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A NOVEL ACYCLIC DITERPENE GLYCOSIDE, CAPSIANSIDE A, FROM CAPSICUM ANNUUM VAR. FASCICULATUM

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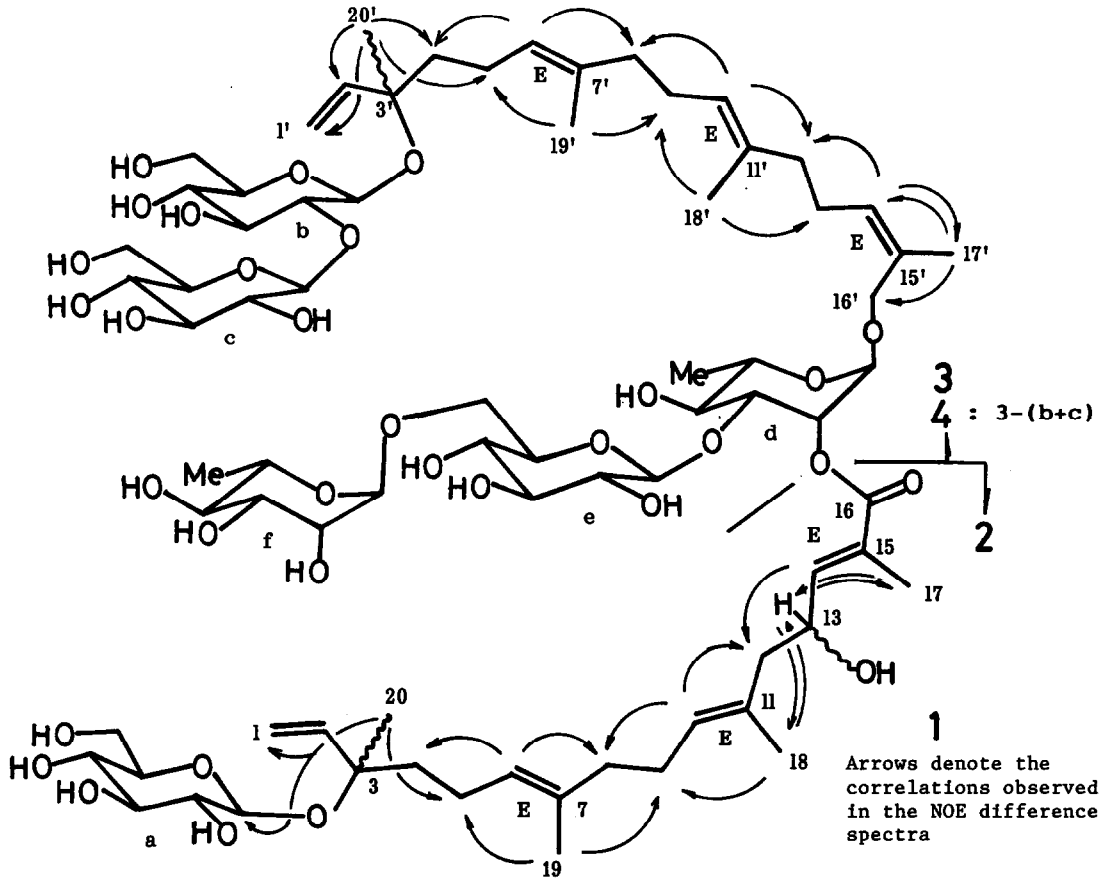
Summary---A novel acyclic diterpene glycoside was obtained from the part of the polar ingredients in the fresh fruits of Capsicum annuum L. var. fasciculatum Irish.

The fruit of Capsicum annuum L. var. fasciculatum Irish is one of the congener crude drugs of Capsici Fructus, which is one of the most important spices and has been used as a medicine for external application. We have now obtained a novel acyclic diterpene glycoside, designated as capsianside A (1), from the fresh fruits in 0.03 % yield. This paper deals with the structure characterization of 1.

Capsianside A (1), colorless amorphous powder, $[\alpha]_D$ -25.1°[1], showed absorption bands at 1716 and 1659 cm^{-1} in the IR spectrum, and a peak due to $(M-H)^-$ at m/z 1563 along with some other fragment ion peaks at m/z 1083, 497 and 479 in the negative FAB-MS. Its ^{13}C-NMR spectrum (Table I) exhibited total seventy-six carbon signals, in which an α,β-unsaturated ester group (δ 127.5, 146.5 and 168.5) and six anomeric carbons of sugars [δ 98.3 (d, J=155 Hz), 99.0 (d, J=168 Hz), 99.7 (d, J=159 Hz), 101.5 (d, J=168 Hz), 102.8 (d, J=159 Hz) and 107.0 (d, J=159 Hz)] were implied. The ^{1}H-NMR spectrum of 1 suggested the presence of eight tert. methyl groups [δ 1.59 (12H, s), 1.64 (3H, s), 1.70 (3H, s), 1.91 (3H, s) and 1.99 (3H, s)]. Acid hydrolysis of 1 afforded L-rhamnose and D-glucose as sugar component. While alkaline treatment of 1 gave two hydrolyzed products, 2 and 3.

