVONOL AND PHENYLPROPANOID GLYCOSIDES FROM *LILIUM CORDATUM*

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(*Received in revised form* 18 *May* 1988)

Key Word Index—*Lilium cordatum*; Liliaceae; flavonoids; isorhamnetin glycosides; phenylpropanoid glucosides.

Abstract—Four flavonol glycosides and four phenyl-propanoid glucosides were isolated from a methanolic petal extract of *Lilium cordatum*. These structures were established as isorhamnetin 3-glucoside, 3-glucoside-7-rhamnoside, 3-rutinoside and 3-rutinoside-7-rhamnoside and isoeugenol, *p*-propenylphenol, coniferyl alcohol and *p*-coumaryl alcohol glucosides, respectively.

INTRODUCTION

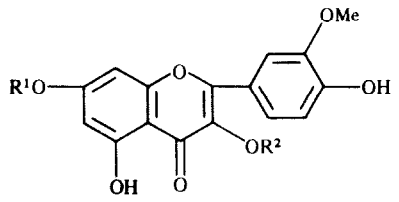
In a previous paper we reported two steroidal alkaloid glycosides [1] and two furostanol glycosides [2] from petals of *Lilium cordatum* (Thunb.) Koidz. In a continuation of our investigation of this plant, we have isolated four flavonol and four phenylpropanoid glycosides and established their structures on the basis of chemical and spectral evidence.

RESULTS AND DISCUSSION

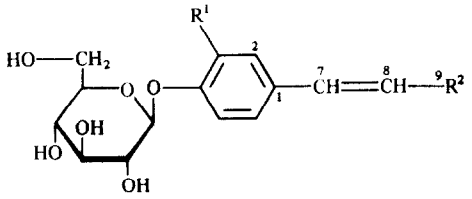
The remaining fractions previously obtained by silica gel column chromatography of the methanolic petal extract of *L. cordatum*, were subjected to a combination of Sephadex LH-20 and silica gel column chromatography with various solvent systems to afford compounds **1–8**.

Compounds **1–4** were all positive to flavonoid colour reactions and their IR and UV spectra suggested they were flavonoid glycosides. Compounds **1–3** were identified as isorhamnetin 3-glucoside, 3-glucoside-7-rhamnoside and 3-rutinoside, respectively by standard procedures (FABMS, acid hydrolysis to aglycone and sugar, UV analysis and ^{13}C NMR) [3–5].

The FABMS spectrum of **4** showed a peak at *m/z* 793 $[M+Na]^+$. Acid hydrolysis gave isorhamnetin, glucose and rhamnose. On enzymic hydrolysis with crude hesperidinase **4** liberated product identical with isorhamnetin 3-rutinoside (**3**), and rhamnose. The ^{13}C NMR spectrum of **4** suggested that one additional rhamnopyranosyl residue



1 R^1 = H, R^2 = -β-D-Glc
2 R^1 = α-L-Rha, R^2 = -β-D-Glc
3 R^1 = H, R^2 = -β-D-Glc^{6}—α-L-Rha
4 R^1 = α-L-Rha, R^2 = -β-D-Glc^{6}—α-L-Rha



5 R^1 = OMe, R^2 = Me
6 R^1 = H, R^2 = Me
7 R^1 = OMe, R^2 = CH_2OH
8 R^1 = H, R^2 = CH_2OH

was bound to the 7-hydroxyl of isorhamnetin. Therefore, compound **4** could be represented as isorhamnetin 3-*O*-rutinoside-7-*O*-α-L-rhamnopyranoside, a new natural product. However a rhamnosylglucoside-7-rhamnoside has been reported from petals of *Eustoma grandiflorum* Griseb (Gentianaceae) [6].

