STRUCTURES OF NEW NON-AROMATIZED *NOR*-CUCURBITACIN GLUCOSIDES IN THE ROOTS OF *CAYAPONIA TAYUYA*

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Six glucosides of novel 29-*nor*-cucurbitacins having non-aromatized A ring were isolated from the roots of *Cayaponia tayuya*. Elucidation of their structures by spectral analyses is described.

KEYWORDS *Cayaponia tayuya*; Cucurbitaceae; cayaponoside; triterpene glucoside; 29-*nor*-cucurbitacin glucoside

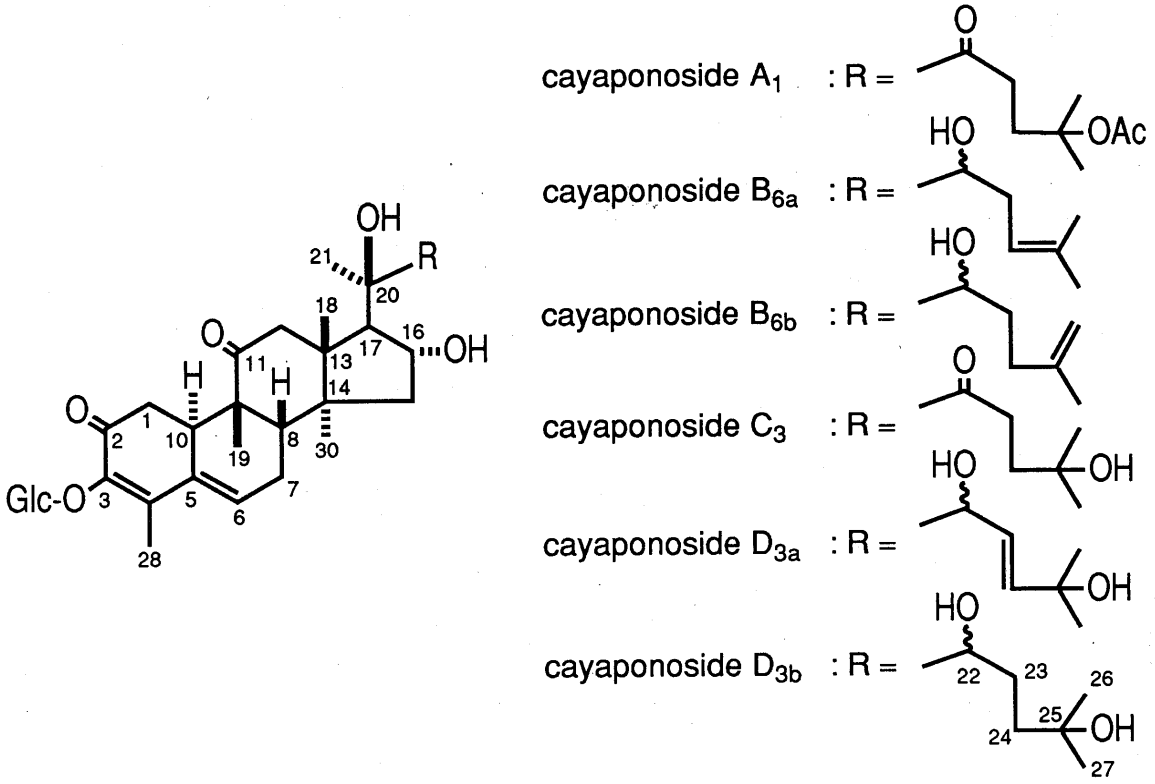
In the first communication[1] on the triterpenoid constituents of the roots of *Cayaponia tayuya*, we reported the isolation and structure determination of four new aromatized *nor*-cucurbitacin glucosides, cayaponosides A, B, C, and D. In the course of examination of the minor constituents, we isolated six new non-aromatized 29-*nor*-cucurbitacin glucosides: cayaponoside A_1 from the fraction A (Fr. A) described in the first communication, B_{6a} and B_{6b} from Fr. B, C_3 from Fr. C, and D_{3a} and D_{3b} from Fr. D. These minor *nor*-cucurbitacins were isolated by preparative high-performance liquid chromatography (HPLC) on reversed-phase material using aqueous acetonitrile and aqueous methanol as the elution solvents. This communication deals with their structures.

