BETAVULGAROSIDES I, II, III, IV, AND V, HYPOGLYCEMIC GLUCURONIDE SAPONINS FROM THE ROOTS AND LEAVES OF *BETA VULGARIS* L. (SUGAR BEET)

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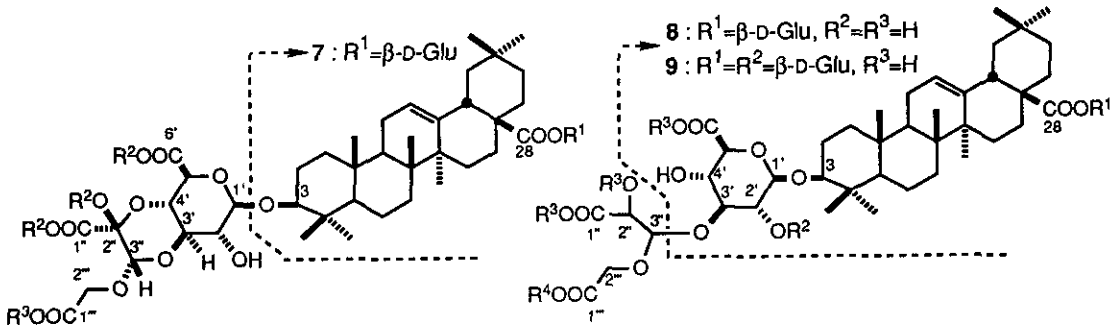
Abstract - Five glucuronide saponins named betavulgarosides I, II, III, IV, and V were isolated from the roots and leaves of *Beta vulgaris* L. (Sugar beet). Their structures were elucidated on the basis of chemical and physicochemical evidence. Betavulgarosides II, III, and IV and the prosapogenol (**6**) were found to exhibit hypoglycemic effect on oral glucose tolerance test in rats.

The roots and leaves of *Beta vulgaris* L. (Sugar beet, Japanese name is Satoudaikon, Chenopodiaceae) are known as a vegetable or garnish foodstuff, particularly, the roots have been used industrially as a raw material of sugar. In Chinese traditional medicine, the roots of this plant have been known to exhibit sedative and emmenagogue-like effects. In regard to the chemical constituents of sugar beet, the presence of saponins, betacyanins, and phenolic compounds has been reported[1] and recently, several oleanolic acid glycosides were characterized from the leaves of this plant.[2]

In the course of our search for biologically active principle in foodstuff,[3] the saponin fraction from the roots and leaves of sugar beet was found to show inhibitory effect on elevation of plasma glucose level on oral glucose tolerance test in rats. As a continuing studies of hypoglycemic saponin constituents,[4] we have engaged in chemical study of the active constituents in the roots and leaves of sugar beet. In this communication, we report the isolation and characterization of saponins named betavulgarosides I (**1**), II (**2**), III (**3**), IV (**4**), and V (**5**).

The water extract[5] from the fresh roots of sugar beet (cultivated in Hokkaido Prefecture) was subjected to reversed phase SiO_2 column (ODS Cosmosil, H_2O-MeOH) and ordinary SiO_2 ($CHCl_3$-MeOH-H_2O) column chromatography and finally hplc (YMC-Pack ODS, MeOH-1%aq. trifluoroacetic acid) separation to furnish betavulgarosides I (**1**, 0.0061% from the fresh roots), II (**2**, 0.0004%), III (**3**, 0.0029%), and IV (**4**, 0.0005%) together with chikusetsusaponin IVa (**8**, 0.0002%).[6] On the other hand, betavulgaroside V (**5**, 0.0011%) was isolated from the leaves of sugar beet by the similar separation methods.[7]

