*Phytochemistry*, Vol 28, No. 6, pp. 1737–1741, 1989
Printed in Great Britain.

0031-9422/89 $3.00+0.00


# LIGNAN GLYCOSIDES FROM *PARSONSIA LAEVIGATA**

FUMIKO ABE and TATSUO YAMAUCHI

Faculty of Pharmaceutical Sciences, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-01, Japan

(*Received in revised form* 3 *October* 1988)

**Key Word Index**—*Parsonsia laevigata*, Apocynaceae, lariciresinol; lignan rhamnoside; pinoresinol-apiosylglucoside.

**Abstract**—Bis-*O*-rhamnosides of lariciresinol, 5,5′-dimethoxylariciresinol and secoisolariciresinol, and pinoresinol-apiosyl(1→2)-glucoside were isolated from *Parsonsia laevigata*.

## INTRODUCTION

*Parsonsia laevigata* Alston is a climbing evergreen shrub, indigenous to the Ryukyu Islands, and known as a feeding plant for the larvae of *Idea leuconoe* Erichson. In the preceding paper of this series, we described parsonine [1], a pyrrolizidine alkaloid having a dienone system as found in danaidone [2], from the stems. This paper deals with bis-*O*-rhamnosides and apiosylglucoside of known lignans from the stems and the leaves.

## RESULTS AND DISCUSSION

The methanol percolate of the air-dried stems was partitioned with chloroform and butanol. The butanol extract on column chromatography gave three lignan glycosides (**1**–**3**). From the air-dried leaves of the same plant, four lignan glycosides (**1**–**4**) were obtained.

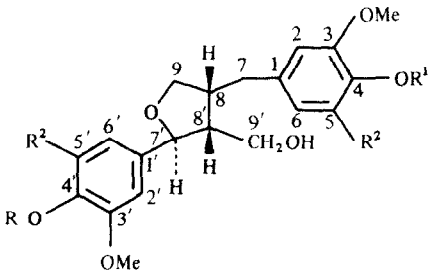
Compound **1** showed the $[M+Na]^+$ peak at *m/z* 675.262 in FABMS, indicating a molecular formula of $C_{32}H_{44}O_{14}$. Upon acetylation, a heptaacetate (**1a**) was obtained. In the $^1H$ NMR spectrum, a pair of three proton signals due to two tri-substituted benzene rings was observed together with a singlet proton peak due to two methoxyl groups, and the presence of two 3-methoxy-4-hydroxyphenyl or 3-hydroxy-4-methoxyphenyl groups was suggested (Table 1). In the 2D-NOESY spectrum, cross peaks were observed between the methoxyl protons and H-2(H-2′), and the structures of the phenyl groups were determined to be 3(3′)-methoxy-4(4′)-hydroxyphenyls. The two component sugars were assignable as rhamnose based on the coupling constants of H-1–H-6, and the chemical shifts in the $^{13}C$ NMR spectrum (Table 2). Since the coupling constant between each anomeric carbon and proton ($^1J_{C-H}$) had a value of 170.9 Hz, the rhamnosyl linkages were considered to be α.

Compound **1** was hydrolysed enzymatically to yield an aglycone (**1b**), which was identified as (+)-lariciresinol [3] based on EIMS (*m/z* 360.158, $C_{20}H_{24}O_6$), the $^1H$ and $^{13}C$ NMR spectra and specific rotation. A rhamnose (2 mol/mol of **1**) molecule was determined to be linked to the *p*-hydroxyl of each phenyl group by a comparison of the $^{13}C$ NMR signals of **1b** and **1**. The rhamnosidic linkages were also assigned on the basis of the cross peaks observed between the anomeric protons and H-5 and H-5′ in the 2D-NOESY spectrum of **1**. Upon acid hydrolysis of **1** with 1 M HCl, L-rhamnose ($[\alpha]_D+9.0°$) and a crystalline aglycone (**1c**) were obtained. Compound **1c** also has a molecular formula, $C_{20}H_{24}O_6$ based on the $M^+$ peak at *m/z* 360.157 and afforded a tetraacetate (**1d**). The C-7′ signal in **1c** showed an upfield shift (−35.2 ppm) in comparison with those in **1** or **1b**. Since the proton signals of one of the two benzene rings were transformed into two singlet peaks, **1c** was assigned as (+)-isolariciresinol formed by acid [3]. The structure of **1** was therefore determined to be lariciresinol-4,4′-bis-*O*-α-L-rhamnoside.

