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IRIDOID GLUCOSIDES FROM *CAMPSIS CHINENSIS*

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Key Word Index—*Campsis chinensis*, Bignoniaceae, iridoid glucosides, 5-hydroxycampenoside, tecomoside, cachineside I, X-ray structure

Abstract—Two new iridoid glucosides, 5-hydroxycampenoside and cachineside I, were isolated together with tecomoside from leaves of *Campsis chinensis* and their structures were elucidated The absolute stereochemistry of 5-hydroxycampenoside has been established by X-ray analysis, and the structural correlation between 5-hydroxycampenoside and tecomoside has been determined by spectral and chemical experiments

INTRODUCTION

From methanol extract of the leaves of *Campsis chinensis* Voss, we isolated two new iridoid glucosides, campsiside (**1**) [1] and 5-hydroxycampsiside (**2**) [1] Further examination of the methanol extract led to the isolation of new iridoid glucosides, campenoside (**3**), 5-hydroxycampenoside (**4**), and cachinoside I (**5**) together with tecomoside (**6**) [2, 3] The structural elucidations of campenoside (**3**) and 5-hydroxycampenoside (**4**) have been reported earlier [4] This paper describes details of the isolation and stereostructural elucidation of 5-hydroxycampenoside (**4**), tecomoside (**6**) and cachineside I (**5**)

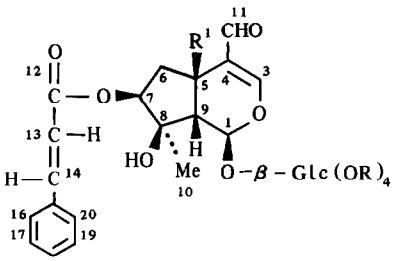
RESULTS AND DISCUSSION

The methanol extract of fresh leaves of *C chinensis* was chromatographed on charcoal–Celite 535 (1 1) with methanol and methanol–acetone (1 1) as solvents The initial methanol eluate gave a yellow powder of a mixture of several components Silica gel column chromatography, and preparative TLC of the mixture led to the isolation of tecomoside (**6**) and cachineside I (**5**), together with campenoside (**3**) [4], 5-hydroxycampenoside (**4**) [4], campsiside (**1**) [1] and 5-hydroxycampsiside (**2**) [1]

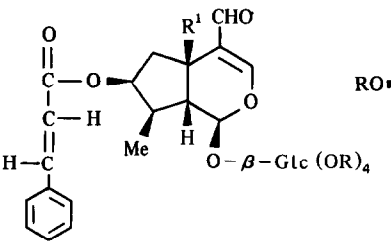
5-Hydroxycampenoside (**4**), $C_{25}H_{30}O_{11}$, mp 191–192°, was assigned structure **4** (but not the absolute stereochemistry) with a formyl group at C-4, a *trans*-cinnamyl ester group at C-7, and a methyl group at C-8 on the basis of the IR, ^{1}H NMR and ^{13}C NMR spectra (see Tables 1 and 2) and the data reported previously [4] Acid hydrolysis of **4** and methanolysis of the penta-*O*-methyl ether (**7**), prepared by treatment of **4** with methyl iodide–silver oxide [5], gave glucose and its penta-*O*-methylated compound, respectively The presence of a β-D-glucose moiety in **4** was shown by the anomeric proton signal at δ4 63 (*d*, *J* = 7 5 Hz) in its ^{1}H NMR spectrum Acetylation of **4** with acetic anhydride–pyridine gave a tetraacetate (**8**), $C_{33}H_{38}O_{15}$, mp 176–179°, which showed a hydroxyl absorption (3560 cm^{-1}) in its IR spectrum The hydroxyl group was located at C-5 since the downfield changes in shifts for C-5 (40 80 ppm), C-6 (7 21 ppm) and C-9 (8 55 ppm) compared with those of **3** (see Table 2) The conformation of the cyclopentane ring and the configurations of H-1, H-7, H-8 and H-9 in **4** were determined by extensive ^{1}H NMR and ^{13}C NMR studies (see Tables 1, 2 and 3) For example, irradiation of the H-8 signal converted the H-9 signal (*dd*, *J* = 12 0 and 2 0 Hz) to a doublet (*J* = 2 0 Hz), the H-7 signal (*m*) to a double-doublet (*J* = 2 0 and 6 0 Hz), and the H-10 signal (*d*, *J* = 7 0 Hz) to a singlet Irradiation of the H-9 signal deformed the H-8 signal and caused the H-1 signal (*d*, *J* = 2 0 Hz) to collapse to a singlet Furthermore, irradiating the H-10 signal indicated the NOE increment in both the H-1 and H-9 signal shown in Scheme 1 On the basis of the assumption that H-9 has the usual β-configuration, the configurations for the methyl group at C-8 and for H-1 would be β and α, respectively In the ^{13}C NMR spectra of **4** and **8**, the C-10 signals [**4** δ12 52, **8** δ12 70] and the C-9 signals [**4** δ53 71, **8** δ53 70] suggest all *cis*-relationships between the β-methyl group at C-8 and the oxygen at C-7, and the proton at C-9 as shown in refs [6] and [7] From these results, the structure of 5-hydroxycampenoside was established as **4** Comparison of the coupling constants of H-6, H-7, H-8 and H-9 in **4** with the calculated values in Table 3 indicates that the cyclopentane ring has the ^7V or $^1V_8$ form (see Scheme 1) in **4**, as well as in **9** and **10** [8]

