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CAPSUGENIN-30-*O*-β-GLUCOPYRANOSIDE: A NEW GLYCOSIDE FROM THE LEAVES OF *CORCHORUS CAPSULARIS*

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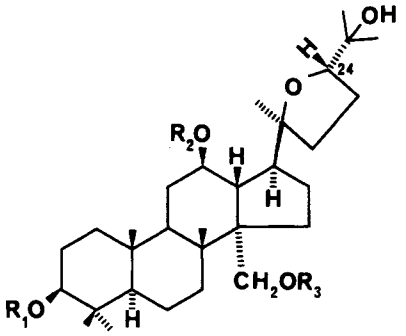
In a previous paper (1) we reported the isolation of a glycoside, capsin, as the major bitter-tasting substance of the leaves of *Corchorus capsularis* L. (Tiliaceae). The genin derived from capsin (capsugenin) was identified (1) as **1** on the basis of a detailed spectral analysis of **1** and the corresponding 3β,30-diacetate [**2**] and 3β,12β,30-triacetate [**3**]. In that previous paper it was noted (1) that capsin appeared to be primarily the 3-*O*-glucoside but that this was accompanied by smaller amounts of two other glycosides. We now report on the isolation and identification of one of those glycosides.

Preparative tlc of the glycoside mixture finally gave a pure compound in a yield of about 15% of that mixture. Hydrolysis of this compound gave glucose, identified by tlc, and capsugenin [**1**]. This new glycoside has been assigned structure **4** on the basis of the following evidence.

Acetylation of **4** under standard conditions gave the penta-acetate [**5**]. The ^{1}H-nmr spectrum of the parent glycoside was ill-defined, but that for **5** allowed resolution of 14 protons occurring downfield of the acetyl methyl resonances including those for the glucose tetraacetate. Salient features noted in the spectrum of **5** when compared to previous data for **1** and its derivatives (1) were: (a) the signals for the H-bonded 12-OH proton, H-3, H-12, H-17, and H-24 agreed well with data for the aglycone diacetate [**2**] and (b) the AB quartet for H-30 occurred at δ3.35 and 4.23 indicating that this position was not acetylated [cf. values of δ 4.16 and 4.32 in **2** (1)] and must, therefore, carry the glycoside link. The ^{13}C-nmr spectra of **4** and **5** were run, and resonances are listed in Table 1 together with previously published data for **2** (1). The close comparability of spectra for **2** and **5** with the exception of the C-30 resonance confirms the placement of the glucose unit at that position.



	R_1	R_2	R_3
1	H	H	H
2	Ac	H	Ac
3	Ac	Ac	Ac
4	H	H	gluc
5	Ac	H	gluc(Ac)$_4$

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Optical rotations were recorded on a Perkin-Elmer 141 polarimeter. Spectra were recorded as follows: ir, Perkin-Elmer 297 as KCl discs; ms, AEI MS902 at 70 eV, inlet temperature 200°; nmr, ^{1}H (360 MHz) and ^{13}C (90.56 MHz) on a Bruker WM 360; chemical shifts given in ppm relative to TMS (δ=0)

TABLE 1. ^{13}C-nmr Chemical Shift Assignments for Capsugenin-30-*O*-glucopyranoside [**4**], its Pentaacetate [**5**], and Capsugenin-3,30-diacetate [**2**]

Carbon Atom	Compounds		
	4	**5**	**2**
C-1	38.9	38.9	38.8
C-2	27.6[b]	23.7	23.7
C-3	78.4	80.3	80.0
C-4	38.7	39.7	39.7
C-5	56.2	56.5	56.5
C-6	18.4	20.0	19.3
C-7	34.5	35.1	35.1
C-8	42.4	41.7	41.0
C-9	49.7	50.4	50.3
C-10	36.2	37.1	37.0
C-11	31.8[c]	32.1[b]	31.8[b]
C-12	70.6	70.4	70.0
C-13	48.4[d]	48.9[c]	48.9[c]
C-14	51.1	52.0	52.0
C-15	31.5[c]	31.8[b]	31.6[b]
C-16	24.7	25.0	25.0
C-17	48.4[d]	48.8[c]	49.0[c]
C-18	17.0	17.6	17.6
C-19	15.7	15.6	16.0
C-20	85.9	87.3	87.0
C-21	22.4	22.3	22.4
C-22	31.2[c]	31.7[b]	32.1[b]
C-23	27.5[b]	28.5	28.4
C-24	87.3	87.1	87.4
C-25	68.9	70.0	70.3
C-26	25.5	24.2	24.2
C-27	27.9	28.8[d]	27.9[d]
C-28(α)	14.5	15.1	15.3
C-29(β)	25.7	27.9[d]	27.8[d]
C-30	72.3	71.6	65.2
C-1′	104.9	101.1	
C-2′	74.2	71.5	
C-3′	77.5	72.8	
C-4′	69.6	68.8	
C-5′	77.5	71.5	
C-6′	61.5	62.1	
Ac		170.3×2	170.7
		170.1	170.3
		169.3	21.2
		168.9	21.0
		21.1	
		20.6	
		20.5×3	

[a]**2** and **5** were run in $CDCl_3$, **4** in C_5D_5N.
[b,c,d]Signals under any compound with the same letter are interchangeable.