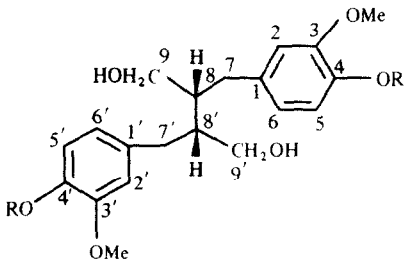
On the basis of the $[M+Na]^+$ peak at *m/z* 735.284 in the FABMS, the molecular formula of **2** was established as $C_{34}H_{48}O_{16}$, having two more methoxyl groups than **1**. The presence of two extra methoxyl groups was confirmed in the $^1H$ NMR spectra in which the methoxyl proton peaks were observed as two singlet peaks of 6H each at δ3.67 and 3.65. In the phenolic proton signals, two singlet peaks for two protons each were observed at δ6.67 and 7.00, suggesting the presence of two 3,5-dimethoxy-4-hydroxyphenyl residues (Table 1). The C-5 and C-5′ signals which appeared at δ118.7 and 118.9 in **1** were shifted downfield and transformed into singlet carbons which duplicated the signals of C-3 and C-3′ at δ154.0, while upfield shifts were observed in C-4(C-4′) and C-6(C-6′). Since the proton and carbon signals due to rhamnose and a furan ring in the lignan were observed with the same chemical shifts as those in **1** (Table 2), and $^1J_{C-H}$ between C-1 and H-1 in the rhamnose was observed as 172.4 ppm, showing to be α-linkage, the structure of **2** was determined to be 5,5′-dimethoxy-lariciresinol-4,4′-bis-*O*-α-L-rhamnoside.

Compound **3** was obtained as crystals and the $[M+Na]^+$ peak was shown at *m/z* 677.277 in the FABMS, indicating the molecular formula ($C_{32}H_{46}O_{14}$) to be two mass units higher than that of **1**. In the $^{13}C$ NMR spectrum, only 16 signals including those from rhamnosyl and 3-methoxy-4-hydroxyphenyl groups were

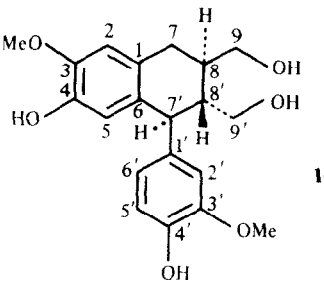
*Part 2 in the series 'Studies on *Parsonsia*'. For Part 1, see ref. [1].



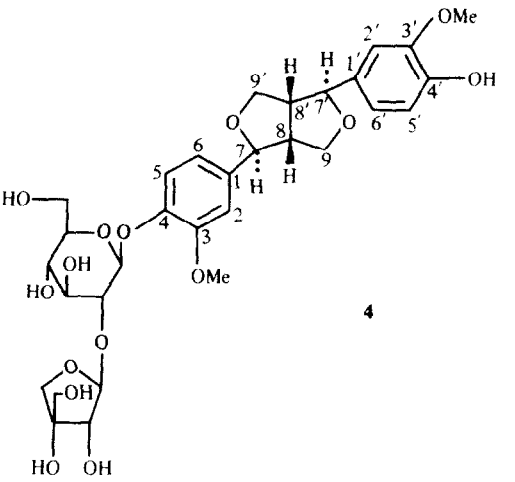
**1** $R^1$ = α-L-rhamnosyl, $R^2$ = H
**1a** 1-heptaacetate
**1b** $R^1$ = $R^2$ = H
**2** $R^1$ = α-L-rhamnosyl, $R^2$ = OMe



