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Studies on Constituents of Bignoniaceae Plants. IV.[1] Isolation and Structure of a New Iridoid Glucoside, Campsiside, from *Campsis chinensis*

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A new iridoid glucoside, campsiside, was isolated along with 5-hydroxycampsiside (pondraneoside) and an alkaloid, boschniakine, from *Campsis chinensis*. The structures of campsiside and 5-hydroxycampsiside (pondraneoside) were established as **5** and **12**, respectively, from chemical and spectral evidence.

Keywords——*Campsis chinensis*; Bignoniaceae; iridoid glucoside; campsiside; 5-hydroxycampsiside; pondraneoside; lamiidol; hexaacetyl caryptoside; tetraacetyl durantoside I; boschniakine

In the preceding papers,[2,3] we reported the isolation and structural determination of four iridoid glucosides having an aldehyde group at C-4, campenoside (**1**),[2] 5-hydroxycampenoside (**2**),[2,3] cachineside I (**3**)[3] and tecomoside (**4**),[3-5] from the leaves of *Campsis chinensis* VOSS. The present paper deals with the isolation and structural elucidation of campsiside (**5**)[6] and 5-hydroxycampsiside (**12**,[6] pondraneoside[7]). These compounds were obtained from the *n*-butanol-soluble portion of a methanolic extract of the leaves by repeated column chromatography as described in Experimental.

Compsiside (**5**) is an amorphous powder, $[\alpha]_D$ −68.5° (MeOH), which gave glucose and a black product (derived from the aglycone) on acid hydrolysis. Infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectral data showed that **5** contained a *trans*-cinnamoyl function [IR(KBr): 1709, 1635 cm^{-1}; ^{1}H-NMR (CD_3OD): δ 6.55 and 7.72 (each 1H, d, J=16.0 Hz), 7.20—7.30 (5H, m, aromatic H)], an α,β-unsaturated aldehyde function [1680, 1645 cm^{-1}; δ 7.41 (1H, br s), 9.18 (1H, s)], a methyl group [δ 1.29 (3H, s)] and a β-D-glucopyranosyl moiety [3400 cm^{-1}; δ 4.67 (1H, d, J=8.0 Hz)]. The signals of H-1, H-9, H-3 and H-6 were assigned on the basis of extensive decoupling experiments as follows. Irradiation of the doublet at δ 5.73 (d, J=1.5 Hz, H-1) collapsed a double doublet at δ 2.70 (dd, J=10.0, 1.5 Hz, H-9) into a doublet, which suggested a *trans*-relatinonship between H-1 and H-9. Irradiation of the broad singlet at δ 7.41 (H-3) caused the multiplet at δ 3.15 (m, H-5) to become deformed. Irradiation at H-5 collapsed the double triplet at δ 1.81 (dt, J=6.0, 12.0 Hz, αH-6) and the double double doublet at δ 2.28 (ddd, J=2.5, 9.0, 12.0 Hz, βH-6), respectively, into double doublets, and also caused the signals of H-9 to change into a doublet ($J_{1,9}$=1.5 Hz), which suggested the absence of a proton at C-8. Acetylation of **5** with acetic anhydride–pyridine gave a tetraacetate (**6**), $C_{33}H_{38}O_{15}$, mp 222—223 °C, in which one hydroxyl group (3510 cm^{-1}) remained unaffected, indicating its tertiary nature, $[\alpha]_D$ −75.3° ($CHCl_3$) and a pentaacetate (**7**), $C_{35}H_{40}O_{16}$, mp 170—171.5 °C, IR: no OH, $[\alpha]_D$ −80.5°

($CHCl_3$). The signals of H-1, H-9 and a methyl group in **7** showed shifts of 0.16, 0.34 and 0.21 ppm downfield from those in **6**. These shifts were due to paramagnetic shifts[8] of the tertiary acetoxy group at C-8, indicating a *cis*-relationship between H-9 and the hydroxyl group at C-8. The *trans*-cinnamoyl group in **5** was concluded to be located at position C-7, since the signals of H-7 in the ^{1}H-NMR spectra of **5** and **6** were observed at δ 4.90 and 4.86, respectively. Furthermore, H-7 was deduced to have the α-configuration from the coupling patterns (see Table I) of protons, H-6 and H-7, of the cyclopentane ring. These assignments were supported by the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **5**, since the signals due to C-7, C-9 and C-10 were observed at δ 81.11 (d), 48.85 (d) and 22.13 (q), respectively, as in other iridoid glucosides[9] with the same functional groups at C-7, C-8 and C-10, respectively. Assuming that H-9 has a usual β-configuration,[10] the structure of campsiside was deduced to be **5** from the above data.

