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STRUCTURES OF ARVENIN I AND II, BITTER PRINCIPLES FROM ANAGALLIS ARVENSIS L.(PRIMULACEAE). NEW CUCURBITACIN GLUCOSIDES

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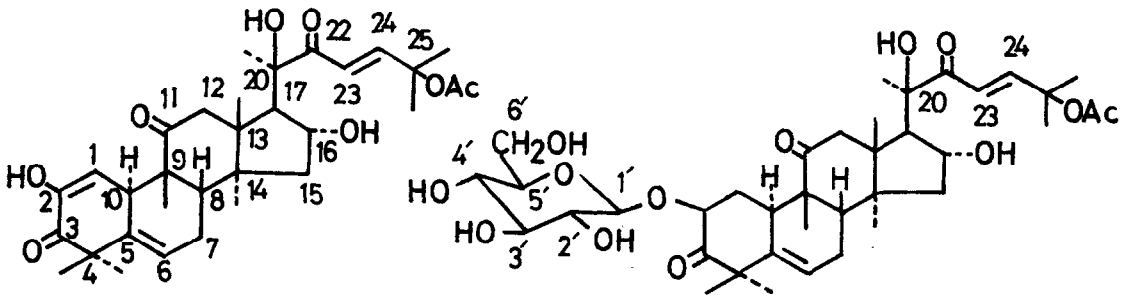
Cucurbitacin glycosides have been received attention owing to their biological activity. Kupchan et al.[1] determined the structure of datiscoside having antileukemic property by X-ray crystallographic analysis. In the course of our investigation on the chemical constituents of Anagallis arvensis L.(Primulaceae), which is used as a herb in Taiwan, two bitter principles, named arvenin I and II, new cucurbitacin glucosides have been isolated from the methanol extract. Now we wish to describe the structure elucidation of arvenin I and II using mainly ^{13}C NMR spectra. Although ^{13}C NMR spectra have been recognized to be useful for the structural studies of terpenoids[2], applications to the field of terpenoid glycosides have been limited[3].

The ethyl acetate insoluble part of the methanol extract,upon successive charcoal chromatography (elution with methanol) and silica gel chromatography [elution with ethyl acetate (saturated with water) : methanol (100:1)], gave arvenin I [m.p. 141-146°C, $[\alpha]_D^{20}$ +40.6(c 1.6, EtOH), $C_{38}H_{56}O_{13}$, UV(EtOH) 228 nm(ϵ 10,900), ^1H NMR($CDCl_3$) δ 0.96(3H,s), 1.06(3H,s), 1.28(6H,s), 1.35(3H,s), 1.45(3H,s), 1.56(6H,s), 2.03(3H,s,OAc), 6.55(1H,d,J=16 Hz,C_{23}-H) and 7.05(1H, d,J=16 Hz,C_{24}-H) ppm], and arvenin II [m.p. 140-143°C, $[\alpha]_D^{20}$ +31.7(c 1.2,EtOH), $C_{38}H_{58}O_{13}$, UV(EtOH) end absorption, ^1H NMR($CDCl_3$) δ 0.98(3H,s), 1.08(3H,s), 1.34(6H,s), 1.47(12H,s) and 1.99(3H,s,OAc) ppm]. The ethyl acetate soluble



(1) cucurbitacin E (2) arvenin I

(3) arvenin II 23,24-dihydro

part of the methanol extract gave cucurbitacin E[4] (1) by repeated silica gel chromatography.

The ^{13}C NMR spectra of cucurbitacin E, arvenin I and arvenin II were examined. Signal assignments of cucurbitacin E were performed by means of chemical shift rules[5] and ^{1}H single frequency off-resonance decoupling experiments, and the results are shown in the Table. Signals of both arvenin I and II are also summarized in the Table as compared with those of cucurbitacin E. The signals attributable to the aglycone of arvenin I were closely related to those of cucurbitacin E, except for the signals underlined in the Table, indicating that arvenin I contained the cucurbitacin carbon skeleton. The remarkably higher shifts of C-1 and C-2 signals together with the lower shift of C-3 signal in arvenin I compared with those of cucurbitacin E demonstrated that the aglycone of arvenin I was a 1,2-dihydro derivative of cucurbitacin E, while the reason of a shift at C-5 position was not clear.