Cayaponoside A_1 was obtained as a colorless amorphous powder by repeated preparative HPLC (yield: 658 mg from 1.7 kg of the material) of Fr. A. Cayaponoside A_1 showed in the positive ion FAB-MS an $[M+Na]^+$ ion at *m/z* 729 and a fragment ion at *m/z* 669, 60 mass units less than the $[M+Na]^+$ ion, and the negative ion FAB-MS showed an $[M-H]^-$ ion at *m/z* 705 and a fragment ion at *m/z* 543 which seemed to be originated by splitting of a hexosyl group. The high-resolution FAB-MS gave a molecular composition $C_{37}H_{54}O_{13}$, the same as that of cayaponoside A. Its ^{1}H-NMR and ^{13}C-NMR spectra revealed the presence of seven tertiary methyl groups, a β-D-glucopyranosyl group, an acetyl group linked to a quaternary carbon, one tertiary hydroxyl group, and one secondary hydroxyl group; and ^{13}C-NMR spectrum showed the presence of three carbonyl carbons, three quaternary olefin carbons, and one olefin carbon which has one hydrogen on it. These data, coupled with the degree (10) of unsaturation, clearly showed that A_1 is a glucoside of a new *nor*-cucurbitacin similar to but different from the aglycone of cayaponoside A. The main difference is that the UV spectrum showed an absorption maximum at 300 nm (log ε 4.12) and it has one more carbonyl group than A, though the molecular formula is the same. Over-all features of ^{1}H-NMR and ^{13}C-NMR spectra suggested that A_1 has one carbonyl group in a non-aromatized ring A. Its NMR spectra were examined in detail and all proton and carbon signals were completely assigned using ordinary NMR techniques, COLOC, and selective INEPT techniques. The structure of A_1 was determined as shown in the chart based on the spectral evidence.

Cayaponosides B_{6a} and B_{6b}, both obtained as colorless amorphous powders (yields: B_{6a}, 40 mg and B_{6b}, 75 mg), have the same molecular formula, $C_{35}H_{52}O_{11}$. Both showed similar NMR spectra to that of A_1 except that they have no acetoxyl

TABLE I. ^{1}H- (400 MHz) and ^{13}C- (100 MHz) NMR Spectral Data of the Aglycone Moieties of Cayaponosides (CD_3OD, TMS as an Internal Standard)