Compound 2, colorless amorphous powder, $[\alpha]_D$ -8.2°, negative FAB-MS(m/z): 497 $(M-H)^-$, showed signals due to four methyl groups [δ 1.59 (6H, s), 1.82 (3H, s) and 2.14 (3H, d, J=1.1 Hz)], six olefinic protons [δ 5.23 (1H, d, J=11.0 Hz), 5.24 (1H, t, J=8.0 Hz), 5.39 (1H, dd, J=1.1, 17.6 Hz), 5.46 (1H, t, J=6.6 Hz), 6.30 (1H, dd, J=11.0, 17.6 Hz) and 7.42 (1H, d, J=7.3 Hz)], a methine proton [δ 5.00 (1H, m)] bearing oxygen atom, five pairs of methylene protons [δ 1.80-2.70 (10H, m)] and one mole of the β-D-glucopyranosyl residue [anomeric proton: δ 4.98 (1H, d, J=8.0 Hz)] in the ^{1}H-NMR spectrum. Moreover, the ^{13}C-NMR spectrum (Table I) indicated the presence of an α,β-unsaturated carboxylic acid [δ 131.4 (s), 144.5 (d) and 171.2 (s)], three double bonds [δ 114.8 (t), 125.2 (d), 127.9 (d), 132.0 (s), 134.9 (s) and 144.5 (d)], two carbons [δ 67.5 (d) and 80.0 (s)] carrying oxygen atom, five methylene carbons (δ 22.9, 27.1, 39.9, 42.1 and



48.0), four methyl carbons (δ 13.4, 16.1, 16.9 and 23.5) and the β-D-glucopyranosyl moiety (δ 99.8, 75.3, 78.8, 71.9, 78.1 and 62.9, C_1-C_6). The full assignments of all of the protons and carbons in **2** were acchieved by the detailed analyses of the 2D (^{1}H-^{1}H, ^{1}H-^{13}C and ^{1}H-^{13}C long range[2]) NMR spectra and NOE difference spectroscopy experiments. Namely, the NMR studies disclosed the connectivities of all of the double bonds, carboxyl-, methyl-, methylene- and hydroxyl-groups, and the geometric configurations of the double bonds. Therefore, the structure of **2** was represented as 3-O-β-D-glucopyranosyl -13-hydroxygeranyl-linalool 16-oic acid.

On the other hand, compound **3**, colorless amorphous powder, $[\alpha]_D$ -37.6°, showed a peak of $(M-H)^-$ at m/z 1083 in the negative FAB-MS. The ^{1}H-NMR spectrum of **3** showed signals due to six methyl groups [δ 1.58 (s), 1.64 (s), 1.65 (d, J=6.0 Hz), 1.69 (s), 1.68 (d, J=6.6 Hz) and 1.92 (s)] , an ABX type signal attributable to the vinyl group [δ 5.07 (d, J=11.0 Hz), 5.28 (d, J=17.6 Hz) and 6.59 (dd, J=11.0, 17.6 Hz)], three olefinic protons (δ 5.24, 5.36 and 5.47) each splitted into triplet, and five anomeric protons [δ 4.73 (d, J=8.1 Hz), 4.98 (d, J=7.7 Hz), 5.22 (d, J=7.3 Hz), 5.36 (br s) and 5.61 (br s)]. In conjunction with the evidence of 2D (^{1}H-^{1}H, ^{1}H-^{13}C) NMR (Table I) spectra, **3** was supposed

Table I. ^{13}C-NMR Assignments (δ) of Casianside A (1), 2, 3 and 4 in pyridine-d_5