The IR spectra of **5**–**8** were similar to each other, suggesting the presence of hydroxyl groups (3400 cm^{-1}) and aromatic ring (1610–1600 and 1520–1500 cm^{-1}). The ^1H NMR spectrum of **5** showed a secondary methyl group [δ1.76 (3H, *d*, J = 6 Hz)], a methoxyl group [δ3.74 (3H, *s*)], one anomeric proton [δ 5.68 (1H, *d*, J = 7 Hz)], two *trans* olefinic protons as ABX_3 type signals δ 6.08 (1H, *dq*, J = 6, 16 Hz) and 6.38 (1H, *d*, J = 16 Hz)] and aromatic protons [δ 6.95 (1H, *dd*, J = 2.0, 8.0 Hz), 7.10 (1H, *d*, J = 2.0 Hz), and 7.48 (1H, *d*, J = 8.0 Hz)]. In a NOE experiment, irradiation of methoxyl signal at δ 3.74 resulted in a 15.8% NOE enhancement of the aromatic proton signal δ7.10 (*d*, J = 2.0 Hz). On enzymic hydrolysis with β-glucosidase, **5** liberated D-glucose and isoeugenol [4-(1-propenyl)-3-methoxyphenol] (TLC and GLC). Accordingly, **5** was concluded to be isoeugenol β-D-glucopyranoside. The ^{13}C NMR spectrum of **5** is given in Table 1.

Compound **6** was obtained as an amorphous powder. The ^1H NMR spectrum of **6** was similar to that of **5**, except for the absence of a methoxyl signal and an A_2B_2 type pattern signals of aromatic protons. And the EIMS spectrum of **6** showed the M^+ peak at *m/z* 296, hexosyl cation at *m/z* 162 and propenylphenol cation at *m/z* 134. The above result was evidenced by the ^{13}C NMR spectrum. Thus, the structure of **6** was established as 4-(1-propenyl)-phenol β-D-glucopyranoside.

Compound **7** showed a M^+ peak at *m/z* 342 in the EIMS spectrum. The ^1H and ^{13}C NMR spectra of **7** were similar to those of **5** except that signals due to a carbinyl methylene group were observed at δ4.28 (2H, *d*, J = 5.6 Hz) and δ63.9 (*t*) instead of signals due to a vinyl methyl at δ1.76 and δ18.1. In addition, the occurrence of a sugar moiety was deduced from the anomeric resonance (δ4.88, *d*, J = 7.3 Hz) and also from the ^{13}C NMR data (Table 1). Moreover, in a NOE experiment, irradiation of the methoxyl signal at δ3.86 resulted in a 15% NOE enhancement of the aromatic proton signal at δ 7.06 (*d*, J = 2.0 Hz). Thus, **7** was identified as coniferin [4-(3-hydroxypropenyl)-3-methoxyphenol β-D-glucopyranoside].

Compound **8** was obtained as an amorphous powder, whose ^1H NMR spectrum showed a pattern similar to that of **7** except that the aromatic proton signals showed as an A_2B_2 type pattern at δ6.98 and 7.35 (2H each, *d*, J = 8.5 Hz). The ^{13}C NMR spectrum of **8** was compared with that of **7** and could be assigned as in Table 1. Accordingly, **8** was deduced to be *p*-coumaryl alcohol [4-(3-hydroxypropenyl)-phenol] β-D-glucopyranoside.

This is the first report of the isoeugenol, *p*-propenylphenol and *p*-coumaryl alcohol glucosides.

EXPERIMENTAL

Isolation of compounds. The remaining fractions previously obtained from the methanolic extract of the petals of *L. cordatum* were chromatographed on silica gel and Sephadex LH-20 columns to afford **1** (244 mg), **2** (100 mg), **3** (29 mg), **4** (21 mg), **5** (130 mg), **6** (258 mg), **7** (98 mg) and **8** (182 mg).

Isorhamnetin 3-rutinoside (**3**). ^1H NMR (d_6-DMSO): 0.94 (3H, *d*, J = 5.0 Hz, rha-Me), 3.78 (3H, *s*, OMe), 4.38 (1H, *br s*, rha 1-H), 5.38 (1H, *d*, J = 7 Hz, glc 1-H), 6.16 (1H, *d*, J = 2.0 Hz, 6-H), 6.38 (1H, *d*, J = 2.0 Hz, 8-H), 6.85 (1H, *d*, J = 8.0 Hz, 5′-H), 7.46 (1H, *dd*, J = 2.0, 8.0 Hz, 6′-H), 7.80 (1H, *d*, J = 2.0 Hz, 2′-H). FABMS *m/z*: 647 $[M+Na]^+$. ^{13}C NMR (d_6-DMSO): 156.4, 133.0, 177.3, 161.1, 98.7, 164.0, 93.7, 156.4, 104.0, 121.0, 113.3, 149.4, 146.8, 115.0, 122.3, 55.7, 101.2, 74.2, 76.4, 70.0, 75.9, 66.8, 100.8, 70.3, 70.6, 71.8, 68.2, 17.6.