**3** R = α-L-rhamnosyl
**3a** 3-octaacetate
**3b** R = H



**1c**



**4**

observed, suggesting that **3** retains a magnetically symmetrical structure (Table 2). While **3** provided an octaacetate (**3a**) and the component sugars were assignable as two mole of rhamnose, the presence of two primary carbinols in the lignan moiety was indicated by a pair of methylene protons at δ4.10 (2H, *dd*) and 3.97 (2H, *dd*). The aglycone of **3** was therefore considered to be secoisolariciresinol [4, 5]. The $^{13}$C NMR signals due to the lignan moiety of **3** were in good agreement with those of secoisolariciresinol [4] with downfield shifts of C-4 (4') and C-1 (1') Upon acid hydrolysis, an aglycone (**3b**) was obtained and identified as secoisolariciresinol based on the $^1$H NMR spectrum and the specific rotation value Based on the glycosylation shifts of the C-4 (4') signal, the rhamnosyl linkages were assigned to the 4 and 4'-OH.

Compound **4** showed the $[M+Na]^+$ peak at *m/z* 675.225 in the FABMS, suggesting the molecular formula, $C_{31}H_{40}O_{15}$ In the $^{13}$C NMR spectrum, the pinoresinol monoglucoside moiety [6] was assignable with a downfield shift of C-2 of glucose (+2 0 ppm) and an upfield shift of C-1 of glucose (−1 6 ppm) The remaining five carbon signals including one oxygenated methylene carbon, one primary carbinol carbon and one tertiary carbon, were in good agreement with those of the terminal β-D-apioside [7, 8]. All proton signals of the sugar moiety of **4** were assignable based on the $^1$H–$^1$H COSY and $^{13}$C–$^1$H COSY spectra Upon partial hydrolysis of **4**, apiose, glucose, (+)-pinoresinol and pinoresinol monoglucoside [6] were identified on TLC. Since only D-types are known for naturally occurring glucose and apiose, the component sugars in **4** are tentatively assigned both as D-type. In the 2D-NOESY spectrum of **4**, cross peaks were observed between H-5 in the pinoresinol and the anomeric proton in the glucose, and also the anomeric proton of the apiose and H-2 of the glucose as observed in 2-*O*-β-D-apiosyl-D-glucose-1β,5'-dibenzoate [9]. The structure of **4** was thus determined to be pinoresinol-4-*O*-β-D-apiosyl-(1→2)-β-D-glucoside

Four lignans were isolated from *P. laevigata*. Although lariciresinol [3], 5,5'-dimethoxylariciresinol [10] and secoisolariciresinol [4, 5] are already known lignans, this is the first isolation of their rhamnosides, and pinoresinol apiosyl-glucoside.

## EXPERIMENTAL

*General.* Mps uncorr NMR 400 and 100 MHz, $C_5D_5N$, TMS as int. standard. TLC and silica gel CC, the following solvent systems were used, 1. $CHCl_3$–MeOH–$H_2O$ (7 2 1, 7 3 1, bottom layer), 2. EtOAc–MeOH–$H_2O$ (4 1 5, top layer)

*Extraction and isolation of the lignan glycosides* Air-dried and powdered stems of *Parsonsia laevigata* (2 4 kg) collected at Kikai-jima in July, 1983, were percolated with MeOH The MeOH percolate was concd *in vacuo* to 1 l, and diluted with $H_2O$ (1 l) The mixture was filtered and the filtrate was partitioned with $CHCl_3$ The $CHCl_3$ extract (9.8 g) was used for the isolation of parsonine [1]

The aq layer, after partition with $CHCl_3$, was concd *in vacuo* and partitioned with BuOH The BuOH extract (26 1 g) was eluted on a polystyrene column (Mitsubishi Chem Co, CHP-