Next, we isolated an iridoid glucoside (**6**), $[\alpha]_D$ −123 5°, as a hygroscopic powder from *C chinensis* Acetylation of **6** with acetic anhydride–pyridine gave its pentaacetate (**11**), $C_{26}H_{34}O_{15}$, mp 122–123°, $[\alpha]_D$ −79 1° The ^{1}H NMR data (see Tables 1 and 3) for **6** were similar to those for **4**, except for the H-7 signal The ^{13}C NMR signals (see Table 2) of **11** corresponded very closely to those of **8**, except for the signals of a *trans*-cinnamoyl group On the basis of these facts, the structural correlation between **11** and **8** was established as follows Treatment of **11** with sodium borohydride gave a reduction product (**12**), which was acetylated with acetic anhydride–pyridine to give a hexaacetate (**13**) On the other hand, the same acetate (**13**) was obtained by reduction of **8** with lithium aluminium hydride followed by acetylation Consequently, **6** was established to be

*To whom correspondence should be addressed



1 R = R¹ = H
2 R = H, R¹ = OH



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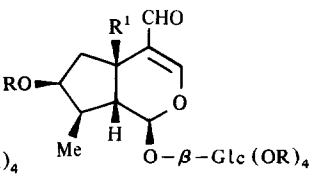
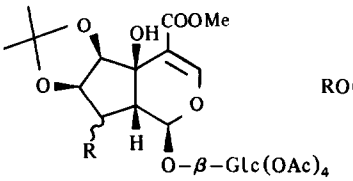
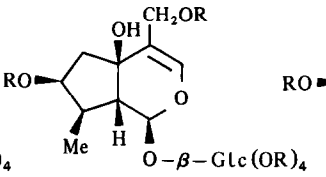
4 R = H, R¹ = OH
7 R = Me, R¹ = OMe
8 R = Ac, R¹ = OH



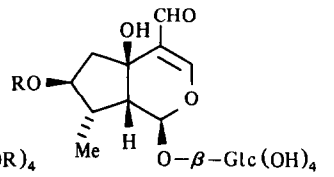
5 R = R¹ = H
6 R = H, R¹ = OH
11 R = Ac, R¹ = OH
16 R = Ac, R¹ = H



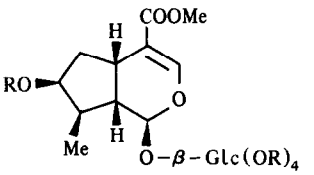
R
9 α-Me
10 β-Me



R
12 H
13 Ac



14



R
15 H
17 Ac

descinnamoyl-5-hydroxycampenoside (**6**), which at first seemed to be a new iridoid glucoside, an epimer of tecomoside (**14**) [2] at C-8 In recent reports [3, 7] the structure of tecomoside has been corrected to **6** with a β-methyl group at C-8, rather than **14** with an α-methyl group Therefore, the iridoid glucoside (**6**) which we isolated from *C chinensis* was tecomoside

For verification of the absolute configurations of **4** and **6**, a single crystal of 5-hydroxycampenoside tetraacetate (**8**) recrystallized from ethanol was subjected to X-ray diffraction analysis Crystal data $C_{33}H_{38}O_{15}$, orthorhombic, space group $P2_12_12_1$, $a = 12\,456\,(7)$, $b = 13\,292\,(8)$, $c = 21\,529\,(14)$ Å, $D_x = 1\,26$ g/cm^3, $Z = 4$, (Mo-K_α) $= 1\,1$ cm^{-1} The structure was solved by the direct method using a MULTAN program with a Syntex XTL Program [9] The atomic positional and thermal parameters were determined by a block diagonal least-squares calculation to $R = 0\,087$ over 1662 statistically significant $|I > 1\,96\,\sigma(I)|$ reflections from Syntex R_3 diffractometer measurements (graphite monochromated Mo-K_α radiation, scan within 2θ less than 45°) The absolute configuration for 5-hydroxycampenoside tetraacetate was established as **8** from data on the configuration of its β-D-glucose moiety, as shown in Fig 1 A complete list of refined co-ordinates, together with any other revelant data, has been deposited at the Cambridge Crystallographic Data Centre

In **8**, the cyclopentane ring is in the envelope form (V_8), as shown in Table 4, and the dihydropyrane ring is in a sofa conformation with C-1 out of the plane of the other atoms, like that in loganin (**15**) [10], as shown in Fig 1 Namely, the results of X-ray diffraction analysis are perfectly consistent in all respects with stereostructure **8** elucidated from the above spectral studies Thus, the absolute configuration of 5-hydroxycampenoside was established as **4** and the stereostructure of tecomoside was confirmed as descinnamoyl-5-hydroxycampenoside (**6**) This is the first X-ray crystallographic analysis of an iridoid glucoside having a hydroxyl group at C-5