Betavulgaroside I (**1**), colorless fine crystals, mp 215~217°C, $[\alpha]_D$ +49.5° (MeOH), positive mode FAB-ms : m/z 977 $(M+Na)^+$, $C_{47}H_{70}O_{20}Na$, negative mode FAB-ms : 953 $(M-H)^-$, $C_{47}H_{69}O_{20}$, ir (KBr) : 3453, 1740, 1736, 1078 cm^{-1}, liberated oleanolic acid, methyl D-glucoside, and methyl D-glucuronide by methanolysis (9% HCl-MeOH, reflux), while



betavulgaroside I (**1**) : R^1=β-D-Glu, R^2=R^3=H
1a : R^1=β-D-Glu, R^2=H, R^3=CH_3
1b : R^1=β-D-Glu, R^2=R^3=CH_3
betavulgaroside II (**2**) : R^1=R^2=R^3=H
betavulgaroside III (**3**) : R^1=β-D-Glu, R^2=R^3=R^4=H
3a : R^1=β-D-Glu, R^2=R^3=H, R^4=CH_3
betavulgaroside IV (**4**) : R^1=R^2=R^3=R^4=H
betavulgaroside V (**5**) : R^1=R^2=β-D-Glu, R^3=R^4=H
5a : R^1=R^2=β-D-Glu, R^3=H, R^4=CH_3
5b : R^1=R^2=β-D-Glu, R^3= R^4=CH_3
6 : R^1=H, R^2=β-D-Glu, R^3=R^4=H

compound O (**7**)[8] was obtained upon the partial acid hydrolysis of **1** (2% aq. H_2SO_4, reflux). The alkaline hydrolysis of **1** (5% aq. NaOH, reflux) furnished betavulgaroside II (**2**), colorless fine crystals, mp 173~174°C, $[\alpha]_D$ +70.1° (MeOH), negative mode FAB-ms : m/z 791 $(M-H)^-$, $C_{41}H_{59}O_{15}$, ir (KBr) : 3432, 1741, 1731, 1080 cm^{-1}. The ^1H nmr (pyridine-d_5) and ^{13}C nmr (Table I) of **1** and **2**,[9] which were assigned by COSY (^1H-^1H, ^1H-^{13}C), HOHAHA, and ROESY experiment, showed the presence of a bis-acetal glucuronide moiety composed of 3-oxopyruvic acid and glycolic acid [**1** : δ 5.00 (d, J=7.3, 1'-H), 4.75 (m, 3'-H), 5.38 (dd-like, 4'-H), 5.99 (s, 3"-H), 4.80 (m, 2"'-H_2)]. The bis-acetal structure at the C-3' and 4' positions of 3-*O*-glucuronide moiety in **1** was confirmed by the HMBC experiment. Namely, long range correlations were observed between the following carbons and protons of **1** (1'-H & 3-C; 3'-H & 3"-C; 3"-H & 3'-C, 2"'-C; 4'-H & 2"-C; 2"'-H_2 & 3"-C, 1"'-C).

By the treatment with MeOH under reflux, **1** was readily converted into the 1"'-methyl ester (**1a**)[10] which was reverted to **1** upon weak alkaline hydrolysis [2% aq. K_2CO_3-CH_3CN (1:1), room temperature]. Observation of the long range correlation between the 1"'-OCH_3 and 1"'-C in the HMBC data of **1a** led us to confirm the 1"'-methylated structure for **1a**. Finally, the methylation of **1** with excess diazomethane in MeOH gave the 6', 1", 2", 1"'-tetra-*O*-methyl derivative (**1b**) which was found to be identical with achyranthoside A methyl ester.[11] Based on the above mentioned evidence, the structures of betavulgarosides I (**1**) and II (**2**) were determined.

