Two New Lignan Xylosides from the Barks of *Prunus ssiori* and *Prunus padus*

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Phytochemical examinations of the barks of *Prunus* species have led to the isolation of two new lignan xylosides, ssioriside (9) and prupaside (12). Compound 9 was obtained from *Prunus* (*P.*) *ssiori* and *P. padus* and 12 from *P. padus*. The spectroscopic data and chemical evidence allowed assignment of the structures of 9 and 12 as (8*S*,8′*S*)-4,4′-dihydroxy-3,5,3′,5′-tetramethoxy-8-8′-butyrolignan 9-*O*-β-D-xylopyranoside and (8*R*,7*S*,8′*R*)-5,5′-dimethoxylariciresinol 9′-*O*-β-D-xylopyranoside, respectively. Several previously reported compounds were also obtained and identified.

Keywords *Prunus ssiori*; *Prunus padus*; Rosaceae; lignan xyloside; ssioriside; prupaside; bark

Prunus (*P.*) *padus* belonging to the subgenus *Padus* grows in the northern area of the Eurasian Continent and its bark is used for the treatment of coughs, headaches, heart trouble and intestinal trouble and as a sedative in Europe and the United States.[1] *P. ssiori* grows in the northern area of Asia and belongs to the same subgenus as *P. padus*. The barks of the two plants taste bitter. Our examinations have shown the barks to be particularly rich in cyanogenic glucoside and phenylpropanoid glucoside derivatives.[2] In this study, we isolated and structurally identified several known compounds and two new bitter lignan xylosides, ssioriside (**9**) and prupaside (**12**), from the above two plants. The isolation of lignan xylosides is of interest from the viewpoint of chemotaxonomy.

Prunus ssiori The concentrated methanol extract of the fresh bark was extracted with chloroform and then with *n*-butanol. Compounds **1**—**9** were isolated from the *n*-butanol-soluble portion by silica gel and Sephadex LH-20 column chromatographies, preparative thin-layer chromatography (TLC) and preparative high-performance liquid chromatography (HPLC).

Fraction **1** (**1a** and **1b**) was a mixture of (+)-catechin and (−)-epicatechin, whose identification was described in another paper.[3] Compound **2** was a cyanogenic glucoside and was identified as prunasin by comparison with an authentic sample. Compound **3** was a phenylpropanoid glucoside and was identified as syringin.[4] Compounds **4** and **5** were phenolic glucosides and their structures were shown to be glucosyringic acid[5] and 1,4-dihydroxy-2,6-dimethoxybenzene 1-*O*-β-D-glucopyranoside, respectively.[6] Compound **6** was a terpenoid glucoside, and was confirmed to be roseoside.[7] Compounds **7** and **8** were tetrahydronaphtalene-type lignan xylosides and were identified as lyoniside[8] and schizandriside, respectively.[9]

Compound **9** was obtained as a colorless amorphous powder. The infrared (IR) spectrum indicated the presence of hydroxyl group(s) (3430 cm^{-1}) and aromatic ring(s) (1615 and 1520 cm^{-1}). The electron impact mass spectrum (EI-MS) showed a molecular ion peak at *m/z* 554. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum displayed the presence of four methoxyl groups, a sugar moiety, two symmetric 1,3,4,5-tetrasubstituted aromatic systems, and two methine and four methylene groups, being typical of a diarylbutane-type lignan. The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of **9** also exhibited typical signal patterns of two methine and four methylene carbons of the diarylbutane-type lignan (Table I).[10] On acetylation with acetic anhydride in pyridine, **9** afforded a hexaacetate (**9a**). The EI-MS of **9a** showed a peak at *m/z* 764 $[M-Ac]^+$, and the ^{1}H-NMR spectrum revealed the existence of two phenolic and four alcoholic acetyl groups. Hydrolysis of **9** with 10% HCl yielded D-xylose and (8*S*,8′*S*)-4,4′-dihydroxy-3,5,3′,5′-tetramethoxy-8-8′-butyrolignan (**9b**). D-Xylose was identified by comparison of TLC behavior and specific rotation $[\alpha]_D$ +22.4° (H_2O) with those of an authentic sample. The spectra of **9b** showed almost the same pattern as those of a diarylbutane-type lignan, (+)-2,3-diveratrylbutane-1,4-diol, and the positive optical rotation ($[\alpha]_D$ +39.4°), suggested that the C-8 and C-8′ configurations are 8*S* and 8′*S*, respectively.[10b] In the ^{1}H-NMR spectrum of **9**, the anomeric proton was observed at δ 4.18 (d, *J*=7.4 Hz), confirming the anomeric center to retain a β-form. The D-xylose moiety was concluded to be attached to either of the two primary hydroxyl groups since in the ^{1}H and ^{13}C-NMR spectra, the chemical shifts showed a difference between the C-9 and C-9′ positions, whereas no difference was observed between those in **9b**.[10] Accordingly, **9**, named ssioriside, was characterized as (8*S*,8′*S*)-4,4′-dihydroxy-3,5,3′,5′-tetramethoxy-8-8′-butyrolignan 9-*O*-β-D-xylopyranoside.