Cachineside I (**5**) was obtained as an amorphous powder, $C_{16}H_{24}O_9$, $[\alpha]_D$ −136 0° Acidic hydrolysis of **5** gave D-glucose and black material due to decomposition of the aglycone Acetylation of **5** with acetic anhydride–pyridine gave a pentaacetate (**16**) ($C_{26}H_{34}O_{14}$,

Table 1 ^{1}H NMR spectral data* of compounds **3–8**, **11–14** and **16** (200 MHz, TMS as internal standard)

	3 (CD_3OD)	**4** (CD_3OD)	**5** (CD_3OD)	**6** (CD_3OD)	**7** ($CDCl_3$)	**8** ($CDCl_3$)	**11** ($CDCl_3$)	**12** (CD_3OD)	**13** ($CDCl_3$)	**14**‡ (D_2O)	**16** ($CDCl_3$)
H-1	5 46 *d*	5 84 *d*	5 46 *d*	5 77 *d*	5 67 *d*	5 62 *d*	5 54 *d*	5 43 *d*	5 37 *d*	6 27 *d*	5 23 *d*
H-3	7 39 *d*	7 40	7 32 *d*	7 35	7 20	7 09	7 03	6 29	6 28	7 82	7 07 *d*
H-5	3 13 *m*		3 07 *q*-like								3 01 *m*
H-6α	†	2 67 *dd*	1 65 *ddd*	2 50 *dd*	2 60 *d*-like	2 64 *dd*	2 55 *dd*	2 42 *dd*	2 57 *dd*	2 40 *dd*	†
H-6β	†	2 27 *dd*	2 22 *ddd*	2 18 *dd*		2 36 *dd*	2 18 *dd*	1 95 *dd*	1 97 *dd*	3 15 *dd*	†
H-7	5 24 *m*	5 08 *m*	4 03 *t*-like	3 91 *m*	5 15 *q*-like	5 19 *m*	4 94 *m*	†	5 01 *m*	4 36 *m*	5 17 *m*
H-8	†	1 88 *m*	1 82 *m*	1 63 *m*	1 85 *m*	†	1 80 *m*	1 78 *m*	1 93 *m*	2 22 *m*	†
H-9	2 14 *m*	2 46 *dd*	2 08 *m*	2 32 *dd*	2 61 *dd*	2 57 *dd*	2 46 *dd*	2 20 *dd*	2 39 *dd*	2 82 *dd*	†
H-10	1 11 *d*	1 13 *d*	1 10 *d*	1 11 *d*	1 09 *d*	1 13 *d*	1 04 *d*	1 10 *d*	1 03 *d*	1 53 *d*	1 03 *d*
H-11	9 19	9 25	9 18	9 25	9 34	9 42	9 34	†		9 62	9 26
H-11a									4 53 *d*		
H-11b									4 75 *d*		
H-13	6 48 *d*	6 50 *d*			6 41 *d*	6 46 *d*					
H-14	7 66 *d*	7 69 *d*			7 68 *d*	7 70 *d*					
H-16 to H-20	7 36–7 60 *m*	7 30–7 60 *m*			7 30–7 60 *m*	7 30–7 60 *m*					
OAc	7 36–7 60 *m*				(3 23)	1 96	1 92		2 01		1 91
(OMe)					(3 39)	2 01	2 01		2 02		1 98
					(3 46)	2 04	2 03		2 03		2 00
					(3 51)	2 12	2 04		2 06		2 05
					(3 59)		2 10		2 07		2 08
									2 08		
H-1′	4 63 *d*	4 63 *d*	4 67 *d*	4 63 *d*	4 61 *d*	†	4 78 *d*	4 59 *d*	4 78 *d*	5 24 *d*	†

*J values (Hz) for the protons of the cyclopentane ring in **3–6**, **11** and **14** are shown in Table 3

†Obscured signal

‡Data taken from ref [2]

J (Hz) **3** 13,14 = 16 0, 1′,2′ = 7 0 **4** 13,14 = 16 0, 1′,2′ = 7 5 **5** 3,5 = 1 0, 1′,2′ = 7 8 **6** 1′,2′ = 7 8 **7** 13,14 = 14 0, 1′,2′ = 7 0 **8** 6α,7 = 6 0, 6β,7 = 2 0, 6α, 6β = 16 0 **11** 1′,2′ = 7 5 **12** 1,9 = 2 2, 6α,7 = 5 8, 6β,7 = 3 5, 6α, 6β = 14 8, 8,9 = 11 1 **13** 1,9 = 1 7, 6α,7 = 6 1, 6β,7 = 2 2, 6α, 6β = 14 8, 8,9 = 12 0, 11a, 11b = 12 7 Unmarked signals are singlets

Table 2 ^{13}C NMR spectral data of compounds **3–6**, **8**, **11–13** and **16** (50 10 MHz, TMS as internal standard)