To confirm this structure, the acetate (**6**) was converted to hexaacetyl caryptoside (**11**).[11] Oxidation of **6** with sodium dichromate in acetic acid, followed by hydrolysis with sodium hydroxide gave a *trans*-cinnamic acid and an acid product (**9**). Acetylation of **9** with acetic anhydride–pyridine followed by methylation with diazomethane afforded pentaacetyl caryptoside (**10**), mp 138—140 °C, $[\alpha]_D$ −119.0° ($CHCl_3$), and a hexaacetyl caryptoside (**11**),[11] mp 157—159 °C, $[\alpha]_D$ −87.5° ($CHCl_3$). The latter compound was confirmed to be identical with

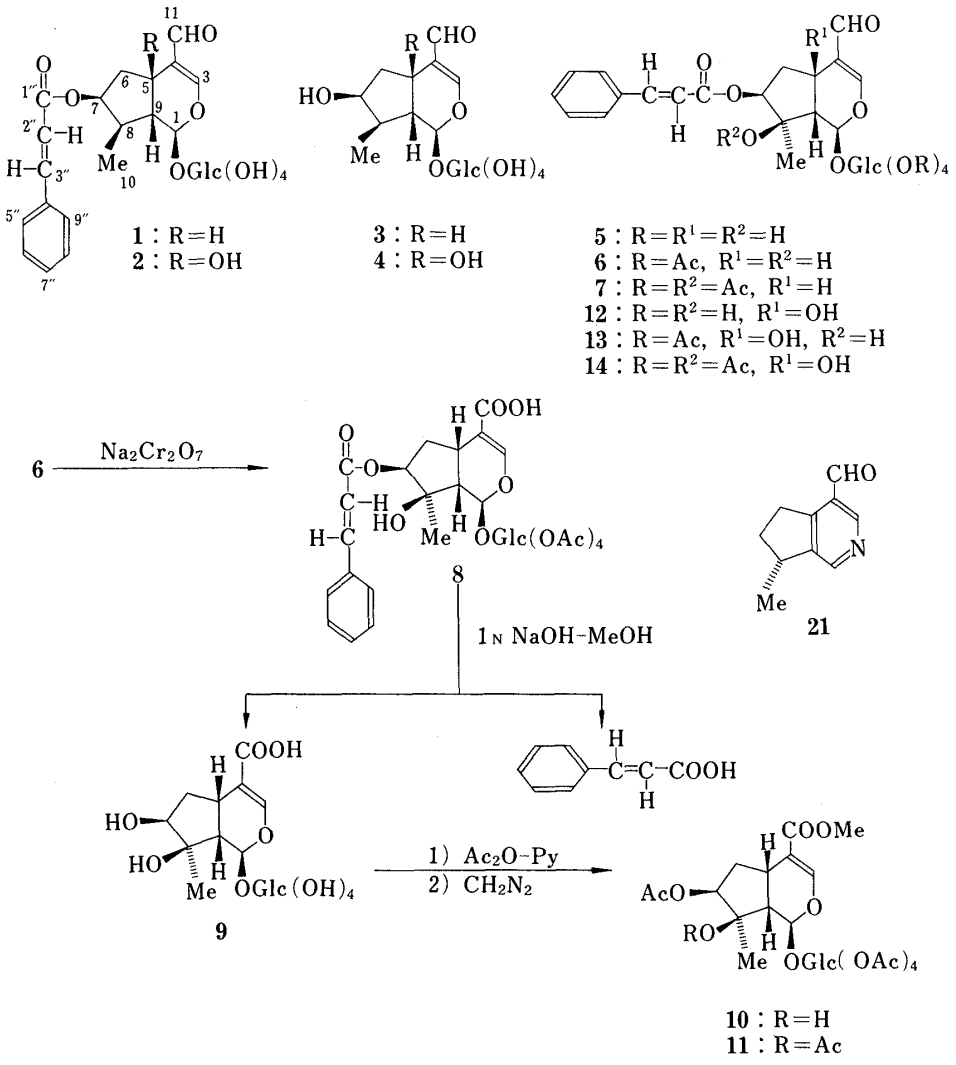


Chart 1

TABLE I. ^{1}H-NMR Spectral Data for **5**—**8**, **10**—**14** and **16**—**18** (δ Values)[a]

