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Studies on the Constituents of Cistanchis Herba. V. Isolation and Structures of Two New Phenylpropanoid Glycosides, Cistanosides E and F

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Two new phenylpropanoid glycosides, named cistanosides E (III) and F (IV), were isolated from Cistanchis Herba, the whole plant of *Cistanche salsa* (C. A. MEY.) G. BECK (Orobanchaceae), together with two known lignan glycosides, liriodendrin (I) and (+)-syringaresinol *O*-β-D-glucopyranoside (II). The structures of III and IV were determined to be 2-(4-hydroxy-3-methoxyphenyl) ethyl *O*-α-L-rhamnopyranosyl-(1→3)-*O*-β-D-glucopyranoside and α-L-rhamnopyranosyl (1→3)-*O*-(4-*O*-caffeoyl)-D-glucopyranose, respectively, on the basis of chemical and spectral data.

Keywords——*Cistanche salsa*; Cistanchis Herba; Orobanchaceae; phenylpropanoid glycoside; cistanoside E; cistanoside F; lignan glycoside; liriodendrin; (+)-syringaresinol *O*-β-D-glucoside; ^{13}C-NMR

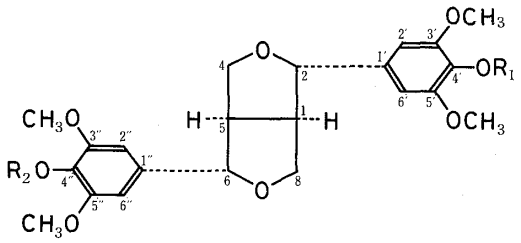
Cistanche salsa (C. A. MEY.) G. BECK (Orobanchaceae) is the plant of origin of the crude drug, Cistanchis Herba (Japanese name: Nikujuyou) which has been used as a staminal tonic in Oriental medicine.

In previous papers, we have reported the isolation of iridoids[1] and phenylpropanoid glycosides[2] from Cistanchis Herba. We now wish to report the isolation and the structure elucidation of two new phenylpropanoid glycosides, cistanosides E (III) and F (IV), as well as the isolation of two known lignan glycosides, liriodendrin [(+)-syringaresinol di-*O*-β-D-glucopyranoside] (I)[3] and (+)-syringaresinol *O*-β-D-glucopyranoside (II),[4] from this crude drug.

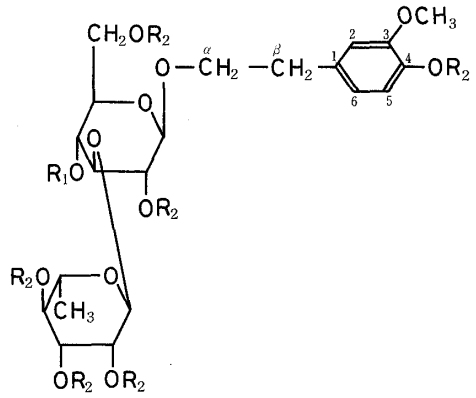
The dried whole plants were extracted with hot methanol and the methanolic extract was suspended in water. This suspension was extracted with ethyl acetate and then the aqueous layer was chromatographed on a Diaion HP-20 column to give three fractions. After repeated chromatography (silica gel, Sephadex LH-20) of each of the three fractions, two lignan glycosides, liriodendrin (I) and (+)-syringaresinol *O*-β-D-glucopyranoside (II), and two phenylpropanoid glycosides, cistanosides E (III) and F (IV), were isolated.

