

CCD ($\text{H}_2\text{O}-\text{Me}_2\text{CO}-\text{cyclohexane}$, 4:6:7) and compared with authentic specimens.

Calceolarioside D (**6**). Colourless amorphous powder. $[\alpha]_D^{25} = -21.5^\circ$ (MeOH; c 2); UV (MeOH), λ_{max} , nm (log ϵ): 331 (4.13), 290 (4.05); IR (KBr), ν_{max} : 3400 (br), 2920, 1700, 1670, 1630, 1050 cm^{-1} . ^1H NMR and ^{13}C NMR δ : Tables 1 and 2, respectively. (Found C, 57.59; H, 5.55; calcd for $\text{C}_{23}\text{H}_{26}\text{O}_{11}$, C, 57.74; H, 5.48%).

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PHENYLPROPANOID GLUCOSE ESTERS FROM *PRUNUS BUERGERIANA*

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(Revised received 4 June 1987)

Key Word Index—*Prunus buergeriana*; Rosaceae; phenylpropanoid glucose esters; caffeic acid esters; *p*-coumaric acid esters; cyanogenic glucoside; mandelonitrile glucoside.

Abstract—Two new phenylpropanoid glucose esters, 6-*O*-caffeoyl-1-*O*-*p*-coumaroyl- β -D-glucopyranose, and 6-*O*-*p*-coumaroyl-D-glucopyranose, along with three known compounds, 1,6-di-*O*-caffeoyl- β -D-glucopyranose, 6-*O*-caffeoyl-D-glucopyranose and (2*R*)-[(6-*O*-caffeoyl)- β -D-glucopyranosyloxy]benzeneacetonitrile were characterized from the bark of the *Prunus buergeriana* using spectroscopic methods.

INTRODUCTION

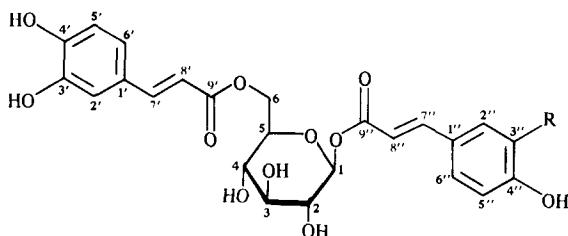
We have previously reported on the isolation and structural determination of a series of phenylpropanoid glucosides from the bark of *Prunus grayana* Maximowicz [1, 2]. In our continuing chemical examination of phenolic compounds in *Prunus* species, we have now isolated two new phenylpropanoid glucose esters from the bark of *Prunus buergeriana* Miquel. This paper describes the isolation and characterization of these compounds.

RESULTS AND DISCUSSION

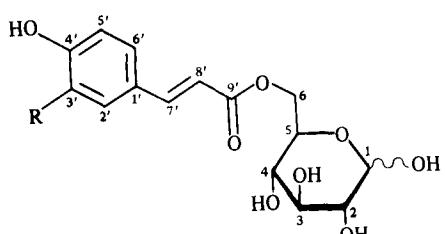
A methanolic extract of *P. buergeriana* bark was partitioned with chloroform, and then *n*-butanol. The *n*-butanol soluble part was repeatedly chromatographed

over silica gel and Sephadex LH-20 column to give compounds **1**–**5** as amorphous powders.

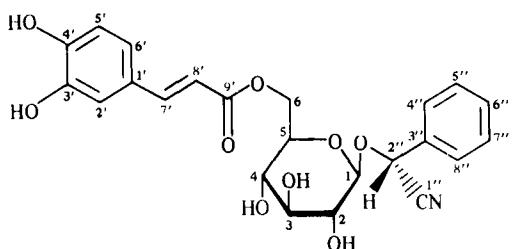
Compound **1** was analysed for $\text{C}_{24}\text{H}_{24}\text{O}_{12}$ (secondary ion mass spectrometry [SIMS] m/z 505 [$\text{M} + \text{H}$] $^+$). The ^1H NMR spectrum of **1** showed the existence of two *trans*-olefin systems, aromatic protons of two ABC systems and sugar protons. An anomeric proton signal (δ 5.60, *d*, $J = 7.7$ Hz) indicated that the C-1 position of the glucose moiety was acylated. In the ^{13}C NMR spectrum, nine pairs of duplicated signals were observed, which were assigned to the phenylpropanoid moieties. On alkaline methanolysis with methanolic sodium methoxide **1** afforded methyl caffeate and D-glucose. Therefore, caffeic acid was attached to some position of 1-*O*-caffeoyl- β -D-glucopyranose. The location of the residual caffeoyl group was determined to be the C-6 position of the glucose moiety from the chemical shift value in the ^{13}C NMR spectrum of