	H-1	H-3	H-5	αH-6	βH-6	H-7	H-9	Me-8	CHO-4	COOMe-4	H-1′
5	5.73 d (1.5)	7.41	3.15 m	1.81 dt (12.0, 6.0)	2.28 ddd (12.0, 9.0, 2.5)	4.90 m	2.70 dd (10.0, 1.5)	1.29	9.18		4.67 d (8.0)
6	5.63 br s	7.09	3.11 m	d)	2.49 ddd (15.0, 9.0, 2.5)	4.86 dd (6.0, 2.5)	2.73 d (10.0)	1.30	9.23		d)
7	5.79 br s	7.11	3.07 m	2.52 m		5.50 dd (6.0, 2.5)	3.07 m	1.51	9.25		d)
8	5.47 br s	7.35	3.08 m	2.40 m		4.76 m	2.69 d-like	1.23			d)
10	5.43 d (1.0)	7.27	3.00 m		2.35 ddd (15.0, 9.0, 2.5)	4.71 m	2.62 dd (10.0, 1.0)	1.25		3.67	d)
11	5.60 br s	7.33	3.00 m	2.44 m		5.38 dd (5.5, 2.0)	3.00 m	1.47		3.70	d)
12	5.95 d (0.8)	7.39		2.48 dd (15.5, 4.4)	2.38 dd (15.5, 2.4)	4.85 m	2.90 d (0.8)	1.17	9.28		4.65 d (8.0)
13[b]	5.80 br s	7.45		2.50 dd (15.0, 4.5)	2.30 dd (15.0, 3.0)	4.78 dd (4.5, 3.0)	2.91	1.18	9.37		d)
13	5.77 br s	7.10		2.48 m		4.84 m	2.95	1.23	9.35		d)
14	5.95 br s	7.14		2.51 d-like		5.28 m	3.19	1.44	9.37		d)
16[c]	5.83 br s	6.56		2.25 m		d)	2.81	1.37			d)
17	5.71 d (1.2)	7.34		2.48 m		4.87 m	2.99 d (1.2)	1.21		3.77	d)
18	5.67 d (1.0)	7.31		2.40 d-like		4.69 t (3.4)	2.89 d (1.0)	1.16		3.76	4.82 d (8.0)

a) Measured in $CDCl_3$ except for **5** and **12** (CD_3OD), with TMS as internal standard. d, doublet; dd, double doublets; d-like, doublet-like; ddd, double double doublets; t, triplet; br s, broad singlet; unmarked signal singlet. Numbers in parentheses are coupling constants J(Hz). *b*) Measured in acetone-d_6. *c*) Measured in D_2O with tetramethylsilane as an external standard. *d*) Obscured signals.

authentic hexaacetyl caryptoside (**11**) by comparison of spectral data and the mixed melting point test.

Thus the stereochemistry of campsiside was established as 8-β-hydroxycampenoside (**5**).

Compound **12** was isolated as a hygroscopic amorphous powder, $[\alpha]_D$ −105.2° (MeOH), which gave a glucose and a black product (derived from the aglycone) on acid hydrolysis. The ^{1}H-NMR and IR spectra of **12** showed the presence of a *trans*-cinnamoyl function [1710, 1640 cm^{-1}; δ 6.61 and 7.77 (each 1H, d, J=16.1 Hz), 7.40—7.70 (5H, m, aromatic H)], an α,β-unsaturated aldehyde group [1670, 1630 cm^{-1}; δ 9.28 (1H, s), 7.39 (1H, s)], a methyl group [δ 1.17 (3H, s)] and a β-D-glucopyranosyl moiety [3420 cm^{-1}; δ 4.65 (1H, d, J=8.0 Hz, anomeric H)].

Acetylation of **12** with acetic anhydride–pyridine gave a tetraacetate (**13**), $C_{33}H_{38}O_{16}$, mp 241—242 °C, $[\alpha]_D$ −83.5° ($CHCl_3$), and a pentaacetate (**14**), $C_{35}H_{40}O_{17}$, mp 168—170 °C, $[\alpha]_D$

TABLE II. ^{13}C-NMR Spectral Data for **5** and **12** (δ Values)[a]

Carbon	**5**	**12**	Carbon	**5**	**12**
Aglycone moiety			Glucose moiety		
1	96.12 d	95.19 d	1′	100.18 d	99.89 d
3	162.41 d	162.23 d	2′	74.60 d	74.46 d
4	126.32 s	127.10 s	3′	77.99 d[b]	77.47 d[b]
5	25.84 d	68.27 s	4′	71.63 d	71.65 d
6	36.09 t	44.59 t	5′	78.28 d[b]	78.43 d[b]
7	81.11 d	80.50 d	6′	62.84 t	62.81 t
8	79.36 s	78.66 s			
9	48.85 d	58.28 d	*trans*-Cinnamoyl moiety		
10	22.13 q	21.43 q	1″	167.95 s	167.98 s
11	192.77 d	192.19 d	2″	119.10 d	119.19 d
			3′	146.40 d	146.43 d
			4″	135.81 s	135.89 s
			5″	129.94 d[c]	129.99 d[c]
			6″	129.18 d	129.24 d
			7″	131.40 d	131.45 d
			8″	129.18 d[c]	129.24 d[c]
			9″	129.94 d	129.99 d

a) Measured in CD_3OD with TMS as an internal standard. s, singlet; d, doublet; t, triplet; q, quartet. *b*, *c*) Assignments in each column may be interchanged.