Although the same ^{13}C chemical shift for the C-20 and C-25 carbons was observed in both cucurbitacin E (79.7 ppm) and arvenin I (79.8 ppm), respectively, the acetoxyl group at C-25 was evidenced by the characteristic lower ^{1}H chemical shift[6] [1.56(6H,s) ppm] for the geminal dimethyl groups at C-25 in arvenin I comparable to that of cucurbitacin E.

^{13}C NMR spectrum provided also satisfactory informations on the sugar moiety of arvenin I. By comparison of the ^{13}C chemical shifts of the sugar moiety with those of several glucopyranosides[8], arvenin I apparently contains

Table. ^{13}C Chemical Shifts[a] of Cucurbitacin E (1), Arvenin I (2) and Arvenin II (3)

Carbon	(1)	(2)	(3)	Carbon	(1)	(2)	(3)
C-1	115.8	34.4	34.3				
2	147.2	78.2	78.1		18.5	18.9	18.8
3	198.7	211.3	211.1		20.2	19.9	19.9
4	48.6	48.5	48.6		20.5	20.4	20.1
5	137.9	140.8	140.7		20.7	20.4	21.7
6	120.6	120.4	120.4		21.7	21.8	22.2
7	24.0[b]	24.2[b]	24.2[b]	CH_3	25.4	25.3	25.5
8	35.3	35.0	35.4		26.3	26.3	26.0
9	48.6	48.9	48.9		26.6	26.6	26.0
10	42.3	42.9	42.8		28.1	28.7	28.7
11	213.5	212.7	212.6				
12	49.4[b]	49.1[b]	49.1[b]				
13	49.4[c]	51.0[c]	50.8[c]				
14	51.0[c]	51.5[c]	51.5[c]				
15	46.6[b]	46.1[b]	46.0[b]				
16	70.9	70.8	70.4	1'		104.0	103.9
17	59.7	59.6	58.9	2'		75.6	75.5
20	79.7	79.8	80.0	3'		78.2	78.1
22	204.1	204.0	214.7	Glc 4'		71.4	71.4
23	122.6	122.5	49.3	5'		78.2	78.1
24	150.1	150.0	32.1	6'		62.6	62.6
25	79.7	79.8	81.7				
$OCOCH_3$	169.7	169.7	170.0				

a ^{13}C-NMR spectra were taken with Varian NV-14 spectrometer (15.1 MHz) at 51-2°C in C_5D_5N with TMS as an internal reference using 5 mm tubes.

b,c Assignments may be reversed in each vertical column.

one glucose, and the unusual low field shift at C-2 (78.2 ppm), which was caused by glucosidation shifts[8,9], indicated obviously that glucose linked with the hydroxyl group at C-2 position, while the glucosidation shifts were not observed for the other carbons (C-16 and C-20) bearing a hydroxyl group.

Stereochemistry at C-2 and C-20 positions was confirmed by the fact that acid-catalyzed hydrolysis of arvenin I gave D-glucose and cucurbitacin D[1] (m.p. 142-143°C), as detectable products, which was formed by the simul-

taneous hydrolysis of the acetoxyl group at C-25 of the aglycone,1,2-dihydrocucurbitacin E*. Furthermore stereochemistry of the anomeric position of glucose was assigned to be β by comparison of the ^{13}C chemical shift of the anomeric carbon (104.0 ppm) to those of related α- and β-glucopyranosides[8,9]. From these results, the structure of arvenin I was unambiguously represented to be 2-O-β-D-glucopyranosyl cucurbitacin B (2).

Hydrogenation of arvenin I over Pd-C afforded arvenin II, indicating that the latter compound was a dihydro derivative of arvenin I. The ^{13}C NMR spectrum of arvenin II are extremely related to those of arvenin I as shown in the Table, except for the side chain signals underlined by a dotted line leading to the structure of arvenin II to be 2-O-β-D-glucopyranosyl 23,24-dihydrocucurbitacin B (3).

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* 1,2-Dihydrocucurbitacin E is same as cucurbitacin B[7].