Isorhamnetin 3-O-rutinoside-7-O-α-L-rhamnopyranoside (**4**). Pale yellow needles, mp 181–184°, $[\alpha]_D^{19}$ −71.0° (pyridine; *c* 1.09), UV λ_{max} nm in MeOH: 254, 263 (sh), 353; +NaOAc: 260, 414; +$AlCl_3$: 268, 296 (sh), 362 (sh), 403. ^1H NMR (C_5D_5N): 1.48 (3H, *d*, J = 6.0 Hz, rha-Me), 1.63 (3H, *d*, J = 6.0 Hz, rha-Me), 3.98 (3H, *s*, OMe), 5.34 (1H, *br s*, rha 1-H), 6.22 (1H, *s*, rha 1-H), 6.29 (1H, *d*, J = 7.0 Hz, glc 1-H), 6.75, 6.91 (each 1H, *d*, J = 2.0 Hz, 6, 8-H), 7.40 (1H, *d*, J = 9.0 Hz, 5′-H), 7.93 (1H, *dd*, J = 2.0, 9.0 Hz, 6′-H), 8.40 (1H, *d*, J = 2.0 Hz, 2′-H). FABMS *m/z*: 793 $[M+Na]^+$. ^{13}C NMR (d_6-DMSO): 156.0, 133.3, 177.4, 160.8, 99.2, 161.5,

Table 1. ^{13}C NMR data of compounds **5**–**8**

C	5	6	7	8
1	131.7	132.4	133.7	131.8
2	109.8	127.3	111.5	127.8
3	145.8	117.1	147.5	117.1
4	149.1	157.6	150.8	157.0
5	115.5	117.1	118.0	117.1
6	118.5	127.3	120.7	127.8
7	130.6	130.9	131.2	129.6
8	123.7	123.7	128.9	129.0
9	18.1	18.3	63.9	62.3
OMe	55.7		56.8	
glc 1′	100.2	102.2	102.8	102.0
2′	73.3	74.9	74.8	74.8
3′	76.9	78.5	78.1	78.3
4′	69.8	71.4	71.3	71.2
5′	77.0	78.8	77.7	78.7
6′	60.8	62.4	62.5	62.9
solv.	d_6-DMSO	C_5D_5N	CD_3OD	C_5D_5N

94.7, 156.8, 105.6, 120.9, 113.2, 149.5, 146.9, 115.2, 122.4, 55.6, 101.0, 74.2, 76.4, 70.0, 75.9, 66.6, 100.7, 70.2, 70.5, 71.7, 68.1, 17.6, 98.3, 70.0, 70.2, 71.5, 69.7, 17.8.

Acid hydrolysis of **1–4**. A soln of **1** (100 mg) in 2 N HCl–MeOH was refluxed for 2 hr, neutralized with 3% KOH–MeOH and concd. The residue was subjected to silica gel CC eluting with $CHCl_3$–MeOH–H_2O (80:20:1) to afford isorhamnetin (37 mg) and methylsides of D-glucose (TLC solv. $CHCl_3$–MeOH–H_2O, 14:6:1). Compounds **2** (10 mg), **3** (6 mg) and **4** (5 mg) were hydrolysed in the same way as for **1** giving D-glucose and L-rhamnose and isorhamnetin.

Acetylation of **2–4**. **2**, **3** and **4** (5 mg of each) were separately acetylated with Ac_2O and pyridine (1:1) at room temp. overnight to give the corresponding peracetate **2a**, **3a** and **4a**. EIMS *m/z*: **2a**; 273, 316, 331, 400, **3a**; 273, 316, 400, 561, **4a**; 273, 316, 561.

Enzymic hydrolysis of **2** *and* **4**. A mixture of **2** (15 mg) and crude hesperidinase (20 mg) in HOAc–NaOAc buffer soln (pH 4.5, 1.5 ml) was incubated at room temp. for 1 min. MeOH was then added to the reaction mixture and evapd *in vacuo* to dryness to give a residue, the MeOH soluble part of which was subjected to silica gel CC eluting with $CHCl_3$–MeOH–H_2O (80:20:1) to yield **1** by TLC (R_f 0.51, solv. $CHCl_3$–MeOH–H_2O = 14:6:1). A small amount of **4** (5 mg) was hydrolysed with crude hesperidinase in HOAc–NaOAc buffer at room temp. for 3 min. The soln treated in the same way as **2** gave **3** by TLC (R_f 0.36, solv. $CHCl_3$–MeOH–H_2O = 14:6:1).