Betavulgaroside III (**3**), colorless fine crystals, mp 212~214°C, $[\alpha]_D$ +10.8° (MeOH), positive mode FAB-ms : m/z 979 $(M+Na)^+$, $C_{47}H_{72}O_{20}Na$, negative mode FAB-ms: m/z 955 $(M-H)^-$, $C_{47}H_{71}O_{20}$, ir (KBr): 3429, 1742, 1736, 1076 cm^{-1}, furnished **7** upon the partial acid hydrolysis. On the other hand, the alkaline hydrolysis of **3** yielded betavulgaroside IV (**4**), colorless fine crystals, mp 186~187°C, $[\alpha]_D$ +43.1° (MeOH), negative mode FAB-ms : m/z 793 $(M-H)^-$, $C_{41}H_{61}O_{15}$, ir (KBr) : 3034, 1740, 1736, 1076 cm^{-1}. The ^1H nmr[12] and ^{13}C nmr (Table I) spectra of **3** and **4** showed the presence of an acetal substituent composed of tartronaldehydic acid and glycolic acid at the 3'-hydroxyl group of 3-*O*-glucuronide moiety in

Table I. ^{13}C Nmr Data for Betavulgarosides I (1), II (2), III (3), IV (4), and V (5) and the Related Compounds (1a, 3a, 5a, 5b, 6)*

	1	1a	2	3	3a	4	5	5a	5b	6
C-1	38.4	38.5	38.5	38.6	38.6	38.6	38.6	38.6	38.6	38.5
C-2	26.4	26.5	26.5	26.6	26.6	26.6	26.4	26.5	26.5	26.5
C-3	89.2	89.4	89.3	89.2	89.2	89.2	89.5	89.5	89.6	89.3
C-4	39.3	39.5	39.5	39.5	39.5	39.5	39.5	39.5	39.5	39.5
C-5	55.5	55.6	55.7	55.7	55.7	55.7	55.8	55.8	55.6	55.7
C-6	18.3	18.5	18.4	18.5	18.5	18.4	18.5	18.5	18.5	18.4
C-7	33.0	33.0	33.3	33.1	33.1	33.1	33.1	33.1	33.2	33.3
C-8	39.7	39.9	39.7	39.9	39.9	39.7	39.9	39.9	39.9	39.7
C-9	47.8	47.9	47.9	48.0	48.0	48.0	48.0	48.0	48.0	47.9
C-10	36.7	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9
C-11	23.2	23.4	23.8	23.4	23.4	23.4	23.4	23.4	23.2	23.8
C-12	122.7	122.9	122.5	122.8	122.8	122.5	122.8	122.8	122.9	122.5
C-13	144.0	144.1	144.8	144.1	144.1	144.8	144.1	144.1	144.2	144.8
C-14	42.0	42.1	42.1	42.1	42.1	42.2	42.1	42.1	42.2	42.1
C-15	28.1	28.2	28.3	28.2	28.2	28.3	28.2	28.2	28.3	28.3
C-16	23.6	23.7	23.8	23.7	23.7	23.8	23.6	23.7	23.7	23.8
C-17	46.8	47.0	46.6	47.0	47.0	46.7	47.0	47.0	47.0	46.6
C-18	41.6	41.8	42.0	41.7	41.7	42.0	41.7	41.7	41.8	42.0