Table 1. $^1$H NMR chemical shifts of lignans (in $C_5D_5N$)

| H | 1 | 1b | 1c | 2 | 3 | 4 |
|---|---|---|---|---|---|---|
| 2 | 6.99 *d* (1)[a] | 7.00 *d* (2) | 6.86 *s* | 6.67 *s* | 7.01 *d* (2) | 7.20 *d* (2)[c,d] |
| 5 | 7.39 *d* (8)[c] | 7.19 *d* (8) | 6.96 *s* | | 7.36 *d* (8) | 7.50 *d* (8)[a] |
| 6 | 6.89 *dd* (8, 1) | 6.91 *dd* (8, 2) | | 6.67 *s* | 6.93 *dd* (8, 2) | 6.96 *dd* (8, 2)[e] |
| 7 | 2.78 *dd* (13, 11) | 2.80 *dd* (13, 12) | 3.13 *dd* (15, 5) | 2.79 *dd* (14, 11) | 3.00–3.09 *m* | 4 91 *d* (5)[c,e] |
| | 3.20 *dd* (13, 4) | 3.26 *dd* (13, 5) | 3 23 *dd* (15, 11) | 3.21 *dd* (14, 4) | | |
| 8 | 2 97 *m* | 3 07 *m* | 2.58 *m* | 3.00 *m* | 2.42 *m* | 3.10–3.24 *m* |
| 9 | 3.99 *t* (8) | 4.07 *dd* (8, 7) | 4.21 *br s* | 4.00 *dd* (8, 7) | 3.97 *dd* (11, 5) | |
| | 4.21 *t* (8) | 4 31 *dd* (8, 7) | | 4 22 *t* (8) | 4.10 *dd* (11, 3) | |
| 2′ | 7.31 *d* (1)[b,e] | 7.33 *d* (2) | 7.06 *d* (2) | 7 00 *s* | 7.01 *d* (2) | 7.24 *d* (2)[f,g] |
| 5′ | 7 46 *d* (8)[d] | 7.26 *d* (8) | 7.18 *d* (8) | | 7.36 *d* (8) | 7.26 *d* (8) |
| 6′ | 7.19 *dd* (8, 1)[e] | 7.20 *dd* (8, 2) | 6.96 *dd* (8, 2) | 7.00 *s* | 6.93 *dd* (8, 2) | 7 08 *dd* (8, 2)[h] |
| 7′ | 5.33 *d* (6)[e] | 5.35 *d* (6) | 4.35 *d* (11) | 5.34 *d* (5) | 3.00–3.09 *m* | 4.94 *d* (5)[g,h] |
| 8′ | 2 69 *m* | 2.83 *m* | 2.34 *m* | 2.71 *m* | 2.42 *m* | 3.10–3.24 *m* |
| 9′ | 4 09 *dd* (11, 7) | 4.14 *dd* (11, 7) | 3 93 *dd* (11, 4) | 4.11 *dd* (10, 7) | 3.97 *dd* (11, 5) | |
| | 4.19 *dd* (11, 7) | 4.26 *dd* (11, 7) | 4 25 *dd* (11, 3) | 4 21 *dd* (10, 7) | 4.10 *dd* (11, 3) | |
| –OMe | 3 67[b], 3 69[a] | 3 73 (× 2) | 3.55, 3 80 | 3.65, 3.67 | 3 64 (× 2) | 3.79[f], 3.84[d] |
| sugar moieties | rha | | | rha | rha | glc |
| 1 | 6.04[c], 6 06[d] *br s* | | | 6.03, 6.05 *br s* | 6 04 (× 2) *br s* | 5 57 *d* (8)[a] |
| 2 | 4.84 (× 2) *br s* | | | 4 97 (× 2) *br s* | 4.85 (× 2) *br s* | 4.57 *t* (8)[b] |
| 3 | 4 74 (× 2) *dd* (9, 3) | | | 4.80 (× 2) *dd* (9, 3) | 4.76 (× 2) *dd* (9, 3) | 4 36 *dd* (8, 9) |
| 4 | 4.35 (× 2) *dd* (10, 9) | | | 4 35 (× 2) *dd* (10, 9) | 4.37 (× 2) *t* (9) | 4 20 *t* (9) |
| 5 | 4.49 *m* | | | 5.03 *m* | 4.52 *m* | 4.00 *m* |
| 6 | 1.60 (× 2) *d* (6) | | | 1 65, 1 67 *d* (6) | 1 61 (× 2) *d* (6) | 4 47 *dd* (12, 2) |
| | | | | | | 4.27 *dd* (12, 4) |
| | | | | | | apiose |
| 1′ | | | | | | 6.62 *s*[b] |
| 2′ | | | | | | 4 85 *s* |
| 4′ | | | | | | 4.43 *d* (9) |
| | | | | | | 4.91 *d* (9) |

[a–h]Cross peaks were observed between the signals marked [a–g] or [h] in the 2D-NOESY spectrum.