1 R = OH
2 R = H



3 R = OH
4 R = H



5

1. The signals assignable to the C-5 and C-6 positions of the glucose moiety were each shifted by -2.6 and $+2.4$ ppm, respectively, as compared with those of 1-O-acyl- β -D-glucopyranose [3]. Thus the structure of 1 is 1,6-di-O-caffeoxy- β -D-glucopyranose, garashangin [4]. Although a trace of the *cis*-isomer of 1 was observed in the ^1H NMR spectrum of a sample of 1 kept at room temperature for a few months, the *cis*-isomer was not detected in the original *n*-butanol extract of the bark by TLC analysis. So, the fresh bark does not apparently contain any of the isomer.

The ^1H NMR spectrum of 2 ($\text{C}_{24}\text{H}_{24}\text{O}_{11}$) SIMS m/z 489 [$\text{M} + \text{H}$]⁺ was similar to that of 1 except for the aromatic region. An AA'BB' and a ABC system were revealed in 2 instead of the two ABC systems in 1. Alkaline methanolysis of 2 gave methyl caffeoate, methyl *p*-coumarate and D-glucose. Therefore, one of the two caffeoxy groups in 1 was replaced by a *p*-coumaroyl group in 2. On stepwise alkaline methanolysis 2 afforded methyl *p*-coumarate and an amorphous powder, which was shown to be identical with 6-O-caffeoxy-D-glucopyranose from ^1H NMR and ^{13}C NMR spectral data. It was clear from

the chemical shift value of the anomeric proton in the ^1H NMR spectra of 2 ($\delta 5.61$, *d*, $J = 7.6$ Hz) that the *p*-coumaric acid was attached to the C-1 position of the glucose moiety. Consequently, 2 is characterized as 6-O-caffeoxy-1-*O*-*p*-coumaroyl- β -D-glucopyranose.

The ^{13}C NMR spectra of 3 ($\text{C}_{15}\text{H}_{18}\text{O}_9$, SIMS m/z 343 [$\text{M} + \text{H}$]⁺) and 4 ($\text{C}_{15}\text{H}_{18}\text{O}_8$, SIMS m/z 327 [$\text{M} + \text{H}$]⁺) were closely correlated in showing duplicated signal patterns of sugar carbons. The dual peaks in the ^1H NMR spectra of these compounds indicated the presence of both the α -and β -anomers. Alkaline methanolysis of 3 and 4 yielded methyl caffeoate and D-glucose from 3, and methyl *p*-coumarate and D-glucose from 4, respectively. In both cases, the locations of the phenylpropanoid groups were concluded to be the C-6 position of the glucose moiety from the evidence of the downfield shift of the C-6 methylene signals in the ^1H NMR and ^{13}C NMR spectra. Therefore, 3 and 4 were 6-O-caffeoxy-D-glucopyranose and 6-O-*p*-coumaroyl-D-glucopyranose, respectively. In an acetone extract of fresh bark both 3 and 4 were detected by TLC. Therefore, 3 and 4 are naturally occurring substances and not artifacts from 1,6-disubstituted sugars such as 1, 2 and 4.

Compound 5 ($\text{C}_{23}\text{H}_{23}\text{NO}_9$, EIMS m/z 457 [M]⁺) was identified as grayanin, (2R)-[(6-O-caffeoxy)- β -D-glucopyranosyloxy]benzeneacetonitrile by the direct comparison with the authentic grayanin previously obtained from *p. grayana* [2].

Some diphenylpropanoid esters of glucose have been isolated from Scrophulariaceae [4], Labiateae [5, 6], Pteridaceae [7] and Cruciferae [8, 9], however, there are few reports on the isolation of two different phenylpropanoids attached to one glucose molecule, such as 6-O-caffeoxy-1-*O*-*p*-coumaroyl- β -D-glucopyranose (2), to our knowledge.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, with TMS as an int. standard. Chemical shifts are given on the δ (ppm) scale.

Isolation. The fresh bark of *Prunus buergeriana* (2.1 kg), collected in the botanical garden of this college in May 1986, was cut into pieces and extracted with hot MeOH under reflux. The concd MeOH extract was suspended in H_2O and extracted with CHCl_3 , and then *n*-BuOH. The *n*-BuOH extract was subjected to silica gel (CHCl_3 -MeOH- H_2O system) and Sephadex LH-20 (MeOH) CC to give 1-5.