Both compound I, colorless needles, mp 253—254 °C, and compound II, amorphous powder, were suggested to have aromatic rings, methoxyl groups, and hydroxyl groups on the basis of ultraviolet (UV), infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectral analyses. On acetylation of I and II with acetic anhydride–pyridine, I gave an octaacetate (Ia), $C_{50}H_{62}O_{26}$, and II afforded a pentaacetate (IIa), $C_{38}H_{46}O_{18}$. The ^{1}H-NMR spectrum of Ia showed the presence of four methoxyl groups [δ 3.83 (12H)] and eight alcoholic acetoxyl groups [δ 2.03 (24H)], while that of IIa showed the presence of four methoxyl groups [δ 3.82 (12H)], four alcoholic acetoxyl groups [δ 2.02 (12H)] and one phenolic acetoxyl group

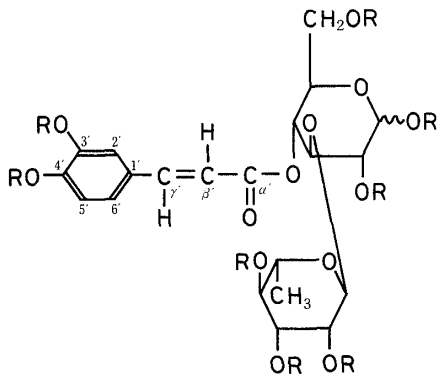
[δ 2.33 (3H)]. On enzymatic hydrolysis with β-glucosidase, both I and II gave the same aglycone (Ib), $C_{22}H_{26}O_8$, which was identified as (+)-syringaresinol[5] by direct comparison [mixed mp, IR and $[\alpha]_D$] with an authentic sample. Furthermore, when compounds I and II were treated with 10% sulfuric acid, glucose was detected on gas liquid chromatography (GLC) in each case. From the above data, I and II were assumed to be liriodendrin [(+)-syringaresinol di-*O*-β-D-glucopyranoside][3] and (+)-syringaresinol *O*-β-D-glucopyranoside,[4] respectively, and these identifications were confirmed by direct comparison (IR and ^{1}H-NMR) with authentic samples.



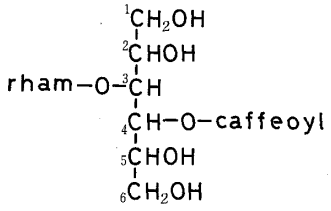
I : $R_1=R_2=$gluc$(OH)_4$
Ia : $R_1=R_2=$gluc$(OAc)_4$
Ib : $R_1=R_2=H$
II : $R_1=H$, $R_2=$gluc$(OH)_4$
IIa: $R_1=Ac$, $R_2=$gluc$(OAc)_4$



III : $R_1=R_2=H$
IIIa: $R_1=R_2=Ac$
V : $R_1=$caffeoyl, $R_2=H$



IV : R=H
IVa: R=Ac



IVb

Chart 1

Cistanoside E (III) was isolated as an amorphous powder and gave a heptaacetate (IIIa), $C_{35}H_{46}O_{19}$, upon acetylation with acetic anhydride and pyridine. The IR spectrum of III suggested the presence of hydroxyl groups (3450 cm^{-1}) and aromatic rings (1620, 1525 cm^{-1}), and the UV spectrum showed absorption maxima at 227 and 281 nm. The field desorption-mass spectrum (FD-MS) of III exhibited ion peaks at *m/z* 476 (M^+), 477 $(M+1)^+$ and 499 $(M+Na)^+$. The presence of glucose and rhamnose in the acid hydrolysate with 10% sulfuric acid in a ratio of 1 to 1 was proved by GLC. The ^{1}H-NMR spectrum of III showed signals due to a methyl group of rhamnose [δ 1.25 (3H, d, $J=6$ Hz)], benzylic methylene protons [δ 2.84 (2H, t, $J=7$ Hz)], a methoxyl group [δ 3.82 (3H, s)], a glucose-anomeric proton [δ 4.50 (1H, d, $J=8$ Hz)], a rhamnose-anomeric proton [δ 5.14 (1H, br s)] and aromatic protons [δ 6.6—6.9 (3H)]. The ^{1}H-NMR spectrum of IIIa revealed the presence of seven acetoxyl signals belonging to six alcoholic [δ 1.94, 1.98, 2.01, 2.11 (3H each) and 2.07 (6H)] and a phenolic [δ 2.28 (3H)] acetoxyl groups. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of III showed almost the same chemical shifts as that of cistanoside C (V),[2b] ex-

