NEW IRIDOID GLUCOSIDES, CAMPENOSIDE AND 5-HYDROXYCAMPENOSIDE, FROM *CAMPSIS CHINENSIS* VOSS

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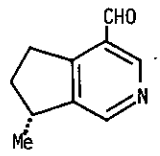
Abstract ——— Two novel iridoid glucosides, campenoside and 5-hydroxycampenoside were isolated from the leaves of *Campsis chinensis* Voss and their structures were shown to be 2 and 3, respectively.

Recently, we have isolated an alkaloid, boschniakine(1)[1] from the roots of *Campsis chinensis* Voss (Bignoniaceae). This isolation prompted us to investigate the iridoid glucosides of *C. chinensis* Voss. Chromatographic examination of a methanolic extract of the leaves of this plant gave two novel iridoid glucosides, campenoside (2) and 5-hydroxycampenoside (3), having a formyl group at C-4 and a cinnamoyl ester group at C-7. This paper describes structural studies of these compounds.

Campenoside (2) [mp 165-167°, $C_{25}H_{30}O_{10}\cdot 1/2H_2O$, $[\alpha]_D^{20}$ - 59.5°(MeOH)] gave D-glucose on acidic hydrolysis. The spectroscopic properties of 2 revealed the presence of a conjugated carbonyl group [$\delta_H(CD_3OD)$: 9.19(s, CHO) and 7.39(s, 3-H); ν_{max} (KBr) 1670 and 1630 cm^{-1}] characteristic of iridoids, a *trans*-cinnamoyl ester group [δ_H 7.66 and 6.48(AB-system, J=16 Hz), 7.6-7.3(5H, aromatic H); ν_{max} 1720 and 1640 cm^{-1}], a methyl group [δ_H 1.11(d, J=6 Hz)], and an anomeric proton [δ_H 4.69(d, J=7 Hz)] of the β-linked D-glucose. Acetylation of 2 with Ac_2O-pyridine gave a tetraacetate(4)[mp 179-181°, $C_{33}H_{38}O_{14}$, $[\alpha]_D^{20}$ -73.7°($CHCl_3$)]. From the fact that the signals of 2 and 4 correspond closely to those of loganin pentaacetate (5)[2] and from the coupling pattern of hydrogen atoms at 6 position of 2 (Table 1), the structures of campenoside and its tetraacetate were considered to be 2 and 4, respectively, although there is still some uncertainty about their stereochemistry. The above assumption was confirmed first by comparison of the ^{13}C-NMR spectrum of 2 with that of 5[3] and then by chemical



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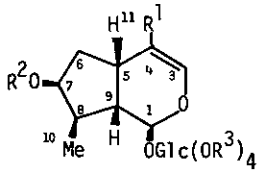
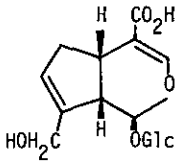


2: R^1=CHO, R^2=-COCH=CHC_6H_5, R^3=H
4: R^1=CHO, R^2=-COCH=CHC_6H_5, R^3=Ac
5: R^1=CO_2Me, R^2=R^3=Ac
6: R^1=CO_2H, R^2=-COCH=CHC_6H_5, R^3=Ac
7: R^1=CO_2H, R^2=R^3=H



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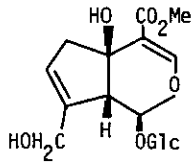

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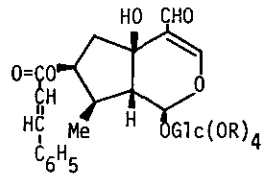
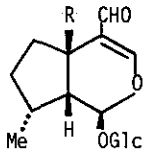
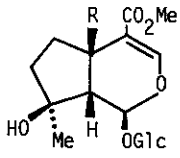


3: R=H
8: R=Ac



11: R=OH
13: R=H



12: R=OH
14: R=H

transformation of 4 into 5.

As shown in Table II, the spectrum of 2 is similar to that of 5, the differences being accounted due to the different functions at C-4 and C-7: a methoxycarbonyl group and an acetate function in 5 and a formyl group and a *trans*-cinnamoyl ester group in 2.

The acetate (4) was converted to 5 as follows: oxidation of 4 with Jones reagent gave an acid (6) [mp 139-143°, $C_{33}H_{38}O_{15}$(Mass spectrum, M^+: Calcd: 674.2211. Found: 674.2227)]. The acid (6) was hydrolyzed with 1N NaOH-MeOH at room temperature to give *trans*-cinnamic acid and an acid (7), which was subjected to acetylation with Ac_2O-pyridine followed by methylation with diazomethane. The ester (5)[mp 131-134°, $[\alpha]_D^{20}$ - 70.0°($CHCl_3$)] thus obtained was found to be identical with authentic loganin pentaacetate[2] by comparison of spectral data and by mixed metlting point.

5-Hydroxycampenoside (3) showed mp 176-179°, $C_{25}H_{30}O_{11}$, $[\alpha]_D^{20}$ - 73.7°(MeOH), and ν_{max} (KBr) cm^{-1}: 3500(OH), 1710(conjugated ester), 1660(conjugated carbonyl group), 1640(C=C). The presence of D-glucose and *trans*-cinnamic acid in 3 was confirmed by hydrolytic experiments. The ^{1}H-NMR spectrum of 3 gave signals which were assigned as shown in Table I, and additional signals due to β-D-glucose(δ_H 4.63, d, J=7.5 Hz) and *trans*-cinnamoyl protons.