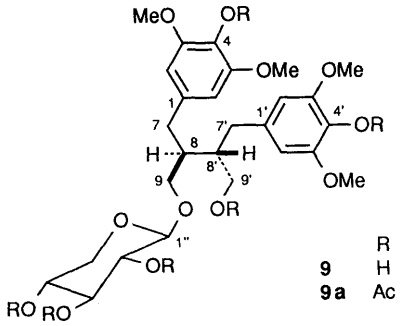
Prunus padus The methanol extract of the fresh bark was treated in the same manner as in the case of *P. ssiori* to give **1** (**1a** and **1b**), **2**, **6**, **7** and **9**—**12**. Compound **10** was a phenylpropanoid glucoside and was identified as melilotoside.[11] Compound **11** was a terpenoid glucoside and was identified as citroside A.[12]

Compound **12** was obtained as a colorless amorphous powder, $[\alpha]_D$ −38.0° (methanol). The IR spectrum indicated the presence of hydroxy group(s) (3400 cm^{-1}) and aromatic ring(s) (1605 cm^{-1}) as in **9**. The EI-MS displayed a molecular ion peak at *m/z* 552. The ^{1}H-NMR spectrum showed the presence of three methines [δ 4.83 (d, *J*= 6.1 Hz), 2.71 (m) and 2.42 (m)] and benzylic protons [δ 2.96 (dd, *J*=13.4, 4.7 Hz) and 2.53 (dd, *J*=13.4, 11.1 Hz)], which were characteristic of a 9—7′ monoepoxy type lignan, as well as two oxymethylene, four methoxyl, sugar, and two sets of symmetric 1,3,4,5-tetrasubstituted aromatic protons. In the ^{13}C-NMR spectrum, **12** showed signal patterns of xylose, three methine and benzylic carbons. The ^{1}H-NMR spectrum of the pentaacetate (**12a**) of **12** showed the existence of two phenolic and three alcoholic acetoxyl groups, and the EI-MS showed a molecular ion peak at *m/z* 762. Hydrolysis of **12** with β-xylosidase (Sigma) in sodium acetate buffer (pH 5.0) yielded D-xylose and 5,5′-dime-

TABLE I. ^{13}C-NMR Spectral Data for **9**, **12** and **12b**[a]

Carbon No.	9	12	12b[b]
1	132.3	133.0	132.9
2	106.6	107.1	107.3
3	148.2	149.3	149.4
4	132.5	134.9	135.2
5	148.2	149.3	149.4
6	106.6	107.1	107.3
7	35.6	34.3	34.0
8	40.7	44.0	43.8
9	70.1	73.8	73.6
1′	132.3	133.0	132.9
2′	106.7	105.3	104.6
3′	148.2	149.3	149.4
4′	132.5	134.9	135.2
5′	148.2	149.3	149.4
6′	106.7	105.3	104.6
7′	35.4	84.2	84.3
8′	43.3	51.8	54.1
9′	62.0	68.4	60.6
1″	104.5	104.4	
2″	74.3	75.1	
3″	77.3	78.1	
4″	70.6	71.3	
5″	66.2	67.1	
OMe	55.9×2 55.8×2	56.9×4	56.9×4

a) Measured in CD_3OD at 100.6 MHz with TMS as an internal standard. *b*) The chemical shifts of **12b** are taken from ref. 12.