TABLE I. ^{13}C-NMR Chemical Shifts[a] of I—V

Carbon No.	I[b]	II[b]	Carbon No.	III	IV	IVb	V
1	53.6	53.6	1	131.6			131.6
5			2	113.9			113.9
4	71.4	71.2	3	148.8			148.8
8			4	145.9			145.9
2	85.0	85.3	5	116.2			116.6
6		85.1	6	122.4			122.4
1′	134.0	131.5	α	72.3			72.3
1″		134.1	β	36.7			36.6
2′	104.5	104.0	1′		127.8	127.8	127.7
2″		104.4	2′		114.9	115.0	114.8
3′	152.6	148.0	3′		149.6	149.6	149.6
3″		152.6	4′		146.7	146.7	146.7
4′	137.1	135.1	5′		116.6	116.6	116.2
4″		137.2	6′		123.1	123.1	123.2
5′	152.6	148.0	α′		168.3	168.6	168.3
5″		152.6	β′		115.4	115.5	115.5
6′	104.5	104.0	γ′		147.8	147.7	147.9
6″		104.4	Gluc-1 α		94.0		
Gluc-1	102.8	102.9	Gluc-1 β	104.2	98.1	64.2[g]	104.1
2	74.2	74.2	2 α		71.2		
3	76.5	76.5	2 β	75.5	74.7	73.4	76.0
4	70.1	70.1	3 α		79.2		
5	77.1	77.1	3 β	84.8	81.6	79.1	81.6
6	61.0	61.1	4 α		70.3[e]		
		56.1	4 β	70.1[c]	70.3[e]	74.0	70.3[i]
OCH_3	56.2	56.5	5 α		76.1		
			5 β	77.7	77.4	72.3	76.1
			6 α		62.5		
			6 β	62.8	62.5	64.0[g]	62.4
			Rham-1	102.7	102.9	103.8	102.8
			2	71.9[d]	72.2[f]	72.3[h]	72.1[j]
			3	72.3[d]	72.3[f]	72.4[h]	72.0[j]
			4	74.0	73.9	73.7	73.8
			5	70.3[c]	70.9[e]	70.9	70.7[i]
			6	17.9	18.4	18.0	18.4
			OCH_3	56.6			56.6

a) δ ppm from TMS in methanol-d_4. *b*) In DMSO-d_6. *c*—*j*) Assignments may be interchanged in each column.

cept for the lack of signals due to the caffeoyl moiety. Methanolysis of III with acetyl chloride in methanol afforded 3-methoxy-4-hydroxyphenethyl alcohol, which was detected by thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC). Compound III was identical with the product which was obtained from cistanoside C (V)[2b] by hydrolysis with sodium methoxide. These results led us to conclude that the structure of cistanoside E is 2-(4-hydroxy-3-methoxyphenyl) ethyl *O*-α-L-rhamnopyranosyl-(1→3)-*O*-β-D-glucopyranoside (III).

Cistanoside F (IV) was isolated as an amorphous powder and gave an octaacetate (IVa), $C_{37}H_{44}O_{21}$, upon acetylation in the usual way. The IR spectrum of IV suggested the presence of hydroxyl groups (3450 cm^{-1}), a conjugated ester (1700 cm^{-1}), a double bond (1638 cm^{-1}) and an aromatic ring (1610, 1523 cm^{-1}). The molecular weight of IV was confirmed by the observation of the ion peak at *m/z* 511 $(M+Na)^+$ on FD-MS. Acid hydrolysis of IV with

