Phytochemistry, Vol. 26, No. 6, pp. 1839–1840, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00

TWO IRIDOID GLYCOSIDES FROM *CAMPSIDIUM VALDIVIANUM**

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(*Revised received* 14 *September* 1986)

Key Word Index—*Campsidium valdivianum*; Bignoniaceae; iridoid diglucosides.

Abstract—Besides stansioside and plantarenaloside, the aerial parts of *Campsidium valdivianum* contain two new iridoid diglucosides, stansiosigenin 1-*O*-β-gentiobioside and plantarenalosigenin 1-*O*-β-gentiobioside.

INTRODUCTION

During our systematic investigation of iridoid components in the Chilean flora, we investigated *Campsidium valdivianum* (Phil.) Skottsb., a monogeneric member of the family Bignoniaceae that grows in the southern region of Chile, where it is known as voqui-bejuco [2]. Previously, we have reported the isolation of two iridoid glucosides, stansioside (1) and plantarenaloside (2), from a methanolic extract of stems and leaves [3]. A reinvestigation of the same plant resulted in the isolation of two more new iridoid diglucosides, the structural determination of which is now described.

RESULTS AND DISCUSSION

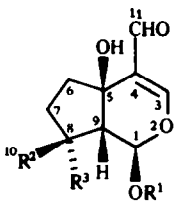
A careful examination of the chromatographic pattern of a methanolic extract of aerial parts of *C. valdivianum* showed, besides 1 and 2 (R_f = 0.44), the presence of a spot with the same pink-red colour with vanillin–HCl reagent, but lower R_f value (0.12). After the usual preliminary purification by the charcoal method and subsequent repeated column chromatography on Si gel, two compounds (3 and 4) were isolated from this area in a *ca* 10:2 ratio.

Substance 3, $C_{22}H_{34}O_{14}$, is an amorphous powder with UV and IR spectra very similar to those of 1 [4]. Also the ^{1}H NMR spectrum is practically identical, apart from several additional peaks between δ3.8–3.2, suggesting the presence of another sugar unit, as also confirmed by the appearance of two anomeric protons, at δ4.72 and 4.57, as doublets with J = 7.5 Hz. Total hydrolysis of 3 afforded, besides the black products arising from the aglycone decomposition, two moles of D-glucose. Partial hydrolysis gave an oligosaccharide, identified as D-gentiobiose by direct comparison. ^{1}H NMR data are well in accordance with this identification: in gentiobiose the anomeric proton resonates at 4.67 (J = 7.0 Hz) and 4.56 (J = 7.0 Hz), for the reducing end unit and for the interglucosidic one, respectively [5].

The ^{13}C NMR spectra of 3 and 4 (Table 1) both contain signals corresponding to a β-gentiobiosyl moiety [4, 6]. Furthermore, by comparison with spectra of stansioside (1) and plantarenaloside (2), the aglucone signals of 3 are almost co-incident with the former, while those of 4 with the latter [4]. Reaction of 3 with pyridine and acetic anhydride afforded the acetyl derivative 5, whose ^{1}H NMR spectrum showed in the sugar resonances region the primary alcoholic functions distinguished between that of the end unit shifted at δ4.22 and 4.10, as a consequence of the acetylation, and that of the interglucosidic linkage at 3.85 and 3.70. Thus, all the data indicate that 3 is stansiosigenin 1-*O*-β-gentiobioside and 4 is plantarenalosigenin 1-*O*-β-gentiobioside. This is the first report of iridoid diglucosides from the Bignoniaceae. Relatively few iridoid diglucosides have been reported in the literature, although this may be due to the difficulty of detecting and separating these compounds amongst other constituents.

EXPERIMENTAL

CC: silica gel 70–230 mesh (Merck). PC: Schleicher & Schüll 2043 b Mgl in *n*-BuOH–HOAc–H_2O 67:10:27. TLC: silica gel 60 F_{254} (Merck) and cellulose (Merck) plates. Spray reagents:



1	R^1 = β-D-glucose	R^2 = Me	R^3 = H
2	R^1 = β-D-glucose	R^2 = H	R^3 = Me
3	R^1 = β-D-gentiobiose	R^2 = Me	R^3 = H
4	R^1 = β-D-gentiobiose	R^2 = H	R^3 = Me
5	R^1 = β-D-gentiobiose (Ac)$_7$	R^2 = Me	R^3 = H
6	R^1 = β-D-gentiobiose (Ac)$_7$	R^2 = H	R^3 = Me

*Part 12 in the series "Iridoids in Equatorial and Tropical Flora". For part 11 see ref. [1].