Compound 1. Amorphous pale yellow powder (75 mg). $[\alpha]_D^{26} + 16.8^\circ$ (MeOH; *c*0.88); SIMS m/z : 505 [$\text{M} + \text{H}$]⁺, 527 [$\text{M} + \text{Na}$]⁺; EIMS m/z : 181, 163, 145, 137, 123; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log *e*): 328 (4.50), 302 sh (4.41), 244 sh (4.29); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3420, 2920, 1700, 1630, 1605, 1525; ^1H NMR (CD_3OD): glucose moiety: δ 5.60 (1H, *d*, $J = 7.7$ Hz, H-1), 3.43-3.50 (3H, overlapping, H-2, H-3 and H-4), 3.68 (1H, *m*, H-5), 4.50 (1H, *dd*, $J = 12.1, 2.1$ Hz, H-6a), 4.32 (1H, *dd*, $J = 12.1, 5.6$ Hz, H-6b); caffeoic acid moiety: δ 7.05, 7.06 (each 1H, *d*, $J = 2.1$ Hz, H-2' or H-2''), 6.77, 6.78 (each 1H, *d*, $J = 8.2$ Hz, H-5' or H-5''), 6.95, 6.96 (each 1H, *dd*, $J = 8.2, 2.1$ Hz, H-6' or H-6''), 7.57, 7.66 (each 1H, *d*, $J = 15.9$ Hz, H-7' or H-7''), 6.29, 6.32 (each 1H, *d*, $J = 15.9$ Hz, H-8' or H-8'').

Alkaline methanolysis of 1. Compound 1 (5 mg) was dissolved in methanolic 1% NaOMe (1 ml) and the soln allowed to stand 1 hr at room temp. The reaction mixture was passed through an Amberlite IR-120 (H^+) column and the eluate concd to afford methyl caffeoate and D-glucose, identified by TLC comparison with authentic samples. Methyl caffeoate: R_f 0.48 (CHCl_3 - Me_2CO , 4:1). D-glucose: R_f 0.29 (*n*-BuOH-HOAC- H_2O , 4:1:2).

Table 1. ^{13}C NMR chemical shift values of compounds 1-4*

Carbon number	1	2	3	4
Glucose†	1	95.8	95.8	94.1, 98.3
	2	74.1	74.1	73.8, 76.3
	3	78.0	78.0	75.6, 78.0
	4	71.4	71.4	72.1, 71.9
	5	76.4	76.4	70.9, 74.9
	6	64.4	64.4	64.9, 65.0
Caffeic acid	1	127.7, 127.8	127.8	127.8
	2	114.4, 114.9	114.6	115.0, 115.1
	3	146.8, 147.3	146.8	146.7
	4	149.6, 149.9	149.6	149.7
	5	116.6	116.6	116.6
	6	123.1, 123.3	123.1	123.0
	7	147.3, 148.5	147.3 ^a	147.1, 147.2
	8	115.3, 115.4	115.3 ^b	115.2
	9	167.2, 169.2	167.7 ^c	169.3
<i>p</i> -Coumaric acid	1		127.1	127.2
	2		131.4	131.2
	3		116.9	116.9
	4		161.5	161.3
	5		116.9	116.9
	6		131.4	131.2
	7		148.3 ^a	146.7, 146.8
	8		114.9 ^b	115.1
	9		169.2 ^c	169.2, 169.3

^{a-c}Assignments with the same superscript may be interchanged in each column.

*Spectra were run in methanol-*d*₄ at 100 MHz.

†The former means α -form, and the latter β -form for compounds 3 and 4.

Compound 2. Amorphous pale yellow powder (270 mg). $[\alpha]_D^{25} + 12.1^\circ$ (MeOH; *c* 0.61); SIMS *m/z*: 489 [$\text{M} + \text{H}$]⁺, 511 [$\text{M} + \text{Na}$]⁺; EIMS *m/z*: 164, 147, 136, 119; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log *e*): 317 (4.46), 300 sh (4.41), 228 sh (4.21); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400, 2930, 1700, 1635, 1605, 1520; ¹H NMR (CD₃OD): glucose moiety: 5.61 (1H, *d*, *J* = 7.6 Hz, H-1), 3.45–3.52 (3H, overlapping, H-2, H-3, H-4), 3.17 (1H, *m*, H-5), 4.51 (1H, *dd*, *J* = 12.0, 2.0 Hz, H-6a), 4.33 (1H, *dd*, *J* = 12.0, 5.6 Hz, H-6b); caffeic acid moiety: 8.705 (1H, *d*, *J* = 2.0 Hz, H-2'), 6.78 (1H, *d*, *J* = 8.2 Hz, H-5'), 6.95 (1H, *dd*, *J* = 8.2, 2.0 Hz, H-6'); *p*-coumaric acid moiety: 8.746 (2H, *d*, *J* = 8.6 Hz, H-2'', H-6''), 6.80 (2H, *d*, *J* = 8.6 Hz, H-3'', H-5''); *trans*-alkene moiety: 8.756, 7.73 (each 1H, *d*, *J* = 15.9 Hz, H-7' or H-7''), 6.29, 6.37 (each 1H, *d*, *J* = 15.9 Hz, H-8' or H-8'').

