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AN IRIDOID GLUCOSIDE FROM *LONICERA CAERUEA**

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Key Word Index—*Lonicera caerulea*; Caprifoliaceae; iridoid; acetal linkage; caeruleoside C.

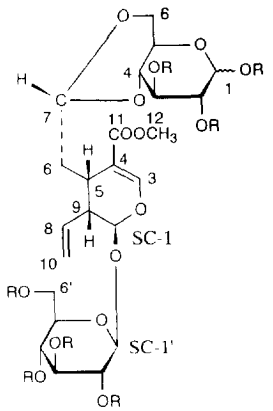
Abstract—A new iridoid glucoside, caeruloside C, has been isolated from the leaves of *Lonicera caerulea*. The structure was elucidated by chemical evidences and 1D, 2D, NMR analysis.

INTRODUCTION

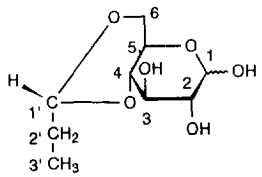
In a previous paper [2], we reported on the isolation of two unusual bis-iridoid glucosides, caeruleoside A and B, consisting of secologanin attached through acetal bonds to C-4′, and C-6′ of the sugar part of loganin and sweroside, respectively, from the leaves of *Lonicera caerulea*. L. var. *emphyllocalyx* Nakai. Further investigation of the this plant led to the isolation of another iridoid glucoside, which we have named caeruleoside C.

RESULTS AND DISCUSSION

Caeruleoside C (**1**) was obtained as an amorphous powder. Its ^{1}H NMR spectrum was similar to that of secologanin isolated from the same plant [2]. The only difference being that **1** had signals due to an equilibrium mixture of α- and β-glucosyl groups instead of the signals of the aldehyde group present in secologanin. The ^{13}C NMR chemical shifts of the secologanin moiety of **1** were good agreement with those of the secologanin moiety of caeruleoside A [2]. Furthermore, the ^{1}H and ^{13}C NMR chemical shifts of an equilibrium mixture of the α- and β-glucosyl moiety of **1** were in good agreement with those of 4,6-propylidene α- and β-glucose (**2**) which we prepared as a model compound (see Experimental). On the basis of the above data, the structure of caeruleoside C was established as **1**.



1; R=H
1a; R=$COCH_3$



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EXPERIMENTAL

The instrument used were the same as described in the previous paper [2].

Extraction and isolation. The extraction and isolation procedure was described in our previous paper [2]. Compound **1** (3 mg) was isolated from fr. 3-1 by prep. HPLC (MeOH–H_2O, 2:3).

Caeruleoside C (**1**). An amorphous powder. ^{1}H NMR (270 MHz, CD_3OD): secologanin moiety; δ1.77 (1H, *m*, H_{SC}-6_A) 2.02 (1H, *m*, H_{SC}-6_B), 2.68 (1H, *m*, H_{SC}-9), 3.03 (1H, *m*, H_{SC}-5), 3.15–3.32 (4H, *m*, H_{SC}-2′, 3′, 4′ and 5′) 3.62 (1H, *m*, H_{SC}-$6'_A$), 3.70 (3H, *s*, H_{SC}-12) 3.89 (1H, *dd*, *J* = 11.7, 2.0 Hz, H_{SC}-$6'_B$), 4.66 (1H, *m*, H_{SC}-7), 4.67 (1H, *d*, *J* = 7.9 Hz, H_{SC}-1′), 5.25 (1H, *br d*, *J* = 8.6 Hz, H_{SC}-10_A), 5.29 (1H, *br d*, *J* = 17.5 Hz, H_{SC}-10_B), 5.54 (1H, *d*, *J* = 5.9 Hz, H_{SC}-1), 5.74 (1H, *br dt*, *J* = 17.5, 8.6 Hz, H_{SC}-8), 7.45 (1H, *d*, *J* = 1.0 Hz, H_{SC}-3); α- and β-glucose moieties: δ3.15–3.40 (5/2H, *m*, α-H-2, 4, β-H-2, 4 and 5), 3.55 (3/2H, *m*, α-H-6_A, β-H-6_A, β-H-3 and 6_A), 3.78 (1H, *m*, α-H-3 and 5), 4.00 (1/2H, *dd*, *J* = 10.2, 5.0 Hz, α-H-6_B), 4.08 (1/2H, *dd*, *J* = 10.2, 4.6 Hz, β-H-6_B), 4.53 (1/2H, *d*, *J* = 7.9 Hz, β-H-1), 5.08 (1/2H, *d*, *J* = 3.6 Hz, α-H-1); ^{13}C NMR (67.8 MHz, CD_3OD): δ29.6 (C_{SC}-5), 35.2 (C_{SC}-6), 45.4 (C_{SC}-9), 51.8 (C_{SC}-12), 62.9 (C_{SC}-6′), 63.6 (C_α-5), 67.9 (C_β-5), 69.5 (C_β-6), 69.9 (C_α-6), 71.7 (C_{SC}-4′), 71.9 (C_{SC}-3), 74.5 (C_α-2), 74.4 (C_β-3 and C_{SC}-2′), 77.2 (C_β-2), 78.0 (C_{SC}-3′), 78.5 (C_{SC}-5′), 82.1 (C_β-4), 82.8 (C_α-4), 94.7

*Part 5 in the series 'Analysis of the Components of *Lonicera* Species'. For part 4 see ref. [1].