Isoeugenol β-D-glucopyranoside (**5**). Colourless needles, mp 170–174°, $[\alpha]_D^{25}$ −39.4° (pyridine; *c* 0.99), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1600, 1587, 1520 (phenyl), 1030 (OMe), 962 (C=C trans), 850 (phenyl). EIMS *m/z*: 164. ^1H NMR (C_5D_5N): 1.76 (3H, *d*, *J* = 6.0 Hz, 9-H_3), 3.74 (3H, *s*, OMe), 5.68 (1H, *d*, *J* = 7.0 Hz, glc 1-H), 6.08 (1H, *dq*, *J* = 6.0, 16.0 Hz, 8-H), 6.38 (1H, *d*, *J* = 16.0 Hz, 7- H), 6.95 (1H, *dd*, *J* = 2.0, 8.0 Hz, 6-H), 7.10 (1H, *d*, *J* = 2.0 Hz, 2-H), 7.48 (1H, *d*, *J* = 8.0 Hz, 5-H).

p-*Propenylphenol β-D-glucopyranoside* (**6**). Powder, $[\alpha]_D^{25}$ −55.0° (pyridine; *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1605, 1508, 963, 840. EIMS *m/z*: 296 [M^+], 162, 134. ^1H NMR (C_5D_5N): 1.75 (3H, *d*, *J* = 6.0 Hz, 9-H_3), 5.60 (1H, *d*, *J* = 7.0 Hz, glc 1-H), 6.00 (1H, *dq*, *J* = 6.0, 16.0 Hz, 8-H), 6.35 (1H, *d*, *J* = 16.0 Hz, 7-H), 7.30 (4H, *m*, arom. H).

p-*Coumaryl alcohol β-D-glucopyranoside* (**8**). Colourless needles, mp 171–174°, $[\alpha]_D^{17}$ −57.4° (MeOH; *c* 0.94), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1603, 1518, 964. ^1H NMR (d_6-DMSO): 4.09 (2H, *t*-like, *J* = 5.1 Hz, 9-H_2), 6.24 (1H, *dt*, *J* = 5.1, 16.0 Hz, 8-H), 6.49 (1H, *d*, *J* = 16.0 Hz, 7-H), 6.98 (2H, *d*, *J* = 8.5 Hz, 2, 6-H), 7.35 (2H, *d*, *J* = 8.5 Hz, 3, 5-H).

Enzymic hydrolysis of **5**. A mixture of **5** (50 mg) and β-glucosidase (30 mg) in HOAc–NaOAc buffer (pH 4.5, 2 ml) was incubated at 37° for 1.5 hr. The reaction mixture was extracted with $CHCl_3$ and the $CHCl_3$ layer was evapd *in vacuo* to dryness to give isoeugenol by TLC and GLC (1.5% neopentylglycol succinate, column temp. 168°).

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Phytochemistry, Vol. 28, No. 1, pp. 303–305, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00

EXTERNAL LEAF FLAVONOIDS OF *POLANISIA TRACHYSPERMA*

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(*Received in revised form* 15 *July* 1988)

Key Word Index—*Polanisia trachysperma*; Capparidaceae; leaf exudate; flavonoid aglycones.

Abstract—*Polanisia trachysperma*, a sticky annual weed, produces a terpenoid leaf resin. This exudate is shown to contain more than a dozen methylated flavonoid aglycones, some of which are rare natural products. Compounds with 6,8-dimethoxy substitution are predominant. *Polanysia trachysperma* is the first Capparaceae species found to accumulate external flavonoids.

INTRODUCTION

Polanisia trachysperma Torr. & Gray (Capparidaceae) is native to the central United States, but has spread widely elsewhere, growing in disturbed soil along roadsides, waste places, denuded areas and in sandy canyon washes or stream beds. It is an erect branching glandular hairy annual, which is very sticky and clammy to the touch [1].