TABLE III. Differences ($\Delta\delta$) between δ in ^{1}H- and ^{13}C-NMR Spectra

Compound	$\Delta\delta$ (ppm)						
	^{1}H-NMR				^{13}C-NMR		
	H-1	H-7	H-9	Me-8	C-5	C-6	C-9
2—**1**[a]	0.38	−0.16	0.37		40.84	7.21	8.55
4—**3**[a]	0.31	−0.12	0.24		42.57	7.68	8.82
12—**5**[a]	0.22	−0.05	0.20		42.43	8.49	9.43
7—**6**[b]	0.16		0.34	0.21			
11—**10**[b]	0.17		0.38	0.22			
14—**13**[b]	0.18		0.24	0.21			
20—**19**[b]	0.15		0.17	0.11			

a) Measured in CD_3OD. *b*) Measured in $CDCl_3$.

−95.3° ($CHCl_3$). The IR spectrum of **14** indicated the presence of a tertiary hydroxyl group (3533 cm^{-1}), which was concluded to be located at C-5 for the following reasons: (i) in the ^{1}H-NMR spectrum of **12**, the signals due to H-1 [δ5.95 (d, J=0.8 Hz)] and H-9 [δ2.90 (d, J=0.8 Hz)] showed shifts of 0.22 and 0.20 ppm downfield, respectively, from those of **5**; namely, similar downfield shifts (see Table III) were observed for the H-1 and H-9 signals in the known 5-hydroxy compounds **2** and **4** compared with those of the corresponding 5-hydrogen compounds **1** and **3**, respectively. (ii) Similarly, in the ^{13}C-NMR spectra, the $\Delta\delta$ values between **12** and **5** at the C-5, C-6 and C-9 signals were similar to those between **2** and **1**, and **4** and **3** as shown in Table III. Furthermore, the *trans*-relationship between the protons of H-1 and H-9 in **12** was deduced from the coupling constant ($J_{1,9}$=0.8 Hz)[12] between the two protons. The hydroxyl and methyl groups at C-8 in **12** were concluded to have the β- and α-configurations, respectively, on the basis of the paramagnetic shifts[8] observed for H-1, H-9

and Me-8 in **14** compared with those in **13**, as seen in the case of **6** and **7** (see Table III). These assignments were supported by the carbon signals at C-7, C-8 and C-10 in the ^{13}C-NMR spectrum (see Table II) of **12**.

The *trans*-cinnamoyl group in **12** was deduced to be at the C-7 position and to have the β-configuration since the proton signal at C-7 in the ^{1}H-NMR spectrum was observed in almost the same region (δ 4.85) as that of **5**, and the carbon signals of C-9 and C-10 in the ^{13}C-NMR spectrum were observed at δ 58.28 (d) and 21.40 (q), respectively, as seen in other iridoid glucosides[9,13] [*e.g.*, lamiide (**15**), δ 56.95 (C-9) and 20.64 (C-10); lamiidol (**16**), δ 58.02 (C-9) and 21.13 (C-10)] which have almost the same functional groups and the same configurations as **12**.

Consequently, the structure of compound **12** was deduced as 5-hydroxycampsiside.