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(C_α-1), 97.7 (C_{SC}-1), 99.0 (C_β-1), 100.0 (C_{SC}-1'), 102.6 (C_{SC}-7), 111.6 (C_{SC}-4), 119.8 (C_{SC}-10), 135.8 (C_{SC}-8), 153.7 (C_{SC}-3), 169.3 (C_{SC}-11).

Acetylation of **1**. Compound **1** (3 mg) was acetylated with Ac_2O in pyridine to give **1a** (1.7 mg) as an amorphous powder, $[\alpha]_D$ −42.8° (MeOH, *c* 0.1). FAB MS *m/z*: 845 $[M + H]^+$; UV λ_{max}^{MeOH} nm (log ε): 229 (3.77); ^{1}H NMR (270 MHz, $CDCl_3$): secologanin moiety; δ 1.72 (1H, *m*, H_{SC}-6_A), 2.05 (1H, *m*, H_{SC}-6_B), 2.69 (1H, *m*, H_{SC}-9), 2.87 (1H, *m*, H_{SC}-5), 3.70 (3H, *s*, H_{SC}-12), 3.75 (1H, *m*, H_{SC}-5'), 4.15 (1H, *m*, H_{SC}-$6'_A$), 4.30 (1H, *dd*, *J* = 12.3, 4.8 Hz, H_{SC}-$6'_B$), 4.63 (1H, *m*, H_{SC}-7), 4.89 (1H, *d*, *J* = 8.1 Hz, H_{SC}-1'), 4.96–5.11 (3H, *m*, H_{SC}-2', 3' and 4'), 5.19–5.29 (3H, *m*, H_{SC}-1, 10_A and 10_B), 5.56 (1H, *m*, H_{SC}-8), 7.34 (1H, *s*, H_{SC}-3); α- and β-glucose moieties; δ 3.41–3.70 (5/2H, *m*, α-H-4, 6_A, β-H-4, 5 and 6_A), 3.87 (1/2H, *m*, α-H-5), 4.12–4.22 (1H, *m*, α-H-6_B and β-H-6_B), 4.96–5.11 (1H, *m*, α-H-2 and β-H-2), 5.19–5.29 (1/2H, *m*, β-H-3), 5.48 (1/2H, *t*, *J* = 9.9 Hz, α-H-3), 5.73 (1/2H, *d* *J* = 8.1 Hz, β-H-1), 6.25 (1/2H, *d*, *J* = 4.0 Hz, α-H-1); acetyl group; δ 1.92, 2.00, 2.02, 2.03, 2.04, 2.10, 2.11 and 2.18 (21H, each *s*).

Preparation of 4,6-*propylidene glucose* (**2**). An equilibrium mixture of α- and β-glucose (27 mg) was suspended in CH_3CH_2CHO (0.05 ml), anhydrous $ZnCl_2$ (23 mg) added and the mixture stirred at room temp. for 3 hr. The EtOAc extract was chromatographed on a silica gel column (hexane–Me_2CO, 3:2) to give a hygroscopic amorphous powder (19 mg), $[\alpha]_D$ +63.5° (MeOH, *c* 1.4). FAB MS *m/z* 243 $[M + Na]^+$; ^{1}H NMR (270 MHz), CD_3OD); δ0.94 (3H, *t* *J* = 7.6 Hz, H-3'), 1.63 (2H, *m*, H-2'), 3.24 (2H, *m*, α-H-4, β-H-2, 4 and 5), 3.40 (1/2H, *dd* *J* = 9.5, 3.6 Hz, α-H-2), 3.54 (3/2H, *m*, α-H-6_A, β-H-3 and 6_A), 3.77 (1/2H, *t*, *J* = 9.5 Hz, α-H-3), 3.78 (1/2H, *m*, α-H-5), 4.01 (1/2H, *dd*, *J* = 10.2, 5.0 Hz, α-H-6_B), 4.09 (1/2H, *dd*, *J* = 10.4, 4.5 Hz, β-H-6B), 4.51 (1H, *m*, H-1'), 4.53 (1/2H, *d*, *J* = 7.9 Hz, β-H-1), 5.08 (1/2H, *d*, *J* = 3.6 Hz, α-H-1); ^{13}C NMR (67.8 MHz, CD_3OD): δ8.7 (C-3'), 28.5 (C-2'), 63.7 (C_α-5), 67.9 (C_β-5), 69.4 (C_β-6), 69.8 (C_α-6), 71.9 (C_α-3), 74.5 (C_α-2),74.8 (C_β-3), 77.2 (C_β-2), 82.0 (C_β-4), 82.7 (C_α-4), 94.7 (C_α-1), 98.9 (C_β-1), 104.6, 104.7 (C_α-1' and C_β-1).

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