Communications to the Editor

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Cynanchoside C_2, a New Steroidal Oligoglycoside from *Cynanchum caudatum* Max.: Applycation of ^{13}C-NMR Spectroscopy to the Structural Elucidation of Plant Glycosides

A new steroidal oligoglycoside, named cynanchoside C_2, was isolated from the rhizome of *Cynanchum caudatum* Max. (Asclepiadaceae). The structure of cynanchoside C_2 was elucidated by the application of ^{13}C-nuclear magnetic resonance spectroscopy and chemical reactions.

Keywords——*Cynanchum caudatum*; Asclepiadaceae; steroidal oligoglycoside; cynanchoside C_2; 2,6-dideoxy-3-*O*-methyl sugars; ^{13}C-NMR; PRFT method

Rhizome of *Cynanchum caudatum* Max. (Asclepiadaceae) is known to contain many kinds of glycosides, which consist of C/D-*cis*-polyoxypregnane derivatives and 2,6-dideoxy-3-*O*-methyl sugars, and this crude glycoside mixture has some physiological activity.[1] This communication describes the isolation and structure of a new steroidal oligoglycoside from this plant source.

The crude glycoside fraction, extracted by the same procedure as before,[1] was treated with benzene–hexane (1:1). Benzene–hexane (1:1)-soluble portion was chromatographed on polyamide (solvent AcOEt–hexane=1:19) and on silica gel (solvent $CHCl_3$ and $CHCl_3$–MeOH=9:1, and benzene–acetone=4:1), and was purified by silica gel preparative TLC, affording a new steroidal oligoglycoside named cynanchoside C_2 (I). By the use of high-performance liquid chromatography (HPLC) on the reversed phase column, Permaphare ODS, I gave a single peak in the chromatogram which was detected with a spectrophotometric detector operating at 220 nm.

Cynanchoside C_2 (I), amorphous, mp 132.5—135.5°, $[\alpha]_D$ −14.6° (c=1.0, $CHCl_3$), showed positive Keller-Kiliani reaction (bluish purple).[2]

Mild acid hydrolysis of I afforded cynanchogenin (III), cymarose (IV), and oleandrose (VI), which were identical with authentic samples by comparison of TLC, and gas-liquid chromatogram (GLC).

On the basis of comparison with ^1H- and ^{13}C-nuclear magnetic resonance (PMR and CMR) spectra of C/D-*cis*-polyoxypregnane derivative,[3] these spectra of I revealed that I must be a glycoside of cynanchogenin (III) and only 3β-OH of which would be bonded with sugar moieties, cymarose and oleandrose (2:1), from the glycosidation shift[4] at C-2, C-3, and C-4 of cynanchogenin moiety (see Table I).

Partially relaxed Fourier transform (PRFT) method, which has been reported to facilitate the identification of carbon resonances of individual sugar units in spectra of oligoglycoside,[5] was applied to the spectrum of I. In the region of sugar carbon signals, a set of signals with longer spin-lattice relaxation time (T_1) than others can be assigned to a terminal sugar,

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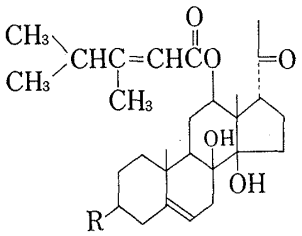
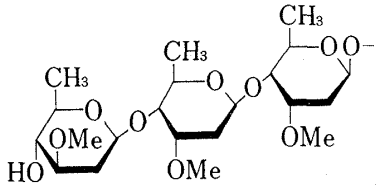
Table I. ^{13}C-NMR Chemical Shifts of I, III, V, VII, and IX in Pyridine-d_5