Alkaline methanolysis of 2. Compound 2 (10 mg) was treated in the same manner as 1 to give methyl caffeate, methyl *p*-coumarate and *D*-glucose, which were identified by TLC comparison with authentic samples. Methyl *p*-coumarate: *R*_f 0.64 (CHCl₃–Me₂CO, 14:1).

Stepwise alkaline methanolysis of 2. Compound 2 (31 mg) was dissolved with MeOH (2.5 ml) and 3% methanolic NaOMe was added dropwise until after 6 hr, the concn of the soln was 0.4% NaOMe in MeOH, when the reaction mixture was passed through an Amberlite IR-120 (H⁺) column. The eluate was subjected to silica gel CC developed with CHCl₃–MeOH to give methyl *p*-coumarate and 6-*O*-caffeoyl-*D*-glucopyranose (2a). Methyl *p*-coumarate was identified by ¹H NMR and TLC comparison with an authentic sample. 2a was an amorphous powder (5 mg). All spectral data was identical with those of 3.

Acetylation of 2. Compound 2 (10 mg) was dissolved in pyridine (0.5 ml) and Ac₂O (2.0 ml), and left at room temp. over night to afford the hexaacetate (2b) (14 mg). $[\alpha]_D^{25} + 6.6^\circ$ (CHCl₃; *c* 0.28); IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3030, 1760, 1640, 1605, 1510, 1430, 1420,

1370; ¹H NMR (CDCl₃): glucose moiety: 8.5.88 (1H, *d*, *J* = 7.9 Hz, H-1), 5.22–5.33 (3H, overlapping, H-2, H-3, H-4), 3.98 (1H, *m*, H-5), 4.35 (2H, *d*, *J* = 3.4 Hz, H-6); caffeic acid moiety: 8.738 (1H, *d*, *J* = 2.0 Hz, H-2'), 7.22 (1H, *d*, *J* = 8.4 Hz, H-5'), 7.41 (1H, *dd*, *J* = 8.4, 2.0 Hz, H-6'); *p*-coumaric acid moiety: 8.7.55 (2H, *d*, *J* = 8.6 Hz, H-2'', H-6''), 7.13 (2H, *d*, *J* = 8.6 Hz, H-3'', H-5''); *trans*-alkene: 8.7.73, 7.64 (each 1H, *d*, *J* = 16.0 Hz, H-7' or H-7''), 6.41, 6.37 (each 1H, *d*, *J* = 16.0 Hz, H-8' or H-8''); acetoxyl groups: 8.2.31 (*x* 2), 2.30, 2.06, 2.03 (*x* 2) (each 3H, *s*, OAc *x* 6).

Compound 3. Amorphous pale yellow powder (930 mg). $[\alpha]_D^{24} + 30.8^\circ$ (MeOH; *c* 0.77); SIMS *m/z*: 343 [$\text{M} + \text{H}$]⁺; EIMS *m/z*: 324 [$\text{M} - \text{H}_2\text{O}$]⁺, 180, 163, 136, 109; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log *e*): 330 (4.03), 302 sh (3.92), 242 sh (3.79), 218 (3.98); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3420, 2920, 1690, 1635, 1610, 1525; ¹H NMR (CD₃OD): glucose moiety: 8.5.11 (1H, *d*, *J* = 3.7 Hz, H-1 α), 4.51 (1H, *d*, *J* = 7.8 Hz, H-1 β), 3.17–4.50 (overlapping, other sugar protons); caffeic acid moiety: 8.7.04 (1H, *d*, *J* = 2.0 Hz, H-2'), 6.78 (1H, *d*, *J* = 8.1 Hz, H-5'), 6.94 (1H, *m*, H-6'), 7.56 (1H, *d*, *J* = 15.9 Hz, H-7'), 6.27 (1H, *d*, *J* = 15.9 Hz, H-8').

