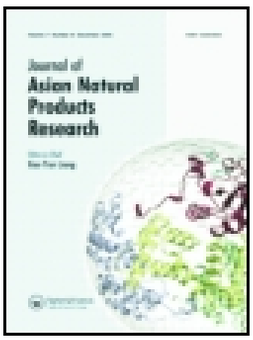

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Two new lignan glycosides from the fruits of *Pyrus ussuriensis*

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ABSTRACT

Two new lignan glycosides, ussuriensislignan A (**1**) and ussuriensislignan B (**2**), together with seventeen known compounds (**3–19**), were isolated from the fruits of *Pyrus ussuriensis*. Their structures were determined by various spectroscopic methods. This is the first report of the isolation of lignans (compounds **1–3**) from the genus *Pyrus*, and compounds **3–6, 12–16** were reported from *Pyrus* for the first time.

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Rosaceae; *Pyrus ussuriensis*; lignan glycosides

1. Introduction

The fruits of *Pyrus ussuriensis* (Rosaceae), widely distributed in North China, are popular for their exceptional fragrance, sweetness, juiciness, and richness of nutrients. The fresh fruits (Qiuzi pear) can be used for prevention and treatment of some ailments, such as coughs and colds. Previous phytochemical studies on the genus *Pyrus* have led to the isolation of flavonoids, phenolic acids, and triterpenoids [1–3]. In order to better understand the functional properties of the fruits and provide evidence for the development of functional food products with this plant, a systematic study was carried out to investigate its antioxidant components of the fruits. Herein, the isolation and structure elucidation of two new lignan glycosides (**1–2**), together with seventeen known compounds (**3–19**), are reported from the fruits of *P. ussuriensis* (Figure 1).

2. Results and discussion

Compound **1** was isolated as an amorphous powder with $[\alpha]_D^{20}$ −5.26 (*c* 0.57, MeOH). Its molecular formula was determined to be $C_{28}H_{36}O_{14}$ based on the pseudo-molecular ion at *m/z* 619.1990 $[M+Na]^+$ in the HRESIMS experiment. The ^1H NMR spectrum displayed two singlet signals at δ 6.78 (2H, H-2, H-6) and δ 6.71 (2H, H-2′, H-6′) attributed to aromatic protons. The ^{13}C NMR spectrum showed two benzene rings, six characteristic aliphatic carbon signals at δ 87.4 and 89.4 (C-7 and C-7′), δ 62.7 and 92.9 (C-8 and C-8′), and δ 72.2 and 76.3 (C-9 and C-9′), four aromatic methoxy groups and resonances corresponding to the presence of a single sugar moiety. Assignments of all ^1H and ^{13}C NMR spectroscopic signals

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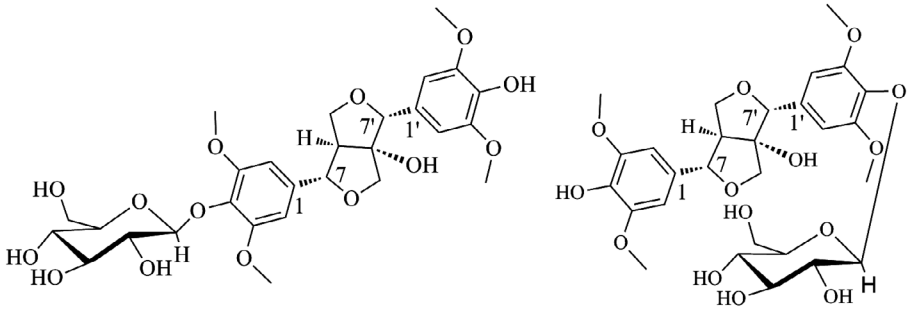
were based on COSY, HSQC, HMBC, and NOESY experiments. The presence of a β-D-glucopyranosyl moiety in the molecule was confirmed by an anomeric proton signal at δ 4.86 (1H, d, J = 7.8 Hz) and six carbon signals at δ 105.3, 75.7, 77.8, 71.3, 78.4, and 62.6 [4], along with acid hydrolysis of **1**. The D configuration of the glucose was assumed from biogenetic consideration [5]. The 1D NMR spectra (Table 1) revealed the presence of 7,9′:7′,9-diepoxylignan skeleton (Figure 1). The position of the glucose moiety at C-4 was confirmed by an HMBC correlation between H-1″ (δ 4.86) and C-4 (δ 135.7). The cross peaks observed in the HMBC spectrum between H-7 (δ 4.88) and C-8/C-8′/C-9/C-9′, H-7′ (δ 4.65) and C-8′/C-9′, H-8 (δ 2.98–3.04) and C-8′, and H_2-9, H_2-9′ and C-7/C-7′/C-8/C-8′ unambiguously provided evidence of the 3,7-dioxabicyclo[3.3.0]octane structure. The HMBC correlations between H-7 and C-1/C-2/C-6 established that ring A was at the C-7 position, and the cross peaks between H-7′ and C-1′/C-2′/C-6′ determined that ring B was attached to C-7′ (Figure 2). The two aryl groups of **1** were all in equatorial positions supported by the chemical shifts of C-7 and C-7′ (δ 87.4 and 89.4, respectively) [5]. The H-7/H-8 relative configuration was assigned as *trans* from the small coupling constant between H-7 and H-8 ($J_{7,8}$ = 4.8 Hz) [6]. The NOE correlations between H-8 and H-2/H-6 indicated that H-8 and ring A were positioned on the same side (Figure 2). Natural tetrahydrofuranoid lignans observed in the literature were usually *cis*-8,8′-fused furfuran lignans [6], and the carbon chemical shifts of compound **1** at the stereogenic centers were similar to those of fraxiresinol-4′-*O*-β-D-glucopyranoside [4], which demonstrated that they have the same relative configuration. Meanwhile, the CD data and specific rotation of **1** were consistent with those of fraxiresinol-4′-*O*-β-D-glucopyranoside [4] and hydroxypinoresinol-4′-*O*-β-D-glucopyranoside [7], suggesting that they possessed the same absolute configuration. In view of all the above evidence, compound **1** was determined as (–)-7*S*,7′*R*,8*R*,8′*S*-3,3′,5,5′-tetramethoxy-4′,8′-dihydroxy-7,9′:7′,9- diepoxylignan-4-*O*-β-D-glucopyranoside and given the trival name ussuriensislignan A.