Table 2 $^{13}$C NMR chemical shifts of lignans (in $C_5D_5N$)

| C | | 1 | 1b | 2 | 3 | 4 | pino glc * |
|---|---|---|---|---|---|---|---|
| 1 | *s* | 136 7 | 132.7 | 135 7 | 137 3 | 136 3 | 136 1 |
| 2 | *d* | 113 8 | 113 5 | 106.3 | 114 3 | 111 3 | 111 2 |
| 3 | *s* | 145 7[a] | 146 3[a] | 154 0 | 144 9 | 147 1 | 147 3 |
| 4 | *s* | 149 9 | 148 6 | 139 9 | 151 2 | 150 2 | 150 1 |
| 5 | *d* | 118.7[b] | 116 5[b] | 154 0 (*s*) | 119.1 | 116 5 | 116 4 |
| 6 | *d* | 119 1[b] | 119 4 | 106 3 | 122 0 | 118 8 | 119 0 |
| 7 | *t* | 33 4 | 35 5 | 34 1 | 35 8 | 86 0 (*d*) | 86 0 (*d*) |
| 8 | *d* | 43.0 | 43 3 | 42 9 | 44 3 | 54 7 | 54 7 |
| 9 | *t* | 73 2 | 73 2 | 73.2 | 61 1 | 71 9 | 71 9 |
| 1′ | *s* | 139 9 | 136 0 | 137.9 | 137 3 | 133 1 | 133 1 |
| 2′ | *d* | 111 1 | 110 9 | 103.8 | 114 3 | 110 0 | 110 9 |
| 3′ | *s* | 145 0[a] | 147 3[a] | 154 0 | 144 9 | 147 8 | 147 8 |
| 4′ | *s* | 151 2 | 148 6 | 141 1 | 151 2 | 148 8 | 148 8 |
| 5′ | *d* | 118 9[b] | 116 3[b] | 154 0 (*s*) | 119 1 | 116 4 | 116 4 |
| 6′ | *d* | 121 2 | 121 8 | 103 8 | 122 0 | 119 7 | 119 6 |
| 7′ | *d* | 83 2 | 83 5 | 83 3 | 35 8 (*t*) | 86 3 | 86 3 |
| 8′ | *d* | 53 6 | 53 7 | 53.5 | 44 3 | 54 7 | 54 7 |
| 9′ | *t* | 60 1 | 60 2 | 60 1 | 61 1 | 71 9 | 71 9 |
| –OMe | *q* | 55 9 (×2) | 56.1 (×2) | 56 0 (×2)<br>55 9 (×2) | 55 9 (×2) | 56 0<br>56 1 | 56 0 (×2) |
| sugar moieties | | rha ×2 | | rha ×2 | rha ×2 | glc | glc |
| 1 | *d* | 101 6† | | 103.5‡ | 101 7§ | 100 6 | 102 2 |
| 2 | *d* | 70 9 | | 71 0 | 70 9 | 76 8 | 74 8 |
| 3 | *d* | 73 8 | | 73 8 | 73 9 | 79 0 | 78 8[a] |
| 4 | *d* | 72 1 | | 72 2 | 72 1 | 71.5 | 71 3 |
| 5 | *d* | 72 6 | | 72 7 | 72 6 | 78 6 | 78 5[a] |
| 6 | *q* | 18 5 | | 18 5 | 18 5 | 62 3 (*t*) | 62 4 (*t*) |
| | | | | | | apiose | |
| 1′ | *d* | | | | | 110 3 | |
| 2′ | *d* | | | | | 78 0 | |
| 3′ | *s* | | | | | 80 8 | |
| 4′ | *t* | | | | | 75 1 | |
| 5′ | *t* | | | | | 66 4 | |