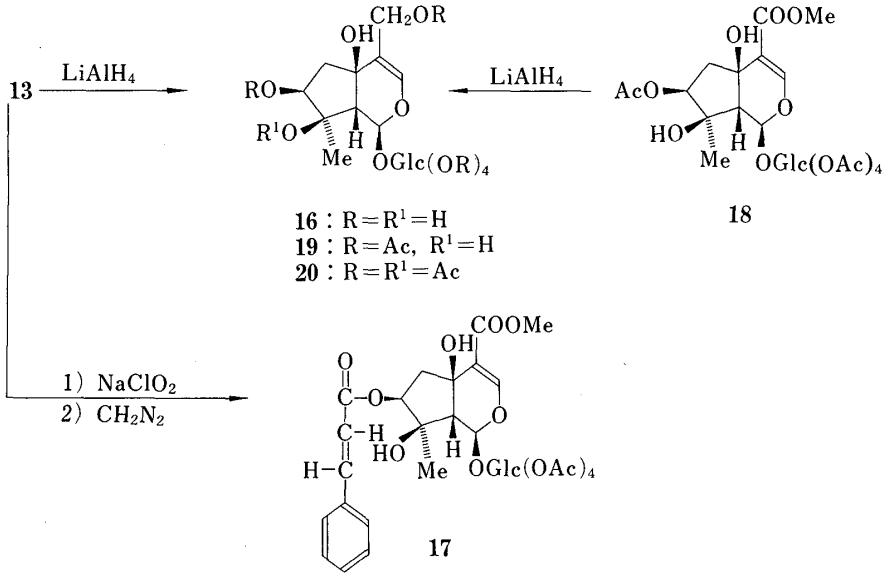


Chart 2

For verification of this structure, 5-hydroxycampsiside was compared chemically with two known compounds, lamiidol (**16**)[14] and tetraacetyl durantoside I (**17**)[15] as shown in Chart 2. Reduction of **13** with lithium aluminum hydride gave **16**, which was identical with **16** prepared by reduction of pentaacetyl lamiide (**18**) with lithium aluminum hydride. Furthermore, acetylation of **16** gave a hexaacetate (**19**) and heptaacetate (**20**). Compound **13**, on oxidation with sodium chlorite,[16] followed by methylation with diazomethane, gave a product (**17**), mp 219—222 °C, that showed the same physical and spectral data as those of tetraacethyl durantoside I,[14] as can be seen in Table I and Chart 3.

Thus, the stereochemistry of 5-hydroxycampsiside was established as **12**, [6] which found to be the same as the structure of pondraneoside reported by Guiso *et al.*[7]

Finally, from an ethanol extract of the roots of *C. chinensis*, a known monoterpene alkaloid, boschniakine (**21**)[17] was isolated as described in Experimental.

Experimental

All melting points are uncorrected. IR spectra and mass spectra (MS) were measured with Hitachi IR-215 and JEOL JMS-D-300 spectrometers, respectively. NMR spectra were taken with a JEOL JNN-PS-100 (^{1}H; 100 MHz) or FX-200 (^{1}H; 200 MHz, ^{13}C; 50.10 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard. For column chromatography, Merck Kieselgel 60 (70—230 mesh) was used. Thin-layer chromatography (TLC) and preparative thin-layer chromatography (PTLC) were performed with Merck Kieselgel GF_{254} and PF_{254}, respectively. Spots were detected under ultraviolet (UV) light or by spraying with 1% $Ce(SO_4)_2$–10% H_2SO_4 and then heating.

Isolations of 5 and 12——The *n*-BuOH-soluble portion (95 g), obtained previously[3] from a methanolic extract (120 g) of the leaves (1.4 kg) of *Campsis chinensis* Voss. was subjected to column chromatography [active charcoal (450 g)–Celite 535 (450 g); MeOH–Acetone (1 : 0—0 : 1) as the eluant] to give seven fractions: Fr.-I (835 mg, fr. 5—7), Fr.-II (2.5 g, fr. 9—13), Fr.-III (1.3 g, fr. 14—16), Fr.-IV (4.9 g, fr. 18—28), Fr.-V (5.5 g, fr. 29—42), Fr.-VI (2.5 g, fr. 43—60) and Fr.-VII (7.0 g, fr. 61—80 (each 500 ml). Material in an aliquot (1.1 g) of Fr.-V was purified by column chromatography [100 g, $CHCl_3$–MeOH–H_2O (50 : 15 : 3, lower layer)] to afford campsiside (**5**, 185 mg) and 5-hydroxycampsiside (**12**, 85 mg).

Campsiside (**5**): Amorphous powder. $[\alpha]_D^{20}$ −68.5° (c=0.43, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1710 (C=O), 1680 (C=O), 1645 (C=C), 1635 (C=C). ^{1}H-NMR: see Table I. ^{13}C-NMR: see Table II.

5-Hydroxycampsiside (**12**): Amorphous powder. $[\alpha]_D^{20}$ −105.2° (c=0.25, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1710 (C=O), 1670 (C=O), 1640 (C=C), 1630 (C=C). ^{1}H-NMR: see Table I. ^{13}C-NMR: see Table II.