Ussuriensislignan B (**2**) was obtained as an amorphous powder with $[\alpha]_D^{20}$ −3.70 (*c* 0.27, MeOH). A molecular formula of $C_{28}H_{36}O_{14}$ was determined from the $[M-H]^-$ ion peak at *m/z* 595.2027, which was the same as that of **1**. The ^1H and ^{13}C NMR spectroscopic data of compound **2** (Table 1) indicated the presence of one glucose, two benzene rings, one 3,7-dioxabicyclo[3.3.0]octane unit, and four aromatic methoxy groups in the molecule (Figure 1). Comparison of NMR spectroscopic data of **1** and **2** indicated that they possessed similar structures. The upfield shifts for C-1 ($\Delta\delta$ 6.4 ppm), C-3/C-5 ($\Delta\delta$ 5.1 ppm), and



1 **2**

Figure 1. Structures of compounds **1–2**.

Table 1. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectroscopic data for compounds **1**–**2** in CD_3OD.

	1		**2**	
Position	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1		139.3		132.9
2	6.78 s	105.3	6.69 s	105.0
3		154.4		149.3
4		135.7		136.3
5		154.4		149.3
6	6.78 s	105.3	6.69 s	105.0
7	4.88 d (4.8)	87.4	4.81 d (4.7)	87.8
8	2.98–3.04 m	62.7	2.96–3.02 m	62.6
9a	4.49 t-like (9.0)	72.2	4.45 t-like (9.0)	72.3
9b	3.78 overlapped		3.73 overlapped	
1′		128.2		134.7
2′	6.71 s	106.2	6.73 s	106.6
3′		149.0		154.0
4′		136.4		135.8
5′		149.0		154.0
6′	6.71 s	106.2	6.73 s	106.6
7′	4.65 (s)	89.4	4.67 s	89.1
8′		92.9		93.1
9′a	4.09 d (9.6)	76.3	4.07 d (9.0)	76.2
9′b	3.86 overlapped		3.84 d (9.3)	
Glc				
1″	4.86 d (7.8)	105.3	4.81 d (7.6)	105.4
2″	3.43–3.47 m	75.7	3.40–3.45 m	75.8
3″	3.37–3.42 m	77.8	3.33–3.39 m	77.9
4″	3.37–3.42 m	71.3	3.33–3.39 m	71.3
5″	3.15–3.20 m	78.4	3.10–3.17 m	78.4
6″a	3.64 dd (11.4, 4.8)	62.6	3.60 dd (12.0, 4.8)	62.6
6″b	3.75 overlapped		3.71 overlapped	
3′-OCH_3	3.84 brs	57.1*	3.82 s	57.1^{+}
5′-OCH_3		57.0*		57.0^{+}
3-OCH_3	3.84 brs	56.8*	3.80 s	56.8^{+}
5-OCH_3		56.7*		56.8^{+}

Note: All assignments were based on COSY, HSQC, HMBC and NOESY experiments. $^{*,+}$The values may be exchanged with each other.