[a,b]Signals may be interchangeable in each vertical column
*Pinoresinol monoglucoside
†$^1J_{C\ H}$ = 170 9 Hz
‡$^1J_{C-H}$ = 172 4 Hz
§$^1J_{C-H}$ = 170 9 Hz

20P) with 0–100% MeOH The eluates with 30–50% MeOH was then chromatographed on a silica gel column with solvent 1 The fractions containing lignan glycosides were again chromatographed on a silica gel column with solvent 2 and then on an ODS column with MeCN–$H_2O$ (1 4) to isolate **1** (125 mg), **2** (40 mg) and **3** (23 mg).

Air-dried leaves of the same plant (500 g) were treated in the same manner as described above From the BuOH extract (5.3 g), **1** (64 mg), **2** (26 mg), **3** (11 mg) and **4** (12 mg) were isolated

*Laricıresinol-4,4′-bis-O-α-L-rhamnoside* (**1**). Fine prisms, mp 124–127° (from MeOH). $[\alpha]_D^{26}$ −100 0° (MeOH; *c* 1.3), FABMS *m/z* 675 262, $C_{32}H_{44}O_{14}Na$ requires 675 263 Upon acetylation with $Ac_2O$ and pyridine at room temp., a heptaacetate was obtained, FDMS *m/z* 946 ($[M]^+$, $C_{46}H_{58}O_{21}$) Compound **1** (40 mg) was dissolved in 4 ml of $H_2O$ and shaken with hesperidinase (Tanabe Pharm Co. Ltd, 25 mg) at 38° for 5 hr The mixture was diluted with $H_2O$ and extracted with BuOH. The BuOH extract was purified on a silica gel column with solvent 1 (14:2 3) to give (+)-laricıresinol as a solid, $[\alpha]_D^{27}$ +32.7° (MeOH; *c* 1.0), EIMS *m/z*: 360 158, $C_{20}H_{24}O_6$ requires 360 157.

Compound **1** (50 mg) was dissolved in 1 M HCl in 50% EtOH (3 ml) and the mixture was refluxed for 30 min The mixture was then deacidified with IR-410A and the EtOH was evapd *in vacuo* The residue was suspended on $H_2O$ and extracted with BuOH. The BuOH extract was crystallized from $CHCl_3$ to give (+)-isolariciresinol as prisms, mp 153–154°, $[\alpha]_D^{28}$ +44 3° (MeOH, *c* 0 35), EIMS *m/z* 360 157, $C_{20}H_{24}O_6$ requires 360 157 $^{13}$C NMR $\delta$ 33 6 (C-7), 40 6 (C-8), 48 0, 48.3 (C-7′,8′), 55 9, 56.2 (–OMe), 62 2 (C-9′), 65 8 (C-9), 112.9 (C-2′), 114.0 (C-2), 116.3 (C-5′), 117 8 (C-5), 123.0 (C-6′), 128.1, 134.3, 139 9, 146 3, 146.5, 147 0, 148 9 (C-1, 3, 4, 6, 1′, 3′, 4′) The $H_2O$ layer, after extraction with BuOH, was concd *in vacuo* and the component sugar examined on TLC (solvent 1, 7 3 1, solvent 2, 4 1 .0 5) and shown to be rhamnose by co-chromatography with authentic L-rhamnose. After purification on a silica gel column with solvent 1 (7·3 1), the rhamnose showed $[\alpha]_D^{28}$ +9 0° (final value, $H_2O$, *c* 0.40) **1c**-tetraacetate (**1d**) Formed on acetylation of **1c** with pyridine and $Ac_2O$, prisms, mp 166–167°, FDMS *m/z* 528 ($[M]^+$, $C_{28}H_{32}O_{10}$)

*5,5′-Dimethoxylaricıresinol-4,4′-bis-O-α-L-rhamnoside* (**2**)

Prisms from MeOH, mp 225–230°, $[\alpha]_D^{28}$ −120.7° (MeOH; *c* 1.45), FABMS *m/z* 735.284, $C_{34}H_{48}O_{16}Na$ requires 735.284.