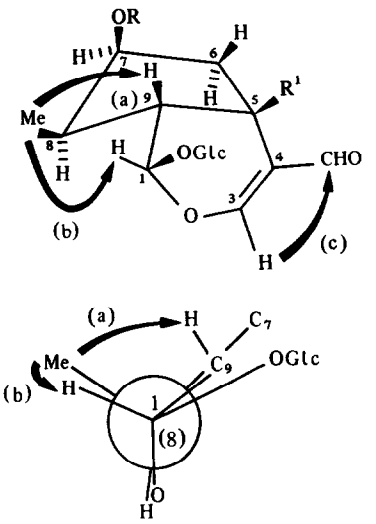
C-Atom	**3** (DMSO-d_6)	**4** (DMSO-d_6)	**5** (CD_3OD)	**6** (CD_3OD)	**8** ($CDCl_3$)	**11*** ($CDCl_3$)	**12** (CD_3OD)	**13*** ($CDCl_3$)	**16*** ($CDCl_3$)
C-1	96 35 *d*	94 37 *d*	98 23 *d*	97 12 *d*	95 19 *d*	95 13 *d*	95 74 *d*	94 05 *d*	95 66 *d*
C-3	160 65 *d*	160 77 *d*	162 41 *d*	162 70 *d*	155 84 *d*	155 98 *d*	139 43 *d*	139 34 *d*	158 73 *d*
C-4	123 21	124 79	126 40	126 78	126 02	125 99	120 38	116 21	125 50
C-5	28 55 *d*	69 39	29 55 *d*	72 12	70 98	70 72	74 57 *d*	71 77 *d*	28 38 *d*
C-6	37 25 *t*	44 46 *t*	41 20 *t*	48 88 *t*	45 20 *t*	45 11 *t*	48 88 *t*	43 01 *t*	37 64 *t*
C-7	76 35 *d*	74 94 *d*	74 81 *d*	73 38 *d*	74 95 *d*	74 93 *d*	73 35 *d*	74 28 *d*	76 79 *d*
C-8	38 45 *d*	37 74 *d*	41 43 *d*	41 23 *d*	38 75 *d*	38 46 *d*	41 40 *d*	38 02 *d*	38 75 *d*
C-9	45 16 *d*	53 71 *d*	45 90 *d*	54 72 *d*	53 70 *d*	53 58 *d*	55 86 *d*	54 02 *d*	45 32 *d*
C-10	12 61 *q*	12 52 *q*	12 96 *q*	13 14 *q*	12 70 *q*	12 56	13 61 *q*	12 91 *q*	12 50 *q*
C-11	190 17 *d*	190 61 *d*	192 95 *d*	192 95 *d*	189 68 *d*	189 68 *d*	60 41 *t*	61 06 *t*	189 97 *d*
C-12	165 20	165 80			166 44				
C-13	118 05 *d*	118 24 *d*			118 02 *d*				
C-14	143 83 *d*	144 39 *d*			145 15 *d*				
C-15	133 78	133 98			134 43				
C-16, 20	128 38 *d*†	128 89 *d*†			128 91 *d*†				
C-17, 19	127 74 *d*†	128 30 *d*†			128 16 *d*†				
C-1′	98 77 *d*	98 58 *d*	98 83 *d*	100 12 *d*	96 27 *d*	96 24 *d*	99 34 *d*	96 33 *d*	95 92 *d*
C-2′	72 87 *d*	72 90 *d*	74 25 *d*	74 37 *d*	70 81 *d*	70 72 *d*	74 57 *d*	71 28 *d*	70 78 *d*
C-3′	76 87 *d*‡	77 28 *d*‡	77 90 *d*‡	78 43 *d*‡	72 44 *d*‡	72 38 *d*‡	78 17 *d*‡	72 18 *d*‡	72 44 *d*‡
C-4′	70 01 *d*	70 03 *d*	71 19 *d*	71 54 *d*	68 33 *d*	68 33 *d*	71 60 *d*	68 44 *d*	68 38 *d*
C-5′	76 50 *d*‡	75 88‡	77 61 *d*‡	77 55 *d*‡	71 95 *d*‡	71 95 *d*‡	77 70 *d*‡	72 09 *d*‡	72 36 *d*‡
C-6′	61 05 *t*	61 08 *t*	62 46 *t*	62 69 *t*	61 67 *t*	61 67 *t*	62 60 *t*	61 79 *t*	61 76 *t*

*The signals of the acetyl groups are not given
†,‡Assignments with the same sign are interchangeable
Unmarked signals are singlets

Table 3 Coupling constants for the protons of the cyclopentane ring in compounds **3–6**, **9–11** and **14**

Compound	$J_{1\alpha\ 9\beta}$	$J_{5\beta\ 6\alpha}$	$J_{5\beta\ 6\beta}$	$J_{6\alpha\ 7\alpha}$	$J_{6\beta\ 7\alpha}$	$J_{7\alpha\ 8\alpha}$	$J_{7\alpha\ 8\beta}$	$J_{8\alpha\ 9\beta}$	$J_{8\beta\ 9\beta}$
Measured value									
3*	3 0	4 0	8 0	6 0	1 0	5 0		10 0	
4*	⩽2 0			6 0	2 0	5 5		12 0	
5*	3 0	6 0	8 0	6 0	1 8	5 0		9 0	
6*	1 7			5 8	2 7	5 8		12 0	
9†	1 5			5 0			1 0		7 5
10†	1 4			5 4		5 4		12 6	
11‡	1 8			6 0	3 0	5 5		12 0	
14§	1 5			6 0	2 0	(5 5)‖	5 5	(12 0)‖	
Calculated value¶									
^7V**	⩽1 0	6 0	7 5	4 5	⩽1 0	5 0	⩽1 0	7 0	7 5
V_8**	2 5	3 0	9 5	6 0	⩽0 5	5 5	⩽1 0	10 5	5 0
V_7††	⩽0 5	0 5	7 5	5 0	10 0	4 0	10 0	⩽0 5	7 5
V_6††	⩽1 0	10 0	5 0	5 0	⩽0 5	7 0	⩽0 5	4 0	9 5