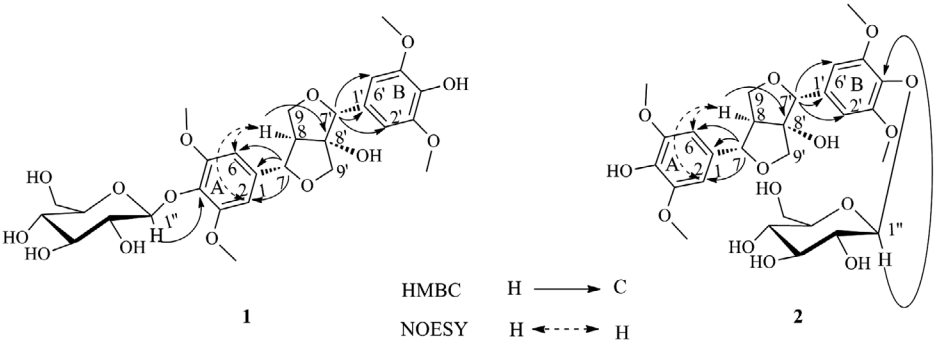


Figure 2. Selected HMBC and NOESY correlations of compounds **1** and **2**.

C-4′ ($\Delta\delta$ 0.6 ppm) and the downfield shifts for C-1′ ($\Delta\delta$ 6.5 ppm), C-3′/C-5′ ($\Delta\delta$ 5.0 ppm), and C-4 ($\Delta\delta$ 0.6 ppm) were observed in the ^{13}C NMR spectrum of **2**, suggesting that the difference between **1** and **2** might be the location of the glucose moiety. Further analysis of HMBC spectrum led to the confirmation of the location of the glucose at C-4′

(Figure 2) by the observation of a correlation between the anomeric proton signal of the glucose (δ 4.81, d, J = 7.6 Hz) and C-4′ (δ 135.8). The D configuration of the glucose was assigned from biogenetic consideration [5]. The specific rotation and the CD data for **2** were in agreement with those of **1**, which suggested that they possessed the same absolute configuration. Thus, ussuriensislignan B was characterized as (–)-7*S*,7′*R*,8*R*,8′*S*-3,3′,5,5′-tetramethoxy-4,8′-dihydroxy-7,9′:7′,9-diepoxylignan-4′-*O*-β-D-glucopyranoside.

In addition to the two new compounds, seventeen known compounds: syringaresinol-β-D-glucoside (**3**) [8], 4-(3′,4′-dihydroxyphenyl)butan-2-one-3′-*O*-β-D-glucopyranoside (**4**) [9–11], vanillyl alcohol-4-*O*-β-D-glucopyranoside (**5**) [12], 3-*O*-(β-D-glucopyranosyl)-1-(3′,5′-dimethoxy-4′-hydroxyphenyl)-1-propanone (**6**) [13], arbutin (**7**) [14], chlorogenic acid methyl ester (**8**) [15], isorhamnetin-3-*O*-β-D-glucoside (**9**) [16], isorhamnetin-3-*O*-rutinoside (**10**) [17], rutin (**11**) [18], quercetin 3-*O*-sophoroside (**12**) [19], *n*-butyl-β-D-fructopyranoside (**13**) [17], ethyl-β-D-fructopyranoside (**14**) [20], 1,5-dimethyl citrate (**15**) [21], 5,5′-oxy(bismethylene)-2-furaldehyde (**16**) [22], ursolic acid (**17**) [23], oleanolic acid (**18**), [23] and daucosterol (**19**), were identified by comparing their spectroscopic data with literature data or co-TLC with authentic samples.