10% sulfuric acid afforded glucose and rhamnose in a ratio of 1 to 1. The ^{1}H-NMR spectrum of IV showed signals due to a methyl group of rhamnose [δ 1.11 (3H, d, J=6 Hz)], a glucose-anomeric proton [δ 4.57 (1H, d, J=8 Hz)], a rhamnose-anomeric proton [δ 5.15 (1H, br s)], two *trans* olefinic protons [δ 6.28, 7.60 (1H each, d, J=16 Hz)] and aromatic protons [δ 6.6—7.2 (3H)]. In the ^{1}H-NMR spectrum of IVa, the signals of six alcoholic acetoxyl groups [δ 1.99, 2.07 (3H each), 2.22, 2.23 (6H each)] and two phenolic acetoxyl groups [δ 2.42 (6H)] were observed. On methanolysis of IV with acetyl chloride in methanol, methyl caffeate was detected by TLC and HPLC. A duplication of the signals due to the glucose moiety was observed in the ^{13}C-NMR spectrum of IV. Furthermore, on reduction with sodium borohydride in methanol, IV afforded 3-*O*-α-L-rhamnopyranosyl-4-*O*-caffeoyl-glucitol (IVb). It follows therefore that the anomeric center of the glucose moiety is not substituted and IV exists as an equilibrium mixture of α- and β-forms in solution. The locations of rhamnose and caffeoyl moieties in the glucose of IV were determined by detailed comparison of the ^{13}C-NMR spectrum with that of V. The signals due to the C-3 and C-4 carbons of β-form were almost identical with those of V, indicating that the rhamnose moiety is attached to the C-3 hydroxyl group of the glucose and the caffeoyl moiety to C-4. On the basis of the above-mentioned observations, the structure of cistanoside F was determined to be α-L-rhamnopyranosyl (1→3)-*O*-(4-*O*-caffeoyl)-D-glucopyranose (IV).

Since cistanosides E (III) and F (IV) were detected in the water extract of fresh plant material on TLC [solvent: $CHCl_3$–MeOH–H_2O (6:4:1); *Rf* value: III (0.81), IV (0.40)], we have confirmed that those compounds are naturally occurring substances and not artifacts formed in the processes of extraction and separation. In the series of phenylpropanoid glycosides, cistanoside F is the first example having a free anomeric hydroxyl group of the glucose.

Experimental

Melting points were determined on a Mitamura micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-140 digital polarimeter. IR spectra were recorded with a Hitachi 270-30 infrared spectrophotometer and UV spectra with a Hitachi 200-20 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a JEOL FX-90Q machine (89.55 and 22.5 MHz, respectively). Chemical shifts are given on the δ (ppm) scale with tetramethylsilane (TMS) as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). FD-MS were measured with a JEOL JMS-01-SG2 mass spectrometer. GLC was run on a Shimadzu GC-4CM apparatus with a flame ionization detector. HPLC was performed on a Kyowa Seimitsu KHP-010 machine equipped with a UV detector operated at 250 nm. Silica gel (Wako gel C-300, Wako Pure Chemical) was used for column chromatography. Kieselgel 60 F_{254} (Merck) precoated plates were used for TLC and detection was carried out by spraying ethanolic $FeCl_3$ solution or 10% H_2SO_4 followed by heating. The conditions for GLC were as follows: column, 1.5% OV-17, 3 mm i.d. × 1.5 m; column temp., 180 °C; carrier gas, N_2 (30 ml/min).

Extraction and Isolation——The dried whole plants of *Cistanche salsa* (C. A. MEY.) G. BECK (10 kg, commercial crude drug produced in China) were chopped and extracted with MeOH (36 l × 2) under reflux. The extract was concentrated under reduced pressure and the residue was suspended in water. This suspension was extracted with EtOAc and then the aqueous layer was chromatographed on a Diaion HP-20 column using an H_2O–MeOH solvent system to give three fractions, fr. 1 (H_2O eluate), 2 (30% MeOH eluate) and 3 (MeOH eluate). Fraction 2 was purified by chromatography on a silica gel column using $CHCl_3$–MeOH–H_2O (7:2:0.2) and then on a Sephadex LH-20 column using H_2O–MeOH (1:1) to afford compounds III (750 mg) and IV (800 mg). Repeated chromatography of fraction 3 on a silica gel column using $CHCl_3$–MeOH–H_2O (8:3:0.3) and then on a Sephadex LH-20 column using H_2O–MeOH (1:1) afforded compounds I (230 mg) and II (200 mg).