*Run in CD_3OD
†Run in $CDCl_3$ Data taken from ref [8]
‡Run in $CDCl_3$
§Run in D_2O Data taken from ref [2]
‖This assignment was made by us from the ^1H NMR data on tecomoside reported by Bianco *et al* (ref [2])
¶The values were calculated from $J = 9\,5\cos^2\alpha - 0\,5\cos\alpha + 0\,4$
Preferred conformers for the cyclopentane ring of iridoid glucosides (3, 4, 5, 6** and **10**) with a β-methyl group at C-8
††Preferred conformers for the cyclopentane ring of the iridoid glucoside (**14**) with an α-methyl group at C-8



R = *trans*-cinnamoyl **(3,4)** or H **(5,6)**

R^1 = OH **(4,6)** or H **(3,5)**

13 R = Ac, R^1 = OH
4-CH_2OAc

	(a)	(b)	(c)
3	13%	~6%	15%
4	17%	~7%	17%
5	14%	~5%	20%
6	16%	~7%	18%
13	13%	~6%	—

Scheme 1 Nuclear Overhauser effect (NOE) observed for compounds **3–6** and **13**

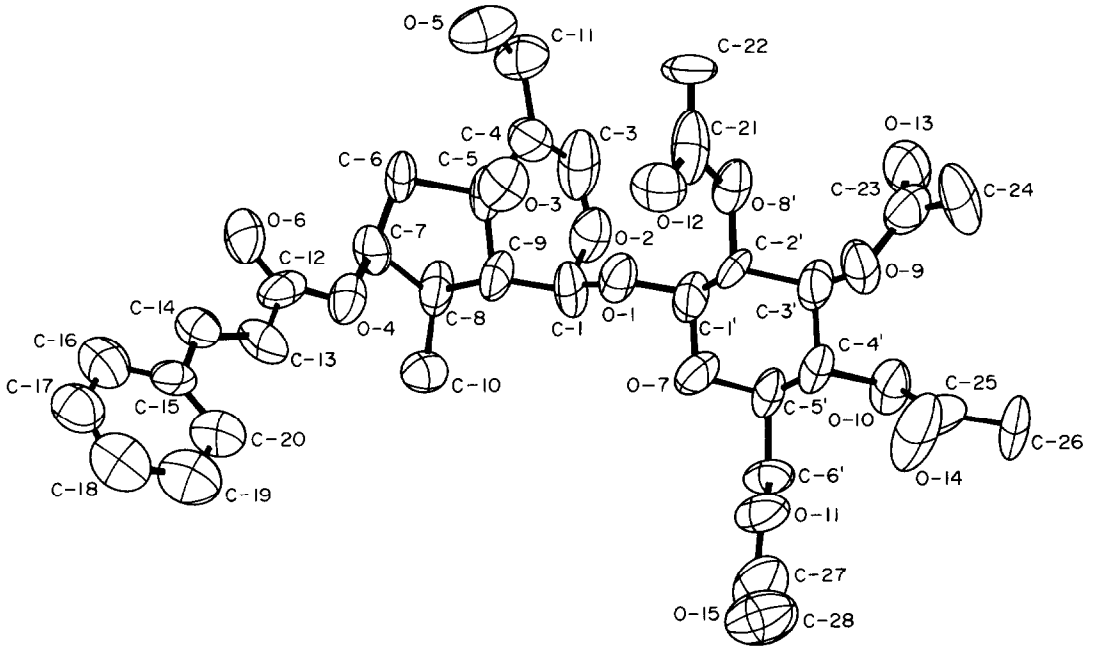


Fig 1 Molecular structure of 5-hydroxycampenoside tetraacetate (**8**)

mp 116–117°, $[\alpha]_D$ −94 1°) showing no hydroxyl absorption in its IR spectrum Taking into account the molecular formula, this indicated the presence of a secondary hydroxyl group in the aglycone moiety of **5**

In addition, the IR, ^{1}H NMR and ^{13}C NMR spectra showed the presence of a conjugated formyl group [1660 and 1630 cm^{-1}, δ9 18 (*s*, CHO-4) and 7 32 (*d*, J = 1 0 Hz, H-3), 192 95 (*d*, C-11), 162.61 (*d*, C-3), and 126 40 (*s*, C-4)], a methyl group [δ1 10 (*d*, J = 6 8 Hz, Me-8), 12 96 (C-10)] and a β-glucosyl moiety [3400 cm^{-1}, δ4 67 (*d*, J = 7 8 Hz, H-1′), 98 83 (*d*, C-1′), 74 25 (*d*, C-2′), 77 90 (*d*, C-3′ or C-5′), 71 16 (*d*, C-4′), 77 61 (*d*, C-5′ or C-3′) and 62 46 (*t*, C-6′)] From the facts that the ^{1}H NMR data (chemical shifts, coupling constants, NOE increments shown in Tables 1 and 3, and Scheme 1, respectively) of **5** are similar to those of **3**, except for the H-7 signal, and that the ^{13}C NMR signals of **16** correspond closely to those of **3**, cachineside I was concluded to have the same functional groups as **3** at the same positions, except for having a hydroxyl group at C-7 Thus, it was assigned the structure **5** To confirm this structure, the acetate (**16**) was converted to loganin pentaacetate (**17**) Oxidation of **16** with sodium chlorite–