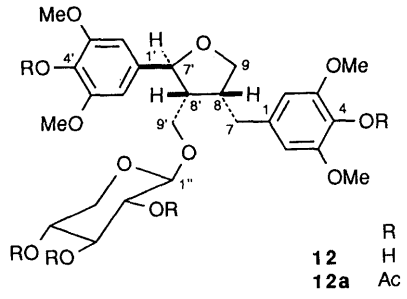
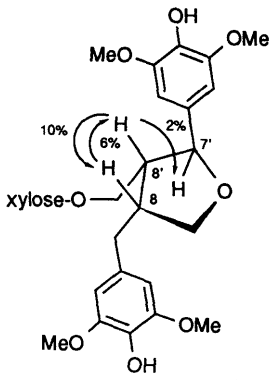


Chart 1

thoxylariciresinol (**12b**). D-Xylose was identified by comparison with an authentic sample in the same manner as described for **9**. The structure of **12b** was confirmed by comparison of the data with the reported values.[13] The anomeric proton (δ 4.35, d, J=6.9 Hz) and the anomeric carbon (δ 104.4) in the ^{1}H- and ^{13}C-NMR spectra indicated the anomeric center to retain a β-form. Comparison of the ^{13}C-NMR spectrum of **12** with the reported data of **12b** (Table I) revealed that the signal assignable to C-9′ was shifted by +7.8 ppm, suggesting the location of D-xylose on



NOEs (⌒) observed in NOE difference spectra

Chart 2

the C-9′ hydroxyl group of the aglycone. The relative configurations, *cis*-configuration between the methine protons at C-8 and C-8′ and the *trans* configurations at C-7′ and C-8′ were established by the proton nuclear Overhauser effect (NOE) difference spectrum as shown in Chart 2. Additionally, the positive optical rotation of **12b** ($[\alpha]_D$ +6.0°, methanol) suggested 8*R*, 7′*S* and 8′*R* stereochemistry in **12**.[13] Finally, compound **12**, named prupaside, was concluded to be (8*R*,7′*S*,8′*R*)-5,5′-dimethoxylariciresinol 9′-*O*-β-D-xylopylanoside.

The two lignan xyloside (**9** and **12**) are new natural products. Lignan glycosides have now been found for the first time in the genus *Prunus*. Further studies on the chemical constituents of some *Prunus* species are in progress at our laboratory.

Experimental

The following instruments were used for the measurements of the spectral and physical data. IR spectra were recorded on a Hitachi 260-30 or a Perkin-Elmer 1710 FT-IR instrument, ultraviolet (UV) spectra on a Hitachi 557 spectrometer, and mass spectrum (MS) on a Hitachi M-80 machine. Optical rotations were measured with a JASCO DIP-360 automatic polarimeter. ^{1}H- and ^{13}C-NMR spectra were taken with a Bruker AM-400 (400 and 100.6 MHz, respectively) spectrometer. Chemical shifts were expressed in ppm (δ) relative to the internal tetramethylsilane (TMS) (s, singlet; d, doublet; dd, doublet of doublets; m, multiplet; br, broad). HPLC: CIG column system (Kusano Scientific Co., Tokyo) with pre-packed column, 20 i.d. × 100 mm (octadecyl silica, 20 μm). Fuji Davison silica gel BW-300 and BW-340 (Fuji Davison Co., Ltd.), and Sephadex LH-20 (Pharmacia Fine Chemicals Co., Ltd.) were used for column chromatographies. TLC was carried out on precoated Kieselgel 60 F_{254} (0.25 mm thick, Merck) and preparative TLC on precoated Kieselgel 60 F_{254} (0.5 mm thick, Merck), and spots were visualized under UV (254 nm) illumination and by spraying the plates with 10% H_2SO_4 solution followed by heating.