PLANT MATERIAL.—Mature leaves of *C. capsularis* were collected from Savar, Dhaka, under the auspices of the Bangladesh Jute Research Institute. A voucher specimen is retained at the herbarium of the Department of Botany, University of Dhaka.

PURIFICATION OF **4**.—Tlc of the glycoside

mixture (Si gel 60; solvent, *n*-BuOH saturated with H_2O) gave a band at Rf 0.73. Elution of this band from preparative tlc plates with MeOH gave **4** in a yield of 15% of the starting mixture.

CAPSUGENIN-30-*O*-β-GLUCOPYRANOSIDE [**4**].—Recrystallized from MeOH as needles, mp 235-237°; $[\alpha]^{25}D-12°$ (*c* 0.5, MeOH); ^1H nmr (C_5D_5N) δ 6.08 (1H, s, OH-12), 5.67 (1H, d, J=7.1 Hz, H-1′), 4.40, 4.29 (2H, ABq, J=9.9 Hz, CH_2-30), 4.18 (1H, dd, J=10.7, 5.2 Hz, H-24), 3.75 (1H, dt, J=10.0, 4.3 Hz, H-12), 3.53 (1H, m, H-3), 1.57, 1.47, 1.33, 1.32, 0.99, 0.88 (6H) (7×Me); ^{13}C nmr (C_5D_5N) see Table 1.

Hydrolysis of **4** (25 mg) was achieved by dissolving it in 0.5M TFA (10 ml) and refluxing for 16 h. The reaction mixture was cooled and precipitated with H_2O to give **1** (12 mg), recrystallized from MeOH as needles, mp 230-231°, identical in all respects (eims, mmp, tlc) with an authentic sample. The H_2O- soluble portion of the hydrolysate was concentrated and analyzed by tlc (cellulose; solvent, *n*-BuOH-pyridine-H_2O, 10:3:3). The only sugar to be found had identical characteristics to glucose.

CAPSUGENIN-30-*O*-β-GLUCOPYRANOSIDE-2′, 3,3′,4′,6′-PENTAACETATE [**5**].—Compound **4** (173 mg) in dry pyridine (2 ml) was treated with Ac_2O (4 ml) for 24 h at room temperature. Normal work-up gave **5** (170 mg) which recrystallized from MeOH as needles, mp 229-230°; $[\alpha]^{25}D-22°$ (*c* 0.6, MeOH); ir ν max 3350, 3220, 1740 cm^{-1}; ^1H nmr ($CDCl_3$) δ 5.73 (1H, s, OH-12), 5.18 (1H, t, J=9.4 Hz, H-3′), 5.09 (1H, t, J=9.6 Hz, H-4′), 5.02 (1H, dd, J=9.5, 7.9 Hz, H-2′), 4.51 (1H, dd, J=11.2, 5.4 Hz, H-3), 4.41 (1H, d, J=7.8 Hz, H-1′), 4.23 (1H, d, J=9.9 Hz, H-30), 4.21 (1H, dd, J=12.2, 4.8 Hz, H-6′), 4.15 (1H, dd, J=12.2, 2.8 Hz, H-6′), 3.87 (1H, dd, J=10.6, 5.3 Hz, H-24), 3.68 (1H, ddd, J=9.8, 4.7, 2.8 Hz, H-5′), 3.51 (1H, dt, J=4.6, 10.3 Hz, H-12), 3.35 (1H, d, J=9.9 Hz, H-30), 2.24 (1H, dt, J=4.3, 10.3 Hz, H-17), 2.07, 2.04, 2.02, 2.02, 1.99, (5×OAc), 1.26 (3H, s, H-26 or H-27), 1.22 (3H, s, H-26 or H-27), 1.09 (3H, s, H-18), 0.99 (3H, s, H-21), 0.94 (3H, s, H-19), 0.92 (3H, s, H-29), 0.87 (3H, s, H-28); ^{13}C nmr see Table 1.

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