Acid Hydrolysis of 5——A solution of **5** (10 mg) in 1 N H_2SO_4–MeOH (1 : 1, 2 ml) was refluxed for 1 h, neutralized with Amberlite IR-45 (OH form) and filtered. The filtrate was evaporated *in vacuo*, and the residue was shown to be identical with authentic D-glucose by paper partition chromatography (PPC) [Toyo Roshi No 50, developed × 3 with iso-PrOH–*n*-BuOH–H_2O (7 : 1 : 2), Rf=0.47, detected with aniline hydrogen phthalate] and TLC [Abiesel SF, Funakoshi Company, developed with PhOH–H_2O–NH_4OH (70 : 25 : 5), Rf=0.43, detected with aniline hydrogen phthalate].

Acetylation of 5——A solution of **5** (75 mg) in acetic anhydride–pyridine (1 : 1, 2 ml) was stirred for 48 h at room temperature. After usual work-up, the crude acetate was purified by PTLC using $CHCl_3$–acetone (10 : 1) as a developer (two developments) to give a tetraacetate (**6**, 41 mg, Rf=0.29) and a pentaacetate (**7**, 12 mg, Rf=0.46).

6: Colorless needles (from EtOH). mp 222—223 °C. $[\alpha]_D^{20}$ −75.3° (c=0.33, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3510 (OH), 1760 (OAc), 1720 (C=O), 1680 (C=O), 1640 (C=C). ^{1}H-NMR: see Table I. *Anal.* Calcd for $C_{33}H_{38}O_{15}$: C, 58.75; H, 5.68. Found: C, 58.64; H, 5.79.

7: Colorless needles (from EtOH). mp 170—171.5 °C. $[\alpha]_D^{20}$ −80.5° (c=0.20, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: no OH, 1760 (OAc), 1750 (OAc), 1715 (C=O), 1680 (C=O), 1640 (C=C). ^{1}H-NMR: see Table I. *Anal.* Calcd for $C_{35}H_{40}O_{16}$: C, 58.65; H, 5.63. Found: C, 58.59; H, 5.68.

Oxidation Followed by Alkaline Hydrolysis, and Acetylation of 6——A solution of $Na_2Cr_2O_7$ (183 mg) in AcOH (5 ml) was added to a solution of **6** (120 mg) in AcOH (4 ml). The reaction mixture was srirred at room temperature for 14 h, poured into ice-water and filtered to give a precipitate (42 mg). The precipitate was purified by PTLC with $CHCl_3$–MeOH (10 : 0.5) as developer to give **8** (35 mg, Rf=0.26. ^{1}H-NMR: see Table I). A solution of **8** (35 mg) in MeOH–1 N NaOH (1.5 : 1, 2.5 ml) was stirred at room temperature for 1 h. The reaction mixture was neutralized with 1 N H_2SO_4, diluted with MeOH (20 ml) and filtered. The filtrate was concentrated *in vacuo* to give a residue, which was washed with Et_2O (5 ml × 2). A solution of the Et_2O-insoluble residue in Ac_2O–pyridine (1 : 1, 2 ml) was stirred at room temperature for 30 h and treated in the usual manner to give the crude acetate. Purification of the crude acetate by PTLC with $CHCl_3$–MeOH (10 : 0.5) as a developer gave a pentaacetate (13 mg, Rf=0.32) and a hexaacetate (9 mg, Rf=0.50), which were converted to **10** (13 mg) and **11** (9.1 mg), respectively, by treatment with CH_2N_2 in Et_2O.

10: Colorless needles (from EtOH). mp 138—140 °C (ref. 9, mp 138—140 °C). $[\alpha]_D^{20}$ −119.0° (c=0.35, $CHCl_3$). ^{1}H-NMR: see Table I.

Acid Hydrolysis of 12——A solution of **12** (15 mg) in 1 N H_2SO_4–MeOH (1 : 1.5, 2.5 ml) was refluxed for 1 h, and treated as described for **5** to give the D-glucose, which was shown to be identical with an authentic D-glucose by PPC and TLC, as employed for **5**.

Acetylation of 12——A solution of **12** (80 mg) in Ac_2O–pyridine (1 : 1, 4 ml) was stirred at room temperature for 48 h. After usual work-up, the crude acetate was purified by PTLC with $CHCl_3$–acetone (4 : 1) as developer to give a tetraacetate (**13**, 39 mg, Rf=0.28) and a pentaacetate (**14**, 19 mg, Rf=0.44).

13: Colorless needles (from EtOH). mp 241—242 °C. $[\alpha]_D^{20}$ −83.5° (c=0.50, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3505 (OH), 1750—1720 (OAc), 1694 (CHO), 1630 (C=C), 1607, 1574, 1495 (aromatic). ^{1}H-NMR: see Table I. *Anal.* Calcd for $C_{33}H_{38}O_{16}$: C, 57.39; H, 5.55. Found: C, 57.18; H, 5.55.