Extraction and Isolation *P. ssiori*: The fresh bark of *P. ssiori* (1.2 kg as dried bark) collected at Mt. Aomatuba (Iwate), in June 1987 was crushed and extracted with hot MeOH under reflux. The extract was concentrated under reduced pressure. The crude residue was suspended in H_2O, and extracted with $CHCl_3$ and then with *n*-BuOH. The *n*-BuOH fraction was repeatedly chromatographed on silica gel with $CHCl_3$–MeOH, $CHCl_3$–MeOH–H_2O, EtOAc–Me_2CO and Me_2CO–MeOH solvent systems, and on Sephadex LH-20 with MeOH to yield **1** (**1a** and **1b**) (2.24 g), **2** (3.00 g) and **3** (10.0 mg). Purification of **4** (30.0 mg) and **5** (107 mg) was carried out by preparative TLC with *n*-BuOH–AcOH–H_2O (3 : 1 : 1), and that of **6** (6.4 mg), **7** (187 mg), **8** (49.4 mg) and **9** (117 mg) by preparative HPLC with MeOH–H_2O (1 : 1).

P. padus: The fresh bark of *P. padus* (1.0 kg as dried bark) collected in Toyoni (Hokkaido), in May 1988 was treated as described in the case of *P. ssiori* to give **1** (**1a** and **1b**) (2.80 g), **2** (719 mg), **6** (33.0 mg), **7** (88.1 mg), **9** (80.9 mg), **10** (18.8 mg), **11** (17.5 mg) and **12** (20.0 mg) from the *n*-BuOH-soluble portion.

A Mixture of (+)-Catechin and (−)-Epicatechin (1) A brownish amorphous powder. Column chromatography of the acetate of **1** (100 mg) gave (+)-catechin pentaacetate (**1a'**) (35.0 mg) and (−)-epicatechin pentaacetate (**1b'**) (51.0 mg) as white amorphous powders. Compound **1a**: $[\alpha]_D^{25}$ +26.9° (c=1.00, $CHCl_3$). Compound **1b'**: $[\alpha]_D^{25}$ −10.0° (c=1.00, $CHCl_3$).

Prunasin (2) Colorless needles. mp 148—149 °C. $[\alpha]_D^{26}$ −26.7° (c=1.09, H_2O).

Syringin (3) Colorless needles. mp 165—166 °C. $[\alpha]_D^{24}$ −15.3° (c=1.00, MeOH).

Glucosyringic Acid (4) A colorless amorphous powder. $[\alpha]_D^{28}$ −11.8° (c=1.06, MeOH).

1,4-Dihydroxy-2,6-dimethoxybenzene 1-*O*-β-D-Glucopyranoside (5) A colorless amorphous powder. $[\alpha]_D^{27}$ −16.5° (c=0.57, MeOH).

Roseoside (6) A colorless amorphous powder. $[\alpha]_D^{28}$ +57.6° (c=0.87, EtOH).

Lyoniside (7) Colorless needles. mp 120—121 °C. $[\alpha]_D^{27}$ +21.3° (c=0.90, MeOH).

Schizandriside (8) Colorless needles. mp 210—211 °C. $[\alpha]_D^{27}$ +28.3° (c=0.52, EtOH).

(8*S*,8'*S*)-4,4'-Dihydroxy-3,5,3',5'-tetramethoxy-8-8'-butyrolignan 9-*O*-β-D-Xylopyranoside (Ssioriside) (9) A colorless amorphous powder. $C_{27}H_{38}O_{12}$. $[\alpha]_D^{24}$ +0.7° (c=1.00, MeOH). UV λ_{max}^{MeOH} nm (log ε): 211 (4.65), 232 shoulder (sh) (4.15), 320 (3.47). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 2925 (CH), 1615, 1520 (aromatic rings), 1110. EI-MS m/z: 554 $[M]^+$, 422, 405, 167, 137. ^{1}H-NMR (CD_3OD) δ, lignan moiety: 6.35 and 6.23 (each 2H, s, H-2, -6, -2', -6'), 3.98 and 3.47 (each 1H, dd, J=10.0, 6.0 Hz, H-9 or -9'), 3.68 and 3.55 (each 1H, dd, J=11.0, 6.0 Hz, H-9 or -9'), 3.75 and 3.74 (each 6H, s, OMe×4), 2.63—2.52 (4H, overlapping, H-7, -7'), 2.06 and 1.94 (each 1H, m, H-8, -8'); D-xylose moiety: 4.18 (1H, d, J=7.4 Hz, H-1''), 3.85—3.15 (5H, overlapping, H-2'', -3'', -4'', -5''). ^{13}C-NMR (CD_3OD): Table I.