Liriodendrin (I)——Colorless needles from MeOH, mp 254—255 °C, $[\alpha]_D^{25}$ −22.8° (c=0.6, pyridine). UV $\lambda_{max}^{H_2O}$ nm (log ε): 230 sh (4.00), 271 (3.10). IR ν_{max}^{KBr} cm^{-1}: 3400, 1595, 1510. ^{1}H-NMR (DMSO-d_6) δ: 3.75 (12H, s, OCH_3 × 4), 6.65 (4H, s, aromatic H). ^{13}C-NMR: Table I. This compound was identified as liriodendrin by direct comparison (IR and ^{1}H-NMR) with an authentic sample.

(+)-Syringaresinol *O*-β-D-Glucopyranoside (II)——Amorphous powder, $[\alpha]_D^{24}$ −20.8° (c=0.7, MeOH). UV λ_{max}^{MeOH} nm (log ε): 221 (4.22), 272 (3.44). IR ν_{max}^{KBr} cm^{-1}: 3450, 1600, 1520. ^{1}H-NMR (DMSO-d_6): 3.75 (12H, s, OCH_3 × 4), 6.61, 6.67 (2H each, s, aromatic H). ^{13}C-NMR: Table I. This compound was identified as (+)-syringaresinol *O*-β-D-glucopyranoside by direct comparison (IR and ^{1}H-NMR) with an authentic sample.

Acetylation of I and II——Compound I (50 mg) or II (40 mg) was dissolved in pyridine (1 ml) and acetic anhydride (1 ml) and the solution was left at room temperature overnight. The reaction mixture was poured into ice-water, and then extracted with EtOAc. Each EtOAc extract was concentrated *in vacuo* and the residue was chromatographed on a silica gel column using benzene–acetone (5 : 1) to give the octaacetate (Ia) (20 mg) or pentaacetate (IIa) (15 mg). Liriodendrin octaacetate (Ia): colorless needles from MeOH, mp 119—120 °C. IR ν_{max}^{KBr} cm^{-1}: 1760, 1600, 1505. ^{1}H-NMR ($CDCl_3$) δ: 2.03 (24H, s, OAc × 8), 3.83 (12H, s, OCH_3 × 4), 6.54 (4H, s, aromatic H). (+)-Syringaresinol *O*-β-D-glucopyranoside pentaacetate: amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 1760, 1606, 1508. ^{1}H-NMR ($CDCl_3$) δ: 2.02 (12H, s, OAc × 4), 2.33 (3H, s, Ar-OAc), 3.82 (12H, s, OCH_3 × 4), 6.55, 6.58 (2H each, s, aromatic H).

Enzymatic Hydrolysis of I and II——Compound I (100 mg) or II (100 mg) was hydrolyzed with β-glucosidase (50 mg, Miles Laboratories) in acetate buffer (pH 5.0) for 2 d at 37 °C. The reaction mixture was extracted with EtOAc. The EtOAc extract was concentrated *in vacuo* to give the residue, which was chromatographed on a silica gel column using $CHCl_3$–MeOH (40 : 1) to give an aglycone (1b) (20 mg from I and 35 mg from II). (+)-Syringaresinol (1b): colorless needles from MeOH, mp 182—183 °C, $[\alpha]_D^{24}$ +21.7° (c=0.2, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3450, 1730, 1614, 1518. ^{1}H-NMR ($CDCl_3$) δ: 2.96—3.20 (2H, m, H-1, 5), 3.89 (12H, s, OCH_3 × 4), 3.70—4.40 (4H, m, H-4, 8), 4.72 (2H, d, J=4 Hz, H-2, 6), 6.58 (4H, s, aromatic H). This compound was identified as (+)-syringaresinol by direct comparison (mixed mp, IR and $[\alpha]_D$) with an authentic sample.