Table 4 Torsional angles of the cyclopentane ring, geometrical parameter (maximum torsional angle) ψ_m* and conformation parameter (phase angle of pseudorotation) Δ† of compounds **8**, **15**, ^7V and V_8

Compound	Torsional angles ψ0 5–9	ψ1 5–6	ψ2 6–7	ψ3 7–8	ψ4 8–9	ψ_m	Δ
8	+27 0°	+3 6°	−22 1°	+39 4°	−39 9°	+43 5°	−103 3°
15‡	+24 0°	+2 7°	−28 7°	+43 2°	−41 6°	+44 7°	−115 1°
^7V form§	+3 5°	+28 5°	−43 5°	+46 5°	−32 5°	+49 2°	−171 8°
V_8 form§	+27 5°	+4 0°	−22 0°	+45 5°	−41 5°	+45 9°	−106 3°

*The values were calculated from $\psi_0 = \psi_m \cos \Delta/2$ (ref [11])

†The values were calculated from $\tan \Delta/2 = \dfrac{(\psi_2 + \psi_4) - (\psi_1 + \psi_3)}{3\,0777\,\psi_0}$ (ref [11])

‡Data taken from ref [10]

§The values were calculated from Dreiding model inspection

sodium hydrogen phosphate in the presence of 2-methyl-2-butene [12], followed by treatment with diazomethane gave a methyl ester (**17**), $C_{27}H_{37}O_{15}$, mp 134–135°, $[\alpha]_D$ −136 6°, which was found to be identical to authentic loganin pentaacetate [13] by comparison of spectral data and by mixed melting point Thus, the stereostructure of cachineside I was established as **5** Cachineside I (**5**) is not new, as a compound with this structure has been described in ref [7] as 7β-hydroxystanside Although only the source and a ^{13}C NMR spectrum have been reported, the latter is apparently identical to that given for **5** in this paper (the small differences are due to different solvents)

EXPERIMENTAL

All mps are uncorr ^1H NMR spectra were recorded at 100 or 200 MHz ^{13}C NMR spectra were determined at 50 10 MHz Chemical shifts are given in δ (ppm) with TMS as internal standard Silica gel (70–230 mesh, Merck) was employed for CC Silica gel 60 (GF_{254}, Merck) was used for TLC and silica gel 60 (PF_{254}, Merck) was used for prep TLC Components were detected under UV light or by spraying with 1% $Ce(SO_4)_2$–10% H_2SO_4 soln and then heating Mass spectra were determined at 70 eV using a direct-inlet system

Plant material Plants were collected at our Faculty Herbary (Faculty of Pharmaceutical Sciences, Tokushima University) in Tokushima Pref in September 1978 A voucher specimen is available at the Herbary in Kokufu-cho, Tokushima 770, Japan

Isolation of iridoid glucosides from leaves of C chinensis Fresh leaves (1 4 kg) were extracted with MeOH and the solvent was evapd *in vacuo* to give a residue (163 g) The residue (120 g) was partitioned in *n*-hexane–H_2O (3 1) The H_2O layer was extracted with *n*-BuOH saturated with H_2O The *n*-BuOH layer gave a brown residue (99 g), which (95 g) was subjected to CC on active charcoal (450 g)–Celite 535 (450 g) with MeOH (until fraction 60) and MeOH–Me_2CO (1 1, from fraction 61), yielding three fractions [fraction I (fractions 18–28) (4 9 g), fraction II (fractions 43–60) (2 5 g) and fraction III (fractions 61–80) (7 0 g) (each fraction 500 ml)] Fraction I (1 5 g) gave by CC on silica gel (150 g) developed with $CHCl_3$–MeOH–H_2O (70 30 3) crude cachineside I (**5**) (198 mg) and tecomoside (**6**) (171 mg) Fraction II (1 1 g) gave by CC on silica gel (100 g) developed with $CHCl_3$–MeOH–H_2O (50 15 3) crude campsiside (**1**) (185 mg) and 5-hydroxycampsiside (**2**) (85 mg) Fraction III (3 6 g) gave by CC on silica gel (250 g) developed with $CHCl_3$–MeOH–H_2O (13 3 2) campenoside (**3**) (316 mg), 5-hydroxycampenoside (**4**) (664 mg) and campsiside (**1**) (80 mg)