Compounds **7–12** exhibited potent antioxidant activity in both DPPH free radical-scavenging assay and ferric reducing power assay.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on a Rudolph Research Analytical Autopol II automatic polarimeter (Rudolph, Flanders, NJ, U.S.A). The UV spectra were measured using an Agilent Cary 60 UV–visible spectrophotometer (Agilent, Santa Clara, CA, U.S.A). The IR spectra were recorded on a Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany). CD measurements were carried out on MOS-500 spectrometer (BioLogic Science Instruments, Claix, France). NMR spectra were collected on a Bruker AV-600 spectrometer (Bruker, Karlsruhe, Germany) with TMS as internal standard. HR-ESI-MS were recorded on a Bruker micrOTOF-Q II mass spectrometer (Agilent, Bruker, U.S.A). Silica gel (100–200 and 200–300 mesh, Qingdao Haiyang Chemical Co., Ltd. Qingdao, China), D101 macroporous resin (Tianjin Haiguang Chemical Co., Ltd. Tianjin, China), ODS silica gel (LiChroprep RP-18, 40–63 μm, Merck KGaA, Darmstadt, Germany), polyamide (60–100 mesh, Zhejiang Sijiashenghua Plastic Co. Ltd., Zhejiang, China), and Sephadex LH-20 (Amersham Pharmacia Biotech AB) were used for column chromatography. Thin Layer Chromatograghy (TLC) was carried out using precoated plates with GF_{254} silica gel (Qingdao Haiyang Chemical Co., Ltd.). Preparative HPLC was performed using ODS columns (Agilent ZORBAX SB-C18, 21.2 mm × 250 mm, 7 μm). All other chemicals and reagents were of analytical grade and purchased locally.

3.2. Plant material

The fresh fruits of *Pyrus ussuriensis* were collected in October 2013 in Jixian County, Tianjin, China, and identified by one of the authors (Prof. Tianxiang Li). A voucher

specimen (S201310002) has been deposited in the Laboratory of Natural Products, School of Pharmaceutical Science and Technology, Tianjin University, China.

3.3. Extraction and isolation

The fresh fruits of *P. ussuriensis* (16 kg) were washed and cut into small pieces, immersed with 95% EtOH (25 L, for a week), and then refluxed with 95% (40 L, twice and each for 2 h) and 60% (20 L, once for 2 h) EtOH (v/v). The ethanol extract (1.28 kg) was evaporated and suspended in distilled water (4 L), and then partitioned with petroleum ether (60–90 °C), EtOAc and *n*-BuOH successively. The *n*-BuOH extract was concentrated in vacuo, and further separated on D101 macroporous resin column chromatography eluting with an increasing concentration of EtOH (0, 50, 95%) in H_2O.

The ethyl acetate extract (76 g) was subjected to silica gel column (66 × 9.6 cm, 100–200 mesh) chromatography (petroleum ether–EtOAc, 8:2, 5:5, EtOAc–MeOH, 100:0, 9:1, 8:2, 5:5, 500 ml each) to obtain six fractions (A–F). Fr. B (100 mg) was subjected to ODS column chromatography (MeOH–H_2O, 75:25, 80:20) to afford **17** (40 mg) and **18** (20 mg). Fraction C (8.5 g) was loaded onto a polyamide column (20 × 6 cm) and eluted with CH_2Cl_2–MeOH (96:4, 94:6, 9:1, 100 ml each) to obtain 60 subfractions. Subfrs. C11–C13 were recrystallized from MeOH to yield **19** (100 mg). Subfrs. C30–C51 were combined and applied to polyamide column (24 × 2.6 cm) chromatography (CH_2Cl_2–MeOH, 96:4, 94:6) and then further purified by Sephadex LH-20 column chromatography (MeOH) to afford **8** (20 mg). Subfrs. C52–C63 (4 g) were combined on the basis of TLC analysis and subjected to polyamide column (24 × 4 cm, 14.3 × 2.5 cm, stepwise) chromatography twice, eluting with CH_2Cl_2–MeOH (96:4, 92:8). Compounds **7** (11 mg) and **9** (18 mg) were furnished by further Sephadex LH-20 column chromatography. Fraction D (4.6 g) was loaded on a silica gel column (27.3 × 4.6 cm, 200–300 mesh) using petroleum ether–Me_2CO (8:2, 74:26) as eluent and the resultant main fractions were recrystallized from MeOH to obtain **15** (103.7 mg). Fraction E (8 g) was loaded on a silica gel column (25 × 7.8 cm, 100–200 mesh) and eluted with EtOAc–MeOH (100:0, 94:6, 92:8, 80:20, 500 ml each) to obtain 76 subfractions. Subfrs. E33–E37 afforded **10** (12 mg) by further purification with Sephadex LH-20 column chromatography (MeOH). Subfrs. E44–E58 were subjected to silica gel column (21 × 2 cm, 200–300 mesh) chromatography (CH_2Cl_2–MeOH, 9:1, 8:2), polyamide column (18.5 × 5 cm) chromatography (CH_2Cl_2–MeOH, 88:12, 86:14, 84:16, 8:2), and ODS column chromatography (MeOH–H_2O, 25:75, 30:70, 40:60, 45:55), successively to yield **11** (11.8 mg) and **12** (10.2 mg).