Acid Hydrolysis of I and II——A solution of a glycoside (*ca.* 2 mg) in 10% H_2SO_4 (1 ml) was heated in a boiling water bath for 30 min. The solution was passed through an Amberlite IR-45 column and concentrated to give a residue, which was reduced with sodium borohydride (*ca.* 3 mg) for 1 h. The reaction mixture was passed through an Amberlite IR-120 column and concentrated to dryness. Boric acid was removed by distillation with MeOH and the residue was acetylated with acetic anhydride (1 drop) and pyridine (1 drop) at 100 °C for 1 h. The reagents were evaporated off *in vacuo*. Glucitol acetate was detected in the hydrolysate from each glycoside by GLC. t_R (min) 5.5.

Cistanoside E (III)——Amorphous powder, $[\alpha]_D^{25}$ −51.5° (c=0.7, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3430, 1614, 1520. UV λ_{max}^{MeOH} nm (log ε): 227 (3.46), 281 (3.04). FD-MS *m/z*: 476 (M^+), 477 (M^+ + 1), 499 (M + Na)$^+$. ^{1}H-NMR (methanol-d_4) δ: 1.25 (3H, d, J=6 Hz, CH_3 of rhamnose), 2.84 (2H, t, J=7 Hz, Ar-CH_2–), 3.82 (3H, s, OCH_3), 4.50 (1H, d, J= 8 Hz, H-1 of glucose), 5.14 (1H, br s, H-1 of rhamnose), 6.6—6.9 (3H, aromatic H). ^{13}C-NMR: Table I.

Cistanoside F (IV)——Amorphous powder, $[\alpha]_D^{25}$ −83.5° (c=0.9, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3430, 1698, 1634, 1606, 1520. FD-MS *m/z*: 511 (M + Na)$^+$. ^{1}H-NMR (methanol-d_4): 1.11 (3H, d, J=6 Hz, CH_3 of rhamnose), 4.57 (1H, d, J=8 Hz, H-1 of glucose), 5.15 (1H, br s, H-1 of rhamnose), 6.28 (1H, d, J=16 Hz, Ar-CH=C<u>H</u>–), 6.7—7.2 (3H, aromatic H), 7.60 (1H, d, J=16 Hz, Ar-C<u>H</u>=CH–). ^{13}C-NMR: Table I.

Acetylation of III and IV——Compound III or IV (each 100 mg) was acetylated in the same way as described for I and II. Each crude acetate was purified by chromatography on a silica gel column using benzene–acetone (10 : 1) to give the heptaacetate (IIIa) (125 mg) from III, or the octaacetate (IVa) (70 mg) from IV. Cistanoside E heptaacetate (IIIa): amorphous powder, *Anal.* Calcd for $C_{35}H_{46}O_{19}$: C, 54.54; H, 6.02. Found: C, 54.29; H, 5.93. IR ν_{max}^{KBr} cm^{-1}: 1760, 1608, 1516, 1436. ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, d, J=6 Hz, CH_3 of rhamnose), 1.94, 1.98, 2.01, 2.11 (3H each, s, OAc), 2.07 (6H, s, OAc × 2), 2.28 (3H, s, Ar-OAc), 2.85 (2H, t, J=7 Hz, Ar-CH_2–), 6.7—7.0 (3H, aromatic H). Cistanoside F octaacetate (IVa): amorphous powder, *Anal.* Calcd for $C_{37}H_{44}O_{21}$: C, 53.88; H, 5.38. Found: C, 53.59; H, 5.38. IR ν_{max}^{KBr} cm^{-1}: 1752, 1642, 1508, 1434. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (3H, d, J=6 Hz, CH_3 of rhamnose), 1.99, 2.07 (3H each, s, OAc), 2.22, 2.23 (6H each, s, OAc), 2.42 (6H, s, Ar-OAc × 2), 6.48 (1H, d, J=16 Hz, Ar-CH=C<u>H</u>–), 7.2—7.6 (3H, aromatic H), 7.80 (1H, d, J=16 Hz, Ar-C<u>H</u>=CH–).