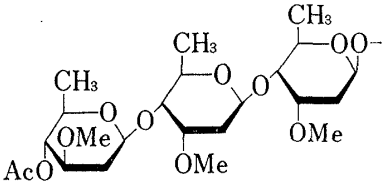
	Aglycone moiety		Sugar moiety I		Methyl glycoside	
	III	I				
C-1	39.2	38.9	Cymarose			V
2	31.9	29.8	C-1	96.3	C-1	99.4
3	71.5	77.9[a]	2	37.2	2	35.1
4	43.1	39.2	3	77.7[a]	3	78.5
5	140.2	139.3	4	83.3	4	74.0
6	118.4	119.1	5	68.9	5	71.0
7	34.1	34.1	6	18.5[b]	6	18.9
8	74.5	74.5	C-3-OMe	58.8	C-1-OMe	57.8
9	44.7	44.7			C-3-OMe	56.0
10	37.4	37.5				
11	25.0	25.0	Cymarose			VII
12	72.3	72.2	C-1	100.3	C-1	101.0
13	55.6	55.7	2	37.2	2	36.6
14	87.4	87.4	3	77.6[a]	3	81.3
15	35.1	35.1	4	83.1	4	76.2
16	21.7	21.7	5	68.9	5	72.6
17	60.5	60.5	6	18.5[b]	6	18.4
18	15.8	15.8	C-3-OMe	58.8	C-1-OMe	56.9
19	18.3	18.1			C-3-OMe	56.0
20	209.0	209.0				
21	32.0	32.0	Oleandrose			IX
C-1′	166.0	165.9	C-1	102.0	C-1	98.7
2′	114.1	114.2	2	37.0	2	35.1
3′	165.1	165.0	3	81.3	3	79.0
4′	38.0	38.1	4	76.1	4	76.6
5′	20.9	20.9	5	72.9	5	68.4
6′	20.9	20.9	6	18.6[b]	6	18.4
7′	16.4	16.4	C-3-OMe	57.0	C-1-OMe	57.0
					C-3-OMe	54.3

^{13}C-NMR spectra were recorded on a JNM FX-100 FT NMR spectrometer at 25.00 MHz in 5-mm spinning tubes with TMS as internal standard (δ_c O):
a) *b*) Assignments may be reversed.

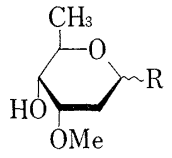




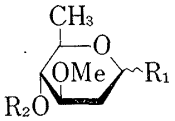
(cynanchoside C_2)



III : R=OH
(cynanchogenin)



IV : R=OH
(cymarose)
V : R=OMe : β



VI : R_1=OH,
R_2=H
(oleandrose)
VII : R_1=OMe : β
R_2=H
VIII : R_1=OH
R_2=Ac
IX : R_1=OMe : α
R_2=H

Chart 1

β-D-oleandroside. Since cymaropyranose possesses only two hydroxy groups at C-1 and C-4, the sugar sequence in I has to be linear and is determined as shown in Chart 1.

We assigned ^{13}C signals of the sugar chain in I as shown in Table I in comparison with the data on ^{13}C chemical shifts of methyl β-D-cymaroside (V) and α,β-D-oleandroside (VII, IX).[6]

From ^{13}C chemical shifts of the anomeric carbon of V and VII, both D-cymarose and D-oleandrose moieties in I are suggested to have a β-configuration at C-1.

In order to confirm the sequence of sugar chain, acetylated cynanchoside C_2 (II) was hydrolyzed under acidic condition and afforded 4-*O*-acetyloleandrose (VIII), cymarose (IV), and cynanchogenin (III).

We have concluded the structure of cynanchoside C_2 to be cynanchogenin-3-*O*-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside (I).

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Intermolecular Photochemical Cycloaddition of 4-Methoxy-2-quinolone with Olefins: A Regioselective Synthesis of 5-Substituted Cyclobuta[*c*]-2-quinolones

Irradiation of 4-methoxy-2-quinolone (IV) in methanol in the presence of substituted ethylenes provided intermolecular addition products. The cycloaddition reaction was shown to be regioselective giving in all cases 5-substituted 3,6-dihydrocyclobuta[*c*]-2-quinolones (V). Base treatment of these cycloadducts afforded the corresponding cyclobuta[*c*]-2-quinolones (VI).

Keywords——cyclobuta[*c*]-2-quinolones; 6-methoxyl-3,6-dihydrocyclobuta[*c*]-2-quinolones; regioselective 2+2 photocycloaddition; biradical intermediate in photochemical cycloaddition reaction; aza-analogs of benzocyclobutene

Recently, we reported that irradiation of 4-allyloxy-2-quinolones (*e.g.* I) produced intramolecular 2+2 cycloaddition products (*e.g.* II) and the successful transformation of the products to the so far unknown cyclobuta[*c*]-2-quinolones (*e.g.* III) by base treatment.[1] An ability of the 3,4-double bond in these quinolones to participate in an intramolecular photocycloaddition reaction seems to suggest that the same bond of 4-alkoxy-2-quinolone may likewise be susceptible to an intermolecular cycloaddition reaction with olefins, though the

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