14: Colorless needles (from EtOH). mp 168—170 °C. $[\alpha]_D^{23}$ −95.3° (c=0.50, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3533 (OH), 1760—1720 (OAc), 1690 (C=O), 1633 (C=C), 1600, 1580, 1500 (aromatic). ^{1}H-NMR: see Table I. *Anal.* Calcd for $C_{35}H_{40}O_{17}$: C, 57.37; H, 5.50. Found: C, 57.15; H, 5.73.

Reduction Followed by Acetylation of 13——A solution of $LiAlH_4$ (40 mg) in dry tetrahydrofuran (THF, 1 ml) was added to a solution of **13** (25 mg) in dry THF (1 ml) under ice-cooling. The resulting mixture was stirred at 21—22 °C for 2 h, treated with wet Et_2O and H_2O to decompose excess $LiAlH_4$, and acidified with aq. 5% HCl. The Et_2O and THF were evaporated off under reduced pressure, and the residue was washed with AcOEt. The AcOEt-insoluble portion was chromatographed on active charcoal–Celite 535 (4 : 1, 5 g) with water (40 ml) and MeOH (40 ml) as solvents. The MeOH fraction was concentrated *in vacuo* to give **16** (20 mg), which was identical with lamiidol (**16**) prepared from lamiide (**18**) on the basis of TLC and ^{1}H-NMR comparisons. **16** (20 mg) was acetylated with Ac_2O–pyridine (1 : 1, 5 ml) at 25 °C for 24 h. After usual work-up, the crude acetate was purified by PTLC with $CHCl_3$–acetone (5 : 1) as developer to give a hexaacetate (**19**, 6 mg, Rf=0.16) and a heptaacetate (**20**, 5 mg, Rf=0.39).

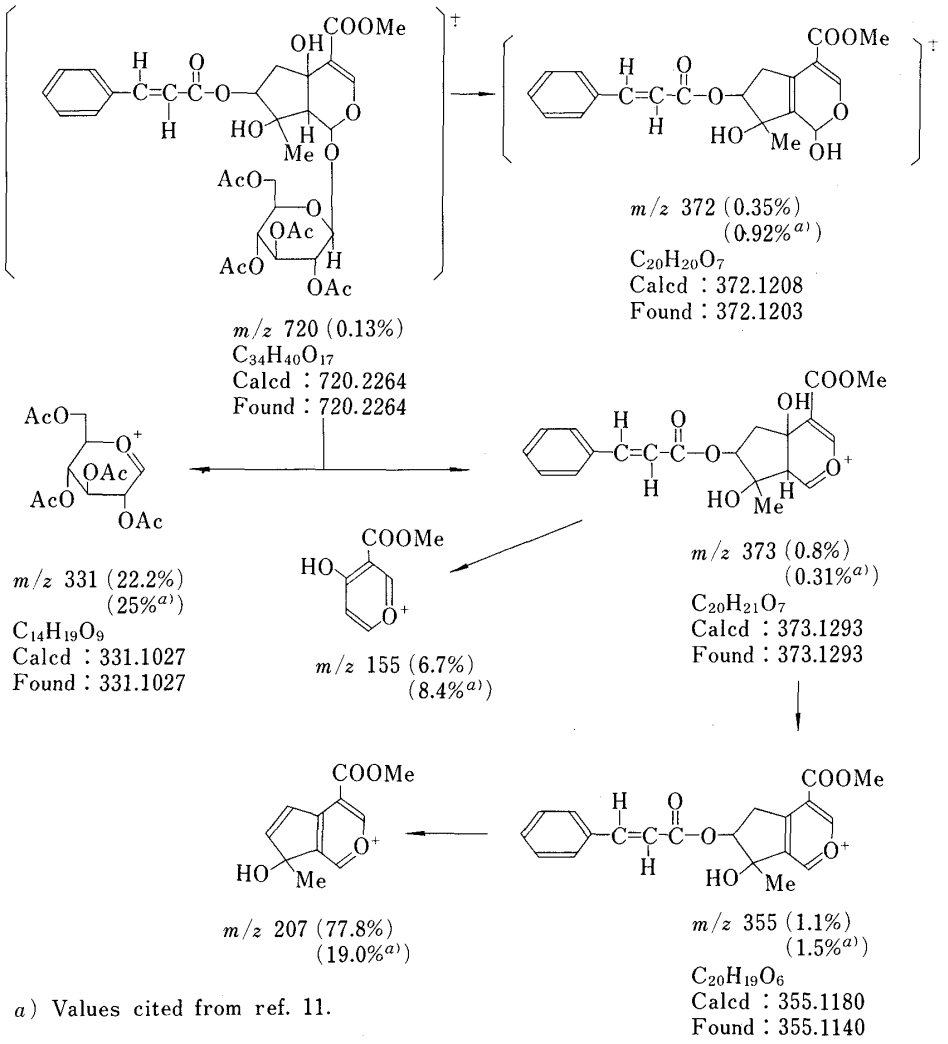
19: Colorless plates (from EtOH). mp 174—176 °C. High-resolution MS: Calcd for $C_{28}H_{36}O_{16}$ ($M^+ - H_2O$),