Acid Hydrolysis of III and IV——Compounds III and IV were hydrolyzed in the same way as described for I and II. Glucitol acetate and rhamnitol acetate were detected in a ratio of 1 to 1 from each glycoside by GLC. t_R (min) 2.0 (rhamnitol acetate), 5.5 (glucitol acetate).

Methanolysis of III and IV——Compound III or IV (*ca.* 1 mg) was refluxed with methanolic 5% CH_3COCl (2 ml) for 30 min, and then the reagents were evaporated off *in vacuo*. The presence of methyl caffeate in the residue of III, or 4-hydroxy-3-methoxyphenethyl alcohol in that of IV was detected by TLC [$CHCl_3$–MeOH (20 : 1)] and HPLC [column, TSK GEL LS-410AK (4 mm i.d. × 300 mm); solvent, H_2O–MeOH (4 : 6); flow rate, 1.0 ml/min]. Methyl caffeate: *Rf* 0.20, t_R (min) 5.5. 4-Hydroxy-3-methoxyphenethyl alcohol: *Rf* 0.31, t_R (min) 3.8.

Alkaline Hydrolysis of Cistanoside C (V)——A solution of V (100 mg) in methanolic 5% NaOMe (10 ml) was allowed to stand for 5 h at room temperature. After dilution with water, the reaction mixture was passed through a Diaion HP-20 column and eluted with water and methanol successively. The methanol eluate was concentrated *in vacuo* to give the residue, which was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (7 : 2 : 0.2) to give III (35 mg), which was identical with natural III (TLC, IR and ^{1}H-NMR).

Reduction of IV——$NaBH_4$ (50 mg) was added to a solution of IV (50 mg) in MeOH (5 ml), and the reaction mixture was stirred at room temperature for 1 h. After dilution with water, the reaction mixture was treated in the same way as described for alkaline hydrolysis of V. The crude reduced product was purified by chromatography on a silica gel column using $CHCl_3$–MeOH–H_2O (8 : 2 : 0.2) to give 3-*O*-α-L-rhamnopyranosyl-4-*O*-caffeoyl-glucitol (IVb) (30 mg). IVb: amorphous powder, $[\alpha]_D^{25}$ −21.2° (c=0.5, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1696, 1634, 1604, 1522. UV λ_{max}^{MeOH} nm (log ε): 219 (4.03), 235 sh (3.88), 246 sh (3.85), 300 sh (3.94), 332 (4.07). ^{1}H-NMR (methanol-d_4)

δ: 1.30 (3H, d, $J=6$ Hz, CH_3 of rhamnose), 6.28 (1H, d, $J=16$ Hz, Ar-CH=C<u>H</u>–), 6.7—7.1 (3H, aromatic H), 7.58 (1H, d, $J=16$ Hz, Ar-C<u>H</u>=CH–). ^{13}C-NMR: Table I.

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4) *a*) Yahara *et al.* isolated (±)-syringaresinol β-D-glucopyranoside [$[\alpha]_D^{19}$ −19.3° ($c=1.1$, MeOH)], the aglycone of which showed $[\alpha]_D^{17}$ −7.5° ($c=1.4$, $CHCl_3$), from *Magnolia officinalis* REHD. *et* WILS. (Magnoliaceae). (M. Yahara, I. Nishioka, A. Koda, and K. Nishiyori, Abstracts of Papers, the 103rd Annual Meeting, Pharmaceutical Society of Japan, Tokyo, April 1983, p. 215.); *b*) Private communication from T. Deyama, Central Research Laboratories, Yomeishu Seizo Co., Ltd. [isolation from the bark of *Eucommia ulmoides* OLIV. (Eucommiaceae)].
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