Table I. ^{1}H-NMR Spectral Data of Iridoids (δ)[a]

Compd.(solvent)	1-H	3-H	5-H	7-H	9-H	10-H	11-H
2[b] (CD_3OD)	5.46(d,3)	7.39(s)	3.13(m)	5.24(m)	2.14(m)	1.11(d,6)	9.19(s)
3[c] (CD_3OD)	5.84(d,2)	7.40(s)		5.08(m)	2.46(dd,12,2)	1.13(d,7)	9.25(s)
4 ($CDCl_3$)	5.34(d,2)	7.06(s)	3.06(m)	5.27(m)	ca. 2.30(m)	1.09(d,7)	9.23(s)
5 ($CDCl_3$)	5.19(d,2)	7.33(s)	2.96(m)	5.13(m)		1.02(d,7)	

a) Numerical values in parentheses are coupling constants in Hz. b) 6-Hα at 1.85(m, $J_{6\alpha-6\beta}$=15, $J_{6\alpha-5}$=6.5, $J_{6\alpha-7}$=6 Hz) and 6-Hβ at 2.32(m, $J_{6\beta-6\alpha}$=15, $J_{6\beta-5}$=8, $J_{6\beta-7}<1$ Hz). c) 6-Hα at 2.67(dd, $J_{6\alpha-6\beta}$=16, $J_{6\alpha-7}$=6 Hz) and 6-Hβ at 2.27(dd, $J_{6\beta-6\alpha}$=16, $J_{6\beta-7}$=2 Hz).

Acetylation of 3 *with* Ac_2O*-pyridine gave a tetraacetate* (8)[*mp* 191-192°, $C_{33}H_{38}O_{15}$, $[\alpha]_D^{20}$ -90.7°($CHCl_3$)], in which one hydroxyl group [ν_{max} (KBr) 3560 cm^{-1}] remained unaffected indicating its tertiary nature. From these data, 3 was concluded to have the same functional groups as 2 at the same positions, and an additional β-hydroxyl group at C-5. This was further confirmed by comparison of the ^{13}C-NMR spectrum of 3 with those of related compounds, as shown in Table II. The relation of the chemical shifts of geniposidic acid (9)[4,5] and theviridoside (10)[4,5] is very similar to that of 2 and 3: (i) the signals for C-5 of 3 (69.39 ppm) and 10 *(76.23 ppm) are shifted ca. 40 ppm downfield from those of* 2 *(28.55 ppm) and* 9 (36.25 ppm); (ii) the signals for C-9 and C-6 in 3 are 8.55 and 7.21 ppm, respectively, downfield from the corresponding signals of 2. This is probably due to β-oxygenation at C-5, since similar deshielding effects were observed by comparing the signals at C-9(9.77 ppm) and C-6(7.36 ppm) of 10 with the corresponding signals of 9. (iii) The signal of C-7 of 3 is shifted 1.41 ppm upfield from that of 2 due to the γ-effect of 5β-hydroxyl group in 3. Similarly the signal of the corresponding carbon of 10 is shifted 1.60 ppm upfield from that of 9. This assignment for the hydroxyl group at C-5 in 3 was also supported by comparison of δ_H of C-9 of 3 with that of 2: the former signal is shifted 0.3 ppm downfied from the latter one, since the H-9 signals in the 5β-hydroxy-iridoides, yuheinoside (11)(δ_H 2.70 ppm)[6] and ipolamiide (12)(δ_H 2.48 ppm)[7], are 0.2-0.1 ppm downfield from those of the corresponding deoxy-compounds, boschnaloside (13)(δ_H 2.35 ppm)[6] and mussaenoside(14)(δ_H 2.36 ppm)[8], respectively. Additional evidence regarding the stereochemistry at C-7, C-8, and C-1 of 3 was obtained from its NMR data: the abnormal high-field shift[3,4] of C-10(12.52 ppm) in 3, as well as that(12.61 ppm)(Table II) in 2, suggests the same *cis*-relationship between the methyl group and the oxygen at C-7. In the NMDR study on 3, irradiation at δ 1.13(H-10) gave a 17% NOE increment in the signal of H-9 and a 12% increment in the signal of 1-H. Thus, the structure of 5-hydroxycampenoside was established as 3.

Table II. ^{13}C-NMR Spectral Data of Iridoids[a)]

Compd.	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
2[b)]	96.35	160.65	123.21	28.55	37.25	76.35	38.45	45.16	12.61	190.17
3[b)]	94.37	160.77	124.79	69.39	44.46	74.94	37.74	53.71	12.52	190.61
5[c)]	94.8	149.1	113.7	29.9	38.9	77.1	38.9	45.6	12.5	167.1
9[d)]	98.06	153.18	112.53	36.25	39.40	128.26	144.22	46.59	61.13	171.11
10[d)]	96.85	153.92	114.14	76.23	46.79	126.66	141.63	56.36	60.78	168.09

a) Chemical shifts in ppm relative to internal $(Me)_4Si$. Additional signals arising from glucose were omitted. Compounds 2 and 3 also showed signals from the cinnamoyl ester part.
b) In DMSO-d_6. c) In $CDCl_3$. d) In CD_3OD.

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