The 50% EtOH eluate (19 g) was chromatographed over a silica gel column (30 × 7 cm, 100–200 mesh) with a step gradient from ethyl acetate to methanol (100:0, 9:1, 8:2, 6:4, 3:7, 500 ml each) to produce seven fractions (A–G). Fr. A (174.1 mg) was sub-fractionated on a silica gel column (15 × 2.7 cm, 200–300 mesh) with CH_2Cl_2–MeOH (99:1, 96:4, 20 ml each) as eluent to give 34 subfractions. Subfrs. A24–A26 were chromatographed on a Sephadex LH-20 column (MeOH) and purified by preparative TLC to yield **16** (2 mg). Fr. B (611 mg) gave **4** (1 mg) by silica gel column (18 × 2.5 cm, 200–300 mesh) chromatography (CH_2Cl_2–MeOH, 96:4) and Sephadex LH-20 column chromatography (MeOH). Separation of fr. C by silica gel column (25 × 3 cm, 200–300 mesh) chromatography (CH_2Cl_2–MeOH, 94:6, 9:1, 8:2, 50 ml each) afforded 23 fractions, and **13** (63 mg) was furnished by further Sephadex LH-20 column chromatography from subfrs. C11–C15. Fr. D (686.4 mg) was subjected to silica gel

column (16.7 × 2.6 cm, 200–300 mesh) chromatography (CH_2Cl_2–MeOH, 92:8, 9:1, 20 ml each) and **14** (33 mg) was yielded by further Sephadex LH-20 column chromatography. Fr. E (1.09 g) was chromatographed on a silica gel column (23.6 × 2.5 cm, 200–300 mesh) eluted with CH_2Cl_2–MeOH (94:6, 8:2, 30 ml each), and subfrs. E14–E16 afforded **3** (3 mg). Subfrs. E30–E41 (300 mg) were purified by preparative HPLC (29% MeOH–H_2O, flow rate 4 ml/min) after Sephadex LH-20 column chromatography (MeOH) to give **5** (11.3 mg, t_R 4.1 min) and **6** (5 mg, t_R 6.0 min). Fr. F (3.4 g) was subjected to silica gel column (20 × 5 cm, 200–300 mesh) chromatography with isocratic elution of CH_2Cl_2–MeOH (84:16), and subfr. F3 yielded **1** (5.7 mg, t_R 39.9 min) and **2** (2.7 mg, t_R 44.6 min) by preparative HPLC (30% MeOH–H_2O, flow rate 4 ml/min).

3.3.1. Ussuriensislignan A (1)

White amorphous powder; $[\alpha]_D^{20}$ −5.26 (*c* 0.57, MeOH); IR ν_{max} (KBr): 3417, 2954, 2838, 1647, 1050, 1019, 684 cm^{-1}; UV (MeOH) λ_{max} (log ε) 210 (5.42), 272 (3.12) nm; CD (MeOH) $\Delta\varepsilon_{242nm}$ −0.524, $\Delta\varepsilon_{217nm}$ +0.867; ^1H and ^{13}C NMR spectroscopic data, see Table 1; HRESIMS: *m/z* 619.1990 $[M+Na]^+$ (calcd for $C_{28}H_{36}O_{14}Na$, 619.1997).

3.3.2. Ussuriensislignan B (2)

White amorphous powder; $[\alpha]_D^{20}$ −3.70 (*c* 0.27, MeOH); IR ν_{max} (KBr): 3453, 1642, 1019, 689 cm^{-1}; UV (MeOH) λ_{max} (log ε) 210 (5.74), 274 (4.46) nm; CD (MeOH) $\Delta\varepsilon_{245nm}$ −0.103, $\Delta\varepsilon_{214nm}$ +0.152; ^1H and ^{13}C NMR spectroscopic data, see Table 1; HRESIMS: *m/z* 595.2027 $[M-H]^-$ (calcd for $C_{28}H_{35}O_{14}$, 595.2021).

3.3.3. TLC acid hydrolysis of compounds 1 and 2

A methanol solution of compounds **1** and **2** was spotted on the TLC plate, respectively, and fumigated by hydrochloric acid vapor at 70 °C for 20 min in the sealed container. Then the plate was removed from the hydrochloric acid vapor. After the plate was air-dried, the authentic sugars were applied to the same plate. Then, the plate was developed by EtOAc–MeOH–H_2O–HAc (4:1:1:2.5), giving yellow spots at R_f 0.5 for glucose. 5% H_2SO_4 in EtOH was employed as a spray for visualization.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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