*Secoisolariciresinol-4,4′-bis-O-α-L-rhamnoside* (**3**). Prisms from MeOH, mp 112–116°, $[\alpha]_D^{27}$ −0.16° (MeOH; *c* 1.04), FABMS *m/z*: 677.277, $C_{32}H_{46}O_{14}Na$ requires 677.278 3-acetate (**3a**): FDMS *m/z*: 990 ($[M]^+$, $C_{48}H_{62}O_{22}$). Upon hydrolysis with 1 M HCl as described for **1**, an aglycone of **3** (**3b**) was obtained as a solid, $[\alpha]_D^{30}$ −28.2° (MeOH, *c* 0.33), EIMS *m/z*: 362.174 $C_{20}H_{26}O_6$ requires 362.173. $^1$H NMR $\delta$: 2.45 (2H, *m*, H-8,8′), 3.07 (4H, *m*, H-7,7′), 4.04 (2H, *dd*, *J* = 11, 5 Hz, H-9a,9′a), 4 16 (2H, *dd*, *J* = 11, 3 Hz, H-9b,9′b).

*Pinoresinol-4-O-β-D-apiosyl-(1→2)-β-D-glucoside* (**4**). Solid, $[\alpha]_D^{25}$ −47.5° (MeOH; *c* 0.75), FABMS *m/z*: 675.225 $C_{31}H_{40}O_{15}Na$ requires 675.226. FABMS (negative) *m/z*. 651 $[M-H]^-$, 537, 501, 433, 357. Compound **4** (12 mg) was refluxed with 0.5 N $H_2SO_4$–50% dioxane (1 ml) for 30 min and the mixture was diluted with MeOH. The mixture was deacidified with IR-410A and concd *in vacuo*. The mixture was then diluted with $H_2O$ and extracted with BuOH. The presence of pinoresinol and pinoresinol monoglucoside in the BuOH extract was shown by TLC of the extract against authentic samples [4] (solvents 1 and 2). (+)-Pinoresinol was obtained by CC on silica gel (solvent 1, 7·1·2), solid, $[\alpha]_D^{30}$ +75.4° (MeOH; *c* 0.18). The $H_2O$ layer showed apiose and glucose on TLC (solvents 1 and 2, with aniline hydrogen phthalate as a colour reagent).

*Acknowledgements*—We thank Messrs S. Yoshitome and T. Iwamoto, then teachers of Kikai High School, for collection of *Parsonsia laevigata*, and Misses Y. Iwase and S. Hachiyama (Fukuoka University) for NMR and MS measurements. Our thanks are also due to Prof. O. Tanaka (Hiroshima University) for supplying hesperidinase.

## REFERENCES

1. Yamauchi, T. and Abe, F. (1987) *Chem. Pharm. Bull.* **35**, 4661
2. Edgar, J. A. and Culvenor, C. C J. (1974) *Nature* **248**, 614.
3. Satake, T., Murakami, T., Saiki, Y. and Chen, C.-M. (1978) *Chem. Pharm. Bull.* **26**, 1619.
4. Fonseca, S. F., Campello, J de P., Barata, L E S and Rúveda, E. A. (1978) *Phytochemistry* **17**, 499.
5 Cambie, R. C., Clark, G R., Craw, P. A., Jones, T. C., Rutledge, P. S and Woodgate, P. D. (1985) *Aust. J. Chem.* **38**, 1631.
6. Deyama, T. (1983) *Chem. Pharm. Bull.* **31**, 2993. Abe, F. and Yamauchi, T. (1988) *Phytochemistry* **27**, 1439.
7 Nagai, M., Kubo, M., Takahashi, K., Fujita, M. and Inoue, T. (1983) *Chem. Pharm Bull.* **31**, 1923.
8. Yamauchi, T., Abe, F. and Wan, A. S. C (1987) *Chem. Pharm Bull.* **35**, 4993.
9 Bowden, B. F. and Collins, D. J. (1988) *J. Nat. Prod.* **51**, 311.
10. Achenbach, H., Stocker, M and Constenla, M. A. (1988) *Phytochemistry* **27**, 1835