628.2001. Obsd., 628.1994. EI-MS *m/z* (%): 628 ($M^+ - H_2O$) (weak), 331 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.22 (3H, s, Me-8), 1.99 (3H, s, OAc), 2.00 (6H, s, OAc × 2), 2.04 (6H, s, OAc × 2), 2.06 (3H, s, OAc), 2.45 (1H, dd, J=15.0, 5.0 Hz, H-6), 2.84 (1H, s, H-9), 5.54 (1H, s, H-1), 6.24 (1H, s, H-3).

20: Colorless needles (from EtOH). mp 112—114 °C. High-resolution MS: Calcd for $C_{30}H_{40}O_{18}$ (M^+), 688.2214. Obsd., 688.2229. EI-MS *m/z* (%): 688 (M^+) (weak), 331 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.43 (3H, s, Me-8), 2.00 (6H, s, OAc × 2), 2.02 (3H, s, OAc), 2.04 (3H, s, OAc), 2.06 (6H, s, OAc × 2), 2.10 (3H, s, OAc), 3.01 (1H, s, H-9), 5.69 (1H, s, H-1), 6.20 (1H, s, H-3).

Oxidation Followed by Methylation of 13——A solution of **13** (56 mg) in *tert*-BuOH (2.5 ml) and 2-methyl-2-butene (0.6 ml) was treated with a solution of $NaClO_2$ (120 mg) and NaH_2PO_4 (120 mg) in water (1 ml) and the reaction mixture was stirred at 25—27 °C for 2.5 h. A solution of $NaClO_2$ (60 mg) and NaH_2PO_4 (60 mg) in water (0.5 ml), *tert*-BuOH (1 ml) and 2-methyl-2-butene (0.3 ml) was added to the reaction mixture. The whole was stirred at 25—27 °C for 3 h, diluted with ice-water (50 ml) and filtered to give the product (50 mg). A solution of CH_2N_2 in Et_2O (10 ml) was added to a solution of the product (50 mg) in Et_2O (10 ml) and the mixture was allowed to stand for 3 h at 25—27 °C. The Et_2O was removed, and the residue was purified by PTLC with $CHCl_3$–MeOH (10 : 0.5) as the solvent to give tetraacetyl durantoside I (**17**, 19 mg, Rf=0.66), which was recrystallized from EtOH–H_2O. The physical and spectral data for **17** were almost the same as those reported by Rimpler and Timm.[15]

17: Colorless needles (from EtOH–H_2O). mp 219—222 °C (ref. 15, mp 220—223 °C). ^{1}H-NMR ($CDCl_3$): see Table I. High-resolutions MS and EI-MS: see Chart 3.



a) Values cited from ref. 11.

Chart 3. Mass Spectrum of **17**

Isolation of 21——Air-dried roots (950 g) of *Campsis chinensis* were extracted three times with EtOH. The solvent was evaporated off *in vacuo*, and the residue was acidified to pH 2.4 with 5% HCl. The acid-soluble fraction was extracted with Et_2O. The aqueous acidic solution was then made alkaline (pH 10.0) with 5% NaOH and extracted twice with $CHCl_3$ to give 1.68 g of crude alkaloid (1.65 g), which was purified by PTLC with $CHCl_3$–acetone

(3 : 1) as a developer to give **21** (95.2 mg, $Rf=0.61$).

Boschniakine (**21**): Yellow oil. $[\alpha]_D^{18}$ +33.7° ($c=1.19$, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.35 (3H, d, $J=6$ Hz, Me-8), 8.58 (1H, s, H-1), 8.80 (1H, s, H-3), 10.18 (1H, s, CHO-4).

Picrate of **21**: mp 126—128 °C. *Anal.* Calcd for $C_{10}H_{11}NO \cdot C_6H_3N_3O_7$: C, 49.24; H, 3.60; N, 14.35. Found: C, 48.95; H, 3.76; N, 14.06.

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