5-Hydroxycampenoside (**4**) Colourless needles from EtOH, mp 191–192°, $[\alpha]_D^{20}$ −73 7° (MeOH, *c* 0 60), IR ν_{max}^{KBr} cm^{-1} 3500, 1710, 1660, 1640, for ^1H NMR ($CDCl_3$) and ^{13}C NMR (DMSO-d_6) spectra, see Tables 1 and 2, respectively (Found C, 58 96, H, 6 12 $C_{25}H_{30}O_{11}$ requires C, 59 28, H, 5 97%)

Acetylation of compound **4** Compound **4** (30 mg) was acetylated with Ac_2O (1 ml)–pyridine (1 ml) at room temp for 30 hr The product (38 mg) was isolated in the usual manner and recrystallized from EtOH to give a tetraacetate (**8**), mp 173–176°, $[\alpha]_D^{20}$ −90 7° ($CHCl_3$, *c* 0 53), IR ν_{max}^{KBr} cm^{-1} 3560, 1760, 1750, 1710, 1700, 1640, for ^1H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra, see Tables 1 and 2, respectively (Found C, 58 65, H, 5 69 $C_{33}H_{38}O_{15}$ requires C, 58 75, H, 5 68%)

Methylation of compound **4** To a soln of **4** (100 mg) in DMF (4 ml) were added Ag_2O (2 5 g) and MeI (5 ml), and the mixture was stirred at room temp for 36 hr The product was isolated in the usual manner and purified by prep TLC to give a penta-*O*-methyl ether (**7**, 43 mg), $[\alpha]_D^{20}$ −80 5° ($CHCl_3$, *c* 0 43), IR ν_{max}^{KBr} cm^{-1} no OH, 3000, 2930, 2830, 1710, 1680, 1630, ^1H NMR (C_6D_6) δ0 90 (*d*, *J* = 7 0 Hz, Me-8), 2 48 (*dd*, *J* = 14 0 and 6 0 Hz, H-6α), 2 61 (*dd*, *J* = 12 0 and 1 5 Hz, H-9), 2 70 (*dd*, *J* = 14 0 and 3 0 Hz, H-6β), 3 16, 3 28, 3 43, 3 52 and 3 58 (each *s*, OMe × 5), 4 74 (*d*, *J* = 7 0 Hz, H-1′), 5 18 (*m*, H-7), 5 58 (*d*, *J* = 1 5 Hz, H-1), 6 39 (*d*, *J* = 14 Hz, C_6H_5–CH=CHCO–), 6 65 (*s*, H-3), 7 79 (*d*, *J* = 14 0 Hz, C_6H_5CH=CHCO–), 9 15 (*s*, CHO)

Acid hydrolysis of compound **4** A soln of **4** (15 mg) in 1 N H_2SO_4 (1 ml)–MeOH (2 ml) was refluxed for 30 min, neutralized with Amberlite IR-45 (OH-form) and filtered The filtrate was evapd *in vacuo* and the residue was identified with glucose by PPC [Toyo Roshi No 50, developed × 3 with *i*-PrOH–*n*-BuOH–H_2O (7 1 2), R_f = 0 49, detected with aniline hydrogen phthalate]

Hydrolysis of compound **4** *with β-glucosidase* A soln of **4** (100 mg) and β-glucosidase (prepared from almonds, Sigma Chemical Co) in 0 1 M acetate buffer (pH 5 1, 9 ml) was stirred at 33–37° for 6 days The mixture was filtered through activated C (1 g) and Celite 535 (1 g) The filter cake was washed with H_2O (50 ml), and the combined filtrate was evapd *in vacuo* The residue was identified by cochromatography with authentic D-glucose on paper (solvent *i*-PrOH–*n*-BuOH–H_2O, 7 1 2)

Methanolysis of compound **7** Compound **7** (8 mg) was refluxed in 6% HCl–MeOH (5 ml) for 1 hr The reaction mixture was neutralized with Ag_2CO_3 and filtered The filtrate was evapd and

the residue was identified by TLC (C_6H_6–Me_2CO, 4 1) with methyl tetra-*O*-methyl-(α, β)-D-glucopyranosides prepared from D-glucose with MeI and Ag_2O

Conversion of compound **8** *to compound* **13** To a soln of **8** (100 mg) in dry THF (15 ml), a suspension of $LiAlH_4$ (100 mg) and dry THF (17 ml) was added dropwise in 5 min, and the mixture was stirred for 2 hr The product (65 mg) was isolated in the usual manner and was purified by CC (*n*-BuOH saturated with H_2O) to give a hygroscopic, amorphous powder (**12**) (43 mg), IR ν_{max}^{film} cm^{-1} 3350, 1660; $[\alpha]_D^{20}$ −52 1° (MeOH, *c* 1 00), for ^1H NMR (CD_3OD) and ^{13}C NMR (CD_3OD) spectra, see Tables 1 and 2, respectively A mixture of **12** (30 mg), Ac_2O (2 ml) and pyridine (2 ml) was stirred at room temp for 2 hr and evapd *in vacuo* The residue was purified by prep TLC ($CHCl_3$–Me_2CO, 10 1) to give **13** (22 mg) as a colourless gum, IR ν_{max}^{film} cm^{-1} 3540, 1760, 1750, 1740, $[\alpha]_D^{20}$ −106 3° ($CHCl_3$, *c* 0 88), MS *m/z* (rel int) 630 2176 $[M]^+$ (0 2), ($C_{28}H_{38}O_{16}$), for ^1H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra, see Tables 1 and 2, respectively