Table 1. ^{13}C NMR chemical shift values for compounds 3–6*

Carbon no.	3†	4†	5‡	6‡
1	97.5	96.3	100.6	100.6
3	164.6	165.4	157.0	157.8
4	124.8	124.9	125.3	124.8
5	73.5	72.9	71.8	72.4
6	37.9	38.2	37.0	37.3
7	31.0	32.2	30.7	31.9
8	35.1	34.2	34.4	33.3
9	56.6	51.7	56.9	51.6
10	19.9	15.9	19.8	15.9
11	194.6	194.8	190.0	190.0
1′	99.7[a]	99.4[a]	96.8[d]	96.8[d]
2′	74.9[b]	74.9[b]	70.7	70.7
3′	77.2[c]	77.2[c]	72.5[e]	72.5[e]
4′	70.8	70.8	68.1[f]	68.1[f]
5′	76.2[c]	76.2[c]	72.9[e]	72.9[e]
6′	69.3	69.3	67.5[f]	67.5[f]
1″	103.6	103.6	96.9[d]	96.8[d]
2″	73.1[b]	73.1[b]	68.7[f]	68.7[f]
3″	76.2[c]	76.2[c]	70.9	70.9
4″	70.7	70.7	67.8[f]	67.8[f]
5″	76.9[c]	76.9[c]	73.5[e]	73.5[e]
6″	61.8	61.8	61.7	61.7

*Chemical shifts in ppm. Values with the same superscript are interchangeable.

†In $CDCl_3$–CD_3OD 6:4.

‡In $CDCl_3$.

2 N H_2SO_4, vanillin–HCl (vanillin 2 g, conc HCl 4 ml, CH_3OH 100 ml) and resorcin (resorcin 5 g, conc H_2SO_4 4 ml, EtOH 296 ml). ^1H NMR: Bruker AM 400. ^{13}C NMR: Varian XL 100. TMS as int. reference. CHO microanalysis of described compounds gave satisfactory results.

Extraction and separation. Campsidium valdivianum (1.5 kg) was collected in Valdivia (Chile) and identified at U.F.S.M., where voucher specimens are deposited. The stems and leaves of *C. valdivianum* were extracted × 2 with CH_3OH at room temp. and the combined extracts evaporated to an aq. suspension. Then charcoal was added until a negative vanillin test occurred and the resulting mixture stratified on a Gooch funnel (ϕ 34 cm). Elution with H_2O and 5% and 10% aq. EtOH removed salts and sugars, whereas 30, 50 and 70% aq. EtOH eluted iridoid-containing fractions. The 30 and 50% fractions were mixed after PC and TLC monitoring and chromatographed on silica gel using *n*-BuOH satd with H_2O as eluent, affording semipurified mixtures of iridoids, which were further separated by repeated CC on silica gel using $CHCl_3$–CH_3OH 7:3 as eluent. The following quantities of pure iridoids were obtained: **1**, 270 mg; **2**, 120 mg; **3**, 230 mg; **4**, 50 mg. Compounds **1** and **2** were identified by direct comparison with authentic samples.

Stansiosigenin 1-O-*β-gentiobioside* **3**. Amorphous white powder with $[\alpha]_D = -13.8$ ($c = 1.8$, CH_3OH). UV (CH_3OH), λ_{max}: 241 nm ($\log\varepsilon = 3.98$). IR (KBr), ν_{max}: 3380, 2850, 2740, 1660, 1620 cm^{-1}. ^1H NMR ($CDCl_3$–CD_3OD 8:2), δ: 9.22 (1H, *s*, H-11), 7.53 (1H, *s*, H-3), 5.80 (1H, *d*, $J_{1,9} = 2.0$ Hz, H-1), 4.72 (1H, *d*, $J_{1',2'} = 7.5$ Hz, H-1′), 4.57 (1H, *d*, $J_{1'',2''} = 7.5$ Hz, H-1″), 3.37 (1H, *dd*, $J_{5,9} = 7.0$ Hz, H-9), 1.14 (3 H, *d*, $J_{8,10} = 5.5$ Hz, CH_3-8).