C-19	46.0	46.0	46.4	46.2	46.2	46.4	46.2	46.1	46.0	46.4
C-20	30.6	30.8	31.0	30.7	30.8	31.0	30.7	30.8	30.8	31.0
C-21	33.8	34.0	34.2	34.0	34.0	34.2	34.0	34.0	34.0	34.2
C-22	32.4	32.5	33.2	32.5	32.5	32.1	32.5	32.5	32.6	33.2
C-23	27.9	28.0	28.1	28.1	28.1	28.2	28.0	28.0	28.0	28.1
C-24	16.7	16.9	16.9	16.9	16.9	16.9	16.7	16.7	16.8	16.9
C-25	15.3	15.5	15.4	15.5	15.5	15.4	15.5	15.5	15.5	15.4
C-26	17.3	17.4	17.3	17.4	17.4	17.4	17.4	17.4	17.6	17.3
C-27	26.0	26.1	26.2	26.1	26.1	26.2	26.1	26.1	26.1	26.2
C-28	176.3	176.4	180.1	176.4	176.4	180.2	176.4	176.4	176.4	180.1
C-29	33.0	33.0	33.3	32.1	33.1	33.1	33.1	33.1	33.2	33.3
C-30	23.5	23.6	23.8	23.6	23.6	23.8	23.4	23.6	23.4	23.8
3-O-Gluc. A										
C-1'	107.4	107.6	107.6	106.7	106.8	106.8	105.1	105.2	104.8	105.3
C-2'	71.9	72.0	72.1	74.8	74.7	74.8	78.3	78.2	79.1	78.3
C-3'	72.4	72.5	72.5	85.4	85.1	85.5	83.9	82.9	84.0	83.9
C-4'	70.0	70.1	70.1	72.3	72.3	72.4	72.9	73.2	71.1	72.9
C-5'	75.1	75.3	75.3	77.5	77.5	77.6	77.2	77.2	76.5	77.3
C-6'	171.4	171.4	171.6	172.4	172.4	172.4	172.2	172.3	170.3	172.2
6'-OMe									51.9	
C-1"	171.0	171.1	171.2	174.8	174.6	174.6	174.5	177.4	170.3	174.5
1"-OMe									52.1	
C-2"	93.8	93.8	94.0	74.2	74.2	74.2	73.0	72.6	82.8	72.8
2"-OMe									58.9	
C-3"	97.9	98.2	98.1	105.4	104.9	105.4	105.2	104.6	102.3	105.2
C-1"'	172.2	170.0	172.3	173.9	171.3	173.9	173.7	171.0	170.3	173.7
1"'-OMe		51.5			51.3			51.2	51.4	
C-2"'	64.7	64.5	64.9	65.1	64.2	64.3	65.7	64.8	64.1	65.7
28-O-Glu.										
C-1""	95.7	95.7		95.7	95.7		95.7	95.7	95.8	
C-2""	74.0	74.1		74.1	74.1		74.1	74.1	74.2	
C-3""	78.7	78.9		78.8	78.9		78.8	78.9	79.0	
C-4""	70.9	71.1		71.1	71.1		71.1	71.1	71.1	
C-5""	79.1	79.3		79.3	79.3		79.2	79.3	79.4	
C-6""	62.0	62.2		62.2	62.2		62.2	62.2	62.2	
2'-O-Glu.										
C-1""							103.6	103.6	103.6	103.7
C-2""							76.3	76.4	76.1	76.4
C-3""							78.1	78.2	78.3	78.2
C-4""							72.4	72.3	72.4	72.5
C-5""							77.8	78.0	78.4	77.8
C-6""							63.2	63.1	63.1	63.3