Acetylation of 9 Compound **9** (13.4 mg) in Ac_2O–pyridine was allowed to stand at room temperature overnight. The crude product was chromatographed on silica gel using n-hexane–Me_2CO (3:1) to give a colorless amorphous powder (13.1 mg) (**9a**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950 (OH), 1750 (C=O), 1600, 1505 (aromatic rings), 1120. EI-MS m/z: 764 $[M-Ac]^+$, 722, 464, 259. ^{1}H-NMR ($CDCl_3$) δ, lignan moiety: 6.33 and 6.31 (each 2H, s, H-2, -6, -2', -6'), 4.23 (1H, dd, J=11.3, 5.3 Hz, H-9'a), 4.00 (1H, dd, J=11.3, 6.5 Hz, H-9'b), 3.92 (1H, dd, J=9.6, 5.5 Hz, H-9a), 3.76 and 3.75 (each 6H, s, OMe×4), 3.40 (1H, dd, J=9.6, 3.4 Hz, H-9b), 2.76—2.60 (4H, overlapping, H-7, -7'), 2.16 (1H, m, H-8 or -8'), 2.05—1.98 (1H, overlapping with acetoxy signals, H-8 or -8'); D-xylose moiety: 5.17 (1H, dd, J=8.8, 8.8 Hz, H-3''), 4.97—4.91 (2H, overlapping, H-2'', -4''), 4.45 (1H, d, J=7.1 Hz, H-1''), 4.09 (1H, dd, J=10.0, 5.2 Hz, H-5''a), 3.33 (1H, dd, J=10.0, 9.3 Hz, H-5''b); acetyl groups: 2.32 and 2.31 (each 3H, s, arom. Ac), 2.05, 2.04, 2.03 and 1.98 (each 3H, s, Ac).

Acid Hydrolysis of 9 Hydrolysis of **9** (15.2 mg) with 10% HCl was carried out at room temperature for 1 h. The reaction solution, after dilution with H_2O, was extracted with $CHCl_3$. The $CHCl_3$ extract was subjected to silica gel column chromatography using $CHCl_3$–MeOH (24:1) to yield the aglycone (**9b**) (1.0 mg) as a colorless amorphous powder. $[\alpha]_D^{24}$ +39.4° (c=0.25, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350 (OH), 2925 (CH), 1610, 1510 (aromatic rings), 1100. EI-MS m/z: 422 $[M]^+$, 404, 168. ^{1}H-NMR ($CDCl_3$) δ: 6.33 (4H, s, H-2, -6, -2', -6'), 3.87—3.80 (2H, overlapping with methoxyl signal, H-9a, -9'a), 3.59 (2H, dd, J=11.3, 4.5 Hz, H-9b, -9'b), 3.83 (12H, s, OMe×4), 2.75 and 2.66 (each 2H, dd, J=13.8, 7.8 Hz, H-7, -7'), 1.87 (2H, m, H-8, -8'). The H_2O residue was purified by silica gel column chromatography with $CHCl_3$–MeOH (2:1) to yield D-xylose as a colorless amorphous powder (1.0 mg), $[\alpha]_D^{26}$ +22.4° (c=0.30, H_2O). TLC, Rf 0.53 (n-BuOH–Me_2CO–H_2O (4:5:1)).

Melilotoside (10) A colorless amorphous powder. $[\alpha]_D^{28}$ −56.1° (c=1.10, MeOH).

Citroside A (11) A colorless amorphous powder. $[\alpha]_D^{28}$ −86.1° (c=0.93, MeOH).