Tecomoside (**6**) Hygroscopic, amorphous powder, $[\alpha]_D^{20}$ −123 5° (MeOH, *c* 0 55) ($[\alpha]_D^{25}$ −118° (MeOH, *c* 2 00) [2]), for ^1H NMR and ^{13}C NMR (CD_3OD) spectra, see Tables 1 and 2, respectively

Acetylation of compound **6** Crude **6** (80 mg) was acetylated with Ac_2O (3 ml) and pyridine (2 5 ml) to give a pentaacetate (**11**, 41 mg), mp 122–123° (from EtOH–H_2O) (mp 124–125° [2] and 118–120° [3]), $[\alpha]_D^{20}$ −79 1° ($CHCl_3$, *c* 0 46) ($[\alpha]_D^{21}$ −97° ($CHCl_3$, *c* 0 60) [3]), IR ν_{max}^{KBr} cm^{-1} 3550, 2720, 1760, 1740, 1680, and 1630, for ^1H NMR and ^{13}C NMR ($CDCl_3$) spectra, see Tables 1 and 2, respectively (Found C, 53 12, H, 5 79 $C_{26}H_{34}O_{15}$ requires C, 53 25, H, 5 84%)

Conversion of compound **11** *to compound* **13** A mixture of **11** (80 mg), $NaBH_4$ (20 mg) and MeOH (3 ml) was stirred at room temp for 1 hr The crude product (**12**, 28 mg) was isolated in the usual manner and identified with authentic **12** obtained from **8**, by TLC The product was acetylated with Ac_2O (1 5 ml)–pyridine (1 5 ml) to give **13** (18 mg) $[\alpha]_D^{20}$ −103 5° ($CHCl_3$, *c* 0 38) which was identical to authentic **13** prepared from **8**, by spectral data and TLC

Cachineside I (**5**) Amorphous powder, $[\alpha]_D^{20}$ −136 0° (MeOH, *c* 0 25), IR ν_{max}^{KBr} cm^{-1} 3400, 1660 and 1625, MS *m/z* (rel int) 360 1420 $[M]^+$ (0 4) ($C_{16}H_{24}O_9$), for ^1H NMR and ^{13}C NMR (CD_3OD) spectra, see Tables 1 and 2, respectively

Acetylation of compound **5** A mixture of **5** (50 mg), Ac_2O (1 ml) and pyridine (1 5 ml) was stirred at room temp for 18 hr The product (43 mg) was isolated in the usual manner and recrystallized from EtOH–H_2O to give **16**, mp 116–117°, $[\alpha]_D^{20}$ −94 1° (MeOH, *c* 0 17), IR ν_{max}^{KBr} cm^{-1} no OH, 1760, 1755, 1745, 1735, 1680 and 1630, for ^1H NMR and ^{13}C NMR ($CDCl_3$) spectra, see Tables 1 and 2, respectively, MS *m/z* (rel int) 571 2012 $[M+1]^+$ (0 3) ($C_{26}H_{35}O_{14}$) (Found C, 54 86, H, 5 62 $C_{26}H_{34}O_{14}$ requires C, 54 73, H, 6 01%)

Acid hydrolysis of compound **5** A mixture of **5** (10 mg), 1 N H_2SO_4 (1 ml) and MeOH (2 ml) was refluxed for 30 min The product (glucose) was isolated in the manner described for **4**, and was identical to an authentic sample of glucose of PPC, as employed for **4**

Conversion of compound **16** *to loganin pentaacetate* (**17**) To a mixture of **16** (50 mg), *t*-BuOH (2 5 ml) and 2-methyl-2-butene (0 6 ml), a soln of $NaClO_2$ (120 mg) and Na_2HPO_4 (120 mg) in H_2O (1 ml) was added dropwise during 2 min with stirring The reaction mixture was stirred at room temp for 1 hr, poured into ice-H_2O, and then extracted with $CHCl_3$ The extract was washed with cold H_2O and concd to dryness The residue was purified by prep TLC ($CHCl_3$–Me_2CO, 10 1) to give **18** (20 mg), which was treated with CH_2N_2 in MeOH–Et_2O The resulting residue was crystallized from EtOH to give **17** (20 mg), mp 134–135° $[\alpha]_D^{20}$ −163 6° (MeOH, *c* 0 16), IR ν_{max}^{KBr} cm^{-1} no OH, 1760, 1740, 1710, 1700, 1640, ^1H NMR ($CDCl_3$) δ 1 02 (*d*, *J* = 6 6 Hz, H_3-8), 1 91 (*s*, OAc), 2 01 (*s*, OAc), 2 03 (*s*, OAc × 2), 2 09 (*s*, OAc), 3 00 (*m*, H-5), 5 23 (*d*, *J* ⩽ 2 0 Hz, H-1), 7 30 (*d*, *J* ⩽ 1 0 Hz, H-3), MS *m/z* (rel int) 601 2145 $[M+1]^+$ (2 2) ($C_{27}H_{37}O_{15}$)

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