Compound 4. Amorphous white powder (75 mg). $[\alpha]_D^{23} + 32.7^\circ$ (MeOH; *c* 1.07); SIMS *m/z*: 327 [$\text{M} + \text{H}$]⁺, 349 [$\text{M} + \text{Na}$]⁺; EIMS *m/z*: 308 [$\text{M} - \text{H}_2\text{O}$]⁺, 164, 147, 120; UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log *e*): 312 (4.50), 301 sh (4.45), 227 (4.19), 211 (4.17); IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3380, 2910, 1695, 1635, 1610, 1590, 1525; ¹H NMR (CD₃OD): glucose moiety: 8.5.13 (1H, *d*, *J* = 3.5 Hz, H-1 α), 4.53 (1H, *d*, *J* = 7.8 Hz, H-1 β), 3.18–4.51 (overlapping, other sugar protons); *p*-coumaric acid moiety: 8.7.45 (2H, *d*, *J* = 8.6 Hz, H-2', H-6''), 6.81 (2H, *d*, *J* = 8.6 Hz, H-3', H-5'), 7.63 (1H, *d*, *J* = 16.0 Hz, H-7'), 6.33 (1H, *d*, *J* = 16.0 Hz, H-8').

Alkaline methanolysis of 3 and 4. Compounds 3 (5 mg) and 4 (5 mg) were each treated in the same manner as 1 affording methyl caffeate and *D*-glucose from 3 and methyl *p*-coumarate

and D-glucose from **4**. All these compounds were identified by TLC comparison with authentic samples.

*Detection of **3** and **4** in the fresh bark.* Fresh cut bark (100 g) was soaked into 500 ml of Me_2CO and extracted in a ultrasonic bath for 30 min. The concd Me_2CO extract was extracted with *n*-BuOH. The *n*-BuOH extract was checked by TLC using silica gel F_{254} (Merck) and $\text{CHCl}_3\text{-MeOH-H}_2\text{O}$ (3:1:0:0.1). R_f value of **3**; 0.19, **4**; 0.28.

Compound 5. Amorphous pale yellow powder (5.50 mg). $[\alpha]_D^{26} -38.7^\circ$ (Me_2CO ; *c*0.60). All spectral data were identical with lit. values [2].

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PHENOLIC GLUCOSIDES FROM *PARABENZOIN PRAECOX*

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Key Word Index—*Parabenzooin praecox*; Lauraceae; bark; thalictoside; thalictoside caffeoylester; phenolic glucoside.

Abstract—From the methanolic extract of the bark of *Parabenzooin praecox* (Sieb. et Zucc.) Nakai, a new phenolic glucoside ester, 4-(2-nitroethyl)phenyl β -D-(6-O-caffeoyle)glucopyranoside, and a new phenolic glucoside, 3,4,5-trimethoxyphenyl β -D-glucopyranoside have been isolated together with a known compound, thalictoside. The structures of these compounds have been determined on the basis of spectroscopic studies and chemical evidence.

In the course of our studies on the constituents of the Lauraceae, new glucosides, 4-(2-nitroethyl)phenyl β -D-(6-O-caffeoyle)glucopyranoside and 3,4,5-trimethoxyphenyl β -D-glucopyranoside together with a known compound, thalictoside, have been isolated from the bark of *Parabenzooin praecox*.

Compound **1** was identified as thalictoside, which was isolated from *Thalictrum aquilegifolium* (Ranunculaceae) [1], by its spectroscopic data and by mixed melting point test with an authentic sample.

Compound **2** was suggested to be a caffeoylester of **1** by its spectroscopic data. Acetylation of **2** with acetic anhydride–pyridine gave a pentaacetate. Alkaline hydrolysis of **2** with sodium methoxide afforded methyl caffeoate and thalictoside. Comparison of the ^1H and ^{13}C NMR spectra with those of **1** (see Table 1 and Experimental) allowed the caffeoylester group to be located on the C-6

hydroxy group in the glucose moiety. Thus, the structure of **2** was determined as 4-(2-nitroethyl)phenyl β -D-(6-O-caffeoyle)glucopyranoside.

Compound **3** showed a molecular ion peak at m/z 346 in the EIMS. By the data of ^1H and ^{13}C NMR spectra, the existence of three methoxyl groups, an aromatic ring and a glucose were indicated. Acetylation of **3** with acetic anhydride–pyridine afforded a tetraacetate. Hydrochloric acid hydrolysis of **3** gave D-glucose and trimethoxyphenol. The data of the ^{13}C NMR spectrum of **3** suggested that three methoxyl groups were located at C-3,4,5 in phenolic moiety [2]. The mode of glucosidic linkage was determined to be β -form based on the coupling constant of the anomeric proton signal [δ 4.82 (1H, *d*, $J=7.6$ Hz)] in the ^1H NMR spectrum. Thus, the structure of **3** was established as 3,4,5-trimethoxyphenyl β -D-glucopyranoside.