(8*R*,7'*S*,8'*R*)-5,5'-Dimethoxylariciresinol 9'-*O*-β-D-Xylopyranoside (Prupaside) (12) A colorless amorphous powder. $C_{27}H_{36}O_{12}$. $[\alpha]_D^{24}$ −38.0° (c=0.87, MeOH). UV λ_{max}^{MeOH} nm (log ε): 210 (4.57), 236 sh (4.03), 321 (3.47). IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 2932 (CH), 1614, 1519 (aromatic rings), 1044. EI-MS m/z: 552 $[M]^+$, 522, 420, 403, 235, 167, 137. ^{1}H-NMR ($(CD_3)_2CO$) δ, lignan moiety: 6.67 and 6.52 (each 2H, s, H-2, -6, -2', -6'), 4.83 (1H, d, J=6.1 Hz, H-7'), 4.13 (1H, dd, J=9.7, 7.0 Hz, H-9'a), 3.97 (1H, dd, J=8.1, 6.8 Hz, H-9a), 3.91—3.50 (2H, overlapping, H-9b, -9'b), 3.81 and 3.80 (each 6H, s, OMe×4), 2.96 (1H, dd, J=13.4, 4.7 Hz, H-7a), 2.71 (1H, m, H-8), 2.53 (1H, dd, J=13.4, 11.1 Hz, H-7b), 2.42 (1H, m, H-8'); D-xylose moiety: 4.35 (1H, d, J=6.9 Hz, H-1''), 3.91—3.50 (2H, overlapping with H-9, -9', -5''), 3.40—3.22 (3H, overlapping, H-2'', -3'', -4''). ^{13}C-NMR (CD_3OD): Table I.

Acetylation of 12 A pyridine solution of **12** (4.2 mg) was treated with Ac_2O. Work-up as usual gave a colorless amorphous powder (**12a**) (4.0 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2925 (OH), 1750 (C=O), 1600, 1500 (aromatic rings), 1110. EI-MS m/z: 762 $[M]^+$, 720, 678, 503, 259, 167. ^{1}H-NMR ($CDCl_3$) δ, lignan moiety: 6.55 and 6.40 (each 2H, s, H-2, -6, -2', -6'), 4.91 (1H, d, J=4.7 Hz, H-7'), 4.14 (2H, overlapping, H-9a, -9'a), 3.83 and 3.80 (each 6H, s, OMe×4), 3.75 (1H, dd, J=8.0, 8.0 Hz, H-9b), 3.60 (1H, dd, J=8.1, 8.1 Hz, H-9'b), 2.89 (1H, dd, J=13.2, 4.3 Hz, H-7a), 2.63 (1H, m, H-8), 2.50—2.43 (2H, overlapping, H-7b, -8'); D-xylose moiety: 5.21 (1H, dd, J=9.0, 9.0 Hz, H-3''), 5.04 (1H, dd, J=9.0, 7.3 Hz, H-2''), 4.99 (1H, m, H-4''), 4.53 (1H, d, J=7.3 Hz, H-1''), 4.06 (1H, dd, J=8.4, 7.0 Hz, H-5''a), 3.38 (1H, dd, J=11.6, 8.4 Hz, H-5''b); acetyl groups: 2.32 and 2.31 (each 3H, s, arom. Ac), 2.05, 2.03 and 1.98 (each 3H, s, Ac).

Enzymatic Hydrolysis of 12 Compound **12** (10.2 mg) was hydrolyzed with β-xylosidase in sodium acetate buffer (pH 5.0) at room temperature for 24 h to afford (8*R*,7'*S*,8'*R*)-5,5'-dimethoxylariciresinol (**12b**) (1.2 mg), D-xylose (0.5 mg) and **12** (5.5 mg). Compound **12b** was a colorless amorphous powder, $[\alpha]_D^{26}$ +6.0° (c=0.5, MeOH). All spectral data were identical with the reported data for (8*R*,7'*S*,8'*R*)-5,5'-dimethoxylariciresinol.[13] D-Xylose was identified by comparison with an authentic sample in the same manner as for **9**.

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