	1	2		1	3	4
C-1	114.8	114.8	C-1'	115.0	115.0	111.2
2	144.4	144.5	2'	144.5	144.5	147.0
3	80.0	80.0	3'	80.6	80.6	72.4
4	42.1	42.1	4'	42.6	42.6	42.3
5	22.9	22.9	5'	23.0	23.0	23.0
6	125.1	125.2	6'	125.1	125.2	125.1
7	135.0	134.9	7'	135.1	135.1	134.8
8	39.8	39.9	8'	40.0	40.0	40.0
9	27.0	27.1	9'	26.4	26.4	26.4
10	127.8	127.9	10'	125.2	125.2	125.4
11	131.9	132.0	11'	134.6	134.6	134.6
12	47.4	48.0	12'	40.1	40.1	40.0
13	67.2	67.5	13'	27.1	27.1	27.0
14	146.5	144.5	14'	130.0	130.0	129.9
15	127.5	131.4	15'	132.0	132.1	132.1
16	168.5	171.2	16'	66.2	66.8	66.8
17	13.0	13.4	17'	21.9	21.9	21.9
18	16.8	16.9	18'	16.0	16.0	16.1
19	16.1	16.1	19'	16.2	16.2	16.1
20	23.5	23.5	20'	23.0	23.0	28.3
Glc-1	99.7	99.8	Glc-1	98.3	98.3	
(a) 2	75.3	75.3	(b) 2	84.6	84.7	
3	78.7	78.8	3	77.7	77.7	
4	71.8	71.9	4	71.4	71.4	
5	78.2	78.1	5	78.0	77.9	
6	62.9	62.9	6	62.6	62.6	
			Glc-1	107.0	106.9	
			(c) 2	76.4	76.6	
			3	77.8	77.8	
			4	70.3	71.4	
			5	78.6	78.5	
			6	62.6	62.9	
			Rha-1	99.0	102.7	102.7
			(d) 2	75.3	72.6	72.6
			3	78.0	79.2	79.3
			4	74.0	73.8	73.8
			5	70.2	70.5	70.5
			6	18.5	18.4	18.4
			Glc-1	102.8	102.7	102.7
			(e) 2	74.9	75.0	75.0
			3	77.2	77.2	76.6
			4	71.5	72.5	72.5
			5	75.3	75.4	75.4
			6	67.1	67.2	67.2
			Rha-1	101.5	101.9	101.9
			(f) 2	72.3	72.1	72.1
			3	72.6	72.9	72.6
			4	74.3	73.9	73.9
			5	69.7	69.7	69.7
			6	18.6	18.6	18.6

to be analogous to **2**. Compound **3** was then hydrolyzed with naringinase to afford compound **4**, an amorphous powder, $[\alpha]_D$ -37.3°. In the same way as **2**, PRFT ^{13}C-NMR and NOE difference spectroscopy revealed **4** to be 16-hydroxygeranyl -linalool 16-O-α-L-rhamnopyranosyl-(1-6)-β-D-glucopyranosyl-(1-3)-α-L-rhamnopyranoside. A comparative study[3] of the ^{13}C-NMR spectra of **3** and **4** showed that the additional β-sophorosyl residue attached to the C_3-OH in **4** to form **3**. Thus, the structure of **1** was represented as a combined form of **2** and **3**. Comparison of the ^{13}C-NMR spectra of **1** and **3** showed that the chemical shifts at the C-1, C-2 and C-3 of the inner rhamnosyl moiety (**d**) in **1** were respectively shifted by -3.7, +2.7 and -1.2 ppm, indicating the carboxyl group linked to the C_2-OH of the rhamnopyranosyl residue.

Consequently, the structure of capsianside A (**1**) was established as shown in the formula. The peracetate of **1** showed peaks at m/z 273 (rha·3Ac), 331 (glc·4Ac), 561 [(rha+glc)·6Ac], 619 [(glc+glc)·7Ac] and 749 [(rha+glc+rha)·7Ac] in the EI-MS, which supported the above sugar linkage.

The novel compound such as capsianside A (**1**) has been first found as the major component in the polar portion of C. annuum var. fasciculatum and it has also become apparent that the related compounds are abundantly distributed in the same genus, e.g., Capsicum annuum L. and C. annuum L. var. angulosum Mill. Studies on their ingredients are now in progress.

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References and Notes

1) Optical rotations were measured in MeOH.
2) Long range couplings were observed between C-3 and 20-H_3, 1-H_2, 2-H; C-4 and 20-H_3; C-6 and 19-H_3; C-8 and 19-H_3; C-10 and 18-H_3; C-12 and 18-H_3; C-13 and 12-H_2; C-14 and 17-H_3; C-15 and 17-H_3; C-16 and 17-H_3, and C-17 and 14-H.
3) R.Kasai, M.Suzuo, J.Asakawa and O.Tanaka, Tetrahedron Lett., **1977**, 175; K.Tori, S.Seo, Y.Yoshimura, H.Arita and Y.Tomita, ibid., **1977**, 179.

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