Plantarenalosigenin 1-O-*β-gentiobioside* (**4**). Amorphous white powder with $[\alpha]_D = -56.0$ ($c = 0.8$, CH_3OH). UV (CH_3OH), λ_{max}: 241 nm ($\log\varepsilon = 3.98$). IR (KBr), ν_{max}: 3380, 2740, 1660, 1620 cm^{-1}. ^1H NMR ($CDCl_3$–CD_3OD 8:2), δ: 9.23 (1H, *s*, H-11), 7.58 (1H, *s*, H-3), 5.93 (1H, *d*, $J_{1,9} = 0.5$ Hz, H-1), 4.72 (1H, *d*, $J_{1',2'} = 7.5$ Hz, H-1′), 4.57 (1H, *d*, $J_{1'',2''} = 7.5$ Hz, H-1″), 0.94 (3 H, *d*, $J_{8,10} = 6.2$ Hz, CH_3-8).

Total hydrolysis of **3**. Compound **3** (30 mg) was dissolved in 1 N H_2SO_4 (5 ml) and refluxed for 6 hr. Black degradation products were removed by filtration and the soln neutralized with satd $Ba(OH)_2$, the suspension was filtered, the soln evaporated and the residue (40 mg) chromatographed on silica gel, using $CHCl_3$–CH_3OH 7:3 as eluent, to give D-glucose (12 mg), identified by direct comparison with an authentic sample.

Partial hydrolysis of **3**. Compound **3** (80 mg) was dissolved in 1 N H_2SO_4 (5 ml) and refluxed for 10 min until the solution gave a negative vanillin test. The soln was rapidly frozen and worked up as above. The neutral soln was treated with charcoal (15 g), the resulting suspension stratified on a Gooch funnel (ϕ 1 cm) and eluted with 200 ml of a continuous gradient of EtOH (0 → 30%). Pure gentiobiose (26 mg) was obtained and identified by direct comparison with an authentic sample.

Heptaacetate of **3** (**5**). Compound **3** (70 mg) was treated with dry pyridine (1 ml) and Ac_2O (2 ml) for 2 hr at room temp. After addition of MeOH the soln was allowed to stand for 20 min the solvents evaporated and the residue purified by CC on silica gel, using C_6H_6–EtOAc 1:1 as eluent, to obtain pure **5** (60 mg) as a viscous oil. ^1H NMR ($CDCl_3$), δ: 9.36 (1H, *s*, H-11), 7.04 (1H, *s*, H-3), 5.40 (1H, *d*, $J_{1,9} = 2.0$ Hz, H-1), 5.19 (1H, *t*, $J_{2',3'} = J_{3',4'} = 9.2$ Hz, H-3′), 5.12 (1H, *t*, $J_{2'',3''} = J_{3'',4''} = 9.2$ Hz, H-3″), 5.02 (1H, *t*, $J_{4',5'} = 9.2$ Hz, H-4′), 4.97 (1H, *dd*, $J_{1',2'} = 7.5$ Hz, H-2′), 4.89 (1H, *dd*, $J_{1'',2''} = 7.5$ Hz, H-2″), 4.86 (1H, *t*, $J_{4'',5''} = 9.2$ Hz, H-4″), 4.79 (1H, *d*, H-1′), 4.54 (1H, *d*, H-1″), 4.22 (1H, *dd*, $J_{gem} = 12.2$ Hz and $J_{5'',6''} = 5.5$ Hz, H-6″$_A$), 4.10 (1H, *dd*, $J_{5'',6''} = 2.2$ Hz, H-6″$_B$), 4.05 (2H, *m*, H-5′ and H-5″) 3.85 (1H, *dd*, $J_{gem} = 12.2$ Hz and $J_{5',6'_B} = 2.2$ Hz, H-6′$_B$), 3.70 (1H, *dd*, $J_{5',6'_B} = 5.5$ Hz, H-6′$_A$), 2.05–1.95 (21H, 7 × $COMe_3$), 1.11 (3H, *d*, $J_{8,10} = 5.5$ Hz, CH_3-8).

Heptaacetate of **4** (**6**). Compound **4** (20 mg) was acetylated, worked up and purified as described above for **5**. ^1H NMR ($CDCl_3$), δ: 9.36 (1H, *s*, H-11), 7.10 (1H, *s*, H-3), 5.50 (1H, *d*, $J_{1,9} = 0.5$ Hz, H-1), 0.92 (3H, *d*, $J_{8,10} = 6.2$ Hz, CH_3-8), signals pertaining to the disaccharide moiety are practically identical to the corresponding ones in **5**.

Acknowledgement—This research was partially supported by a grant (No. 861303) from DGDCYT, Universidad Federica Santa Maria.

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