	Cayaponoside A_1		Cayaponoside B_{6a}		Cayaponoside B_{6b}		Cayaponoside C_3		Cayaponoside D_{3a}		Cayaponoside D_{3b}	
	δH	δC	δH	δC	δH	δC	δH	δC	δH	δC	δH	δC
1	2.22 (dd, 4, 15) 2.38 (dd, 14, 15)	40.7	2.21 (dd, 5, 15) 2.38 (t, 15)	40.7	2.20 (dd, 5, 14) 2.37 (t, 14)	40.6	2.23 (dd, 5, 14) 2.38 (t, 14)	40.7	2.19 (dd, 5, 14) 2.38 (t, 14)	40.6	2.21 (dd, 5, 15) 2.38 (t, 15)	40.6
2	-	197.1	-	197.1	-	197.1	-	197.1	-	197.1	-	197.1
3	-	147.1	-	147.1	-	147.1	-	147.1	-	147.1	-	147.1
4	-	134.3	-	134.4	-	134.3	-	134.3	-	134.3	-	134.3
5	-	145.8	-	145.8	-	145.9	-	145.8	-	145.8	-	145.8
6	6.48 (m)	132.6	6.49 (m)	132.7	6.48 (m)	132.6	6.48 (m)	132.6	6.48 (m)	132.7	6.49 (m)	132.6
7	2.28 (ddd, 2,6,20) *ca.* 2.6	26.7	2.30 (m) 2.60 (m)	26.8	2.27 (m) 2.60 (m)	26.8	2.29 (br dd, 8, 22) 2.60 (m)	26.7	2.31 (br dd,6,20) 2.61 (m)	26.8	2.31 (br dd, 5, 21) 2.62 (m)	26.8
8	2.10 (d, 8)	44.5	2.12 (d, 8)	44.5	2.12 (d, 8)	44.5	2.10 (d, 8)	44.6	2.11 (d, 8)	44.5	2.12 (d, 9)	44.5
9	-	50.8	-	50.4	-	50.4	-	50.6	-	50.4	-	50.4
10	3.02 (br d, 14)	37.8	3.02 (br d, 14)	37.8	3.02 (br d, 14)	37.7	3.02 (br d, 14)	37.8	3.00 (br d, 14)	37.8	3.10 (br d, 14)	37.8
11	-	215.8	-	216.2	-	216.2	-	215.8	-	216.3	-	216.2
12	2.57 (d, 15) 3.27 (d, 15)	50.6	2.56 (d, 14) 3.18 (d, 14)	51.2	2.56 (d, 14) 3.19 (d, 14)	51.2	2.58 (d, 15) 3.27 (d, 15)	50.8	2.53 (d, 14) 3.15 (d, 14)	51.0	2.56 (d, 14) 3.19 (d, 14)	51.2
13	-	52.4	-	53.0	-	53.0	-	52.4	-	53.1	-	53.0
14	-	50.3	-	50.4	-	50.4	-	50.4	-	50.1	-	49.9
15	*ca.* 1.43 1.87 (dd, 9, 13)	47.6	1.55 (d, 13) 1.93 (dd, 9, 13)	46.7	1.54 (d, 13) 1.92 (dd, 9, 13)	46.8	1.43 (d, 13) 1.88 (dd, 9, 13)	47.7	1.54 (d, 14) 1.93 (dd, 10, 14)	46.6	1.54 (d, 13) 1.92 (dd, 9, 13)	46.7
16	4.44 (dd, 7, 9)	72.1	4.60 (dd, 7, 9)	72.9	4.60 (dd, 7, 9)	72.8	4.44 (dd, 7, 9)	72.2	4.64 (dd, 7, 10)	73.0	4.60 (dd, 7, 9)	72.9
17	2.53 (d, 7)	60.4	2.38 (d, 7)	57.4	2.36 (d, 7)	57.5	2.55 (d, 7)	60.2	2.37 (d, 7)	57.4	2.39 (d, 7)	57.5
18	0.92 (s)	21.4	0.97 (s)	21.2	0.97 (s)	21.2	0.93 (s)	21.4	0.96 (s)	21.1	0.97 (s)	21.3
19	1.11 (s)	20.6	1.11 (s)	20.6	1.11 (s)	20.6	1.11 (s)	20.7	1.11 (s)	20.5	1.11 (s)	20.6
20	-	81.6	-	77.7	-	77.7	-	81.6	-	77.9	-	77.9
21	1.37 (s)	26.4	1.23 (s)	24.5	1.21 (s)	24.3	1.37 (s)	26.4	1.22 (s)	25.1	1.22 (s)	24.3
22	-	217.3	*ca.* 3.36	82.9	*ca.* 3.38	81.8	-	218.0	3.96 (d, 6)	82.7	*ca.* 3.30	82.9
23	2.69 (ddd,6,10,18) 2.84 (ddd,6,10,18)	33.6	2.13 (m) 2.28 (m)	32.0	*ca.* 1.5 (m) *ca.* 1.75 (m)	31.3	2.72 (ddd,6,10,18) 2.85 (ddd,6,10,18)	33.9	5.77 (dd, 6, 16)	142.4	1.45 (m)	27.8
24	*ca.* 2.0 (2H, m)	36.6	5.25 (t, 7)	124.2	2.05 (m) *ca.* 2.77 (m)	37.1	1.72 (2H, m)	39.0	5.85 (d, 16)	142.4	1.45 (m) 1.80 (m)	43.3
25	-	83.9	-	134.3	-	147.1	-	71.6	-	72.0	-	72.1
26	1.44 (s)	27.0	1.70 (s)	26.8	4.70 (2H, br s)	111.4	1.18 (s)	30.2	1.27 (s)	30.9	1.18 (s)	30.0
27	1.44 (s)	27.1	1.62 (s)	18.9	1.72 (s)	23.4	1.18 (s)	30.0	1.27 (s)	30.7	1.19 (s)	30.3
28	2.14 (s)	14.4	2.15 (s)	14.4	2.15 (s)	14.4	2.15 (s)	14.4	2.14 (s)	14.4	2.15 (s)	14.4
30	1.30 (s)	19.6	1.31 (s)	19.5	1.30 (s)	19.5	1.30 (s)	19.7	1.28 (s)	19.5	1.31 (s)	19.5
Ac	1.94 (s)	23.1 173.2										



group but have one more hydroxyl group instead of one carbonyl group. The NMR spectra suggested that both have similar structures to that of A_1 but differ in their side chain structures. Examination of the NMR spectra revealed that B_{6a} has the 22-hydroxy-24-ene structure and B_{6b} is the isomer which has an end-methylene group.

Cayaponoside C_3, $C_{35}H_{52}O_{12}$, an amorphous powder (yield: 700 mg), showed almost the same NMR spectra as that of A_1, differing only in the chemical shifts of the side chain carbons and protons. It has no acetyl group, and C_3 was concluded to be desacetyl cayaponoside A_1 by comparison of the spectral data.

The structures of cayaponosides D_{3a} ($C_{35}H_{52}O_{12}$, yield: 126 mg) and D_{3b} ($C_{35}H_{54}O_{12}$, yield: 366 mg), both obtained as amorphous powders, were determined in the same way as shown in the chart. Cayaponoside D_{3a} is a non-aromatized *nor*-cucurbitacin glucoside corresponding to cayaponoside D, and D_{3b} is the 23,24-dihydro derivative of D_{3a}.

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