*(68MHz, pyridine-d_5, δc)

3 (HMBC correlations : 1'-H & 3-C; 3"-H & 3'-C, 2"'-C; 2"-H & 1"-C, 3"-C; 2"'-H_2 & 3"-C, 1"'-C). Based on this evidence and comparison of the ^{13}C nmr data for 3 with those for 8, the structure of 3 was characterized.

The MeOH treatment of 3 provided the 1"'-methyl ester (3a)[13] which was reverted to 3 upon the weak alkaline hydrolysis. The 1"'-methyl ester structure (3a) was corroborated by observation of the HMBC correlation between the 1"'-OCH_3 and 1"'-C of 3a. Detailed comparison of ^1H nmr and ^{13}C nmr (Table I) for 3 with those for 3a and 4 led us to formulate the structure of betavulgarosides III (3) and IV (4).[14]

Betavulgaroside V (5), colorless fine crystals, mp 205~206°C, $[\alpha]_D$ +12.5° (MeOH), positive mode FAB-ms : m/z 1141 $(M+Na)^+$, $C_{53}H_{82}O_{25}Na$, negative mode FAB-ms : m/z 1117 $(M-H)^-$, $C_{53}H_{81}O_{25}$, ir (KBr) : 3432, 1740, 1736, 1076 cm^{-1}, liberated 7 upon the partial acid hydrolysis. The ^1H nmr and ^{13}C nmr (Table I) data of 5 indicated the presence of 3-*O*-glucuronide moiety [δ 4.97 (d, J=8.9, 1'-H)] having 2'-*O*-β-D-glucopyranosyl [δ 5.69 (d, J=7.3, 1""-H)] and 3'-*O*-acetal substituent [δ 4.40 (m, 3'-H), 4.63 (m, 4'-H)], which was composed of tartronaldehydic acid [δ 5.38 (br s, 2"-H), 6.32 (br s, 3"-H)] and glycolic acid [δ 4.92, 5.17 (ABq, J=16.1, 2"'-H_2)]. The HMBC correlations were observed between the following protons and carbons (1'-H & 3-C; 1""-H & 2'-C; 3"-H & 3'-C, 2"-C, 2"'-C; 2"-H & 1"-C, 2"'-H & 1"'-C). Based on this evidence and comparison of the ^{13}C nmr data for 5 with those for chikusetsusaponin V (9),[6] the structure of 5 was deduced.

The MeOH treatment of 5 furnished the 1"'-methyl ester (5a)[15] which was reverted to 5 upon the weak alkaline hydrolysis. The 1"'-methyl ester structure (5a) was corroborated by the HMBC experiment. On the other hand, the diazomethane methylation of 5 yielded the tetramethyl derivative (5b)[16] and by the alkaline hydrolysis of 5, the prosapogenol (6)[17] was obtained. Based on those findings and comparison of the ^1H nmr and ^{13}C nmr data for 5 with those for 5a, 5b, and 6, the structure of betavulgaroside V (5) was characterized.[13]

Table II. Inhibitory Effects of Betavulgarosides I (1), II (2), III (3), IV (4), and V (5) and the Prosapogenol (6) on the Elevation of Plasma Glucose Level by Oral Glucose Tolerance Test

	Dose (mg /kg, *p.o.*)	n	Plasma glucose concentration (mg / dl) 0.5 h	1 h	2 h
Control (normal)		10	72.4±3.3**	95.8±5.0**	90.6±4.8*
Control (glucose tolerance)		9	148.6±4.7 (76.2±4.7)	138.3±4.6 (42.5±4.6)	107.9±4.1 (17.3±4.1)
1	100	5	153.5±5.9 (81.1±5.9)	144.7±4.7 (48.9±4.7)	114.0±5.3 (23.4±5.3)
2	100	5	108.5±9.1** (36.1±9.1**)	137.7±5.4 (41.9±5.4)	121.8±4.9 (31.2±4.9)
3	100	5	139.3±3.3 (66.9±3.3)	135.1±4.9 (39.3±4.9)	103.0±1.9 (12.4±1.9)
4	100	3	111.5±5.7** (39.1±5.7**)	125.8±5.9 (30.0±5.9)	114.0±0.6 (23.4±0.6)
5	100	5	147.0±3.4 (74.6±3.4)	138.5±3.1 (42.7±3.1)	108.3±5.7 (17.7±5.7)
6	100	6	124.1±5.9** (51.7±5.9)**	139.3±4.8 (43.5±4.8)	119.3±3.0 (28.7±3.0)

*p<0.05, ** p<0.01

Each sample was orally administered to rats 30 min before oral administration of D-glucose (0.5 g / kg). Values in parenthesis showed the difference in plasma glucose concentration between normal control and each sample treatment.

Inhibitory effects of betavulgarosides I (**1**), II (**2**), III (**3**), IV (**4**), and V (**5**) and the prosapogenol (**6**) on the elevation of plasma glucose level by oral glucose tolerance test in rats are summarized in Table II. Among the glycosides tested, betavulgarosides II (**2**), III (**3**), and IV (**4**) and the prosapogenol (**6**) showed hypoglycemic activity. It is noteworthy that the 3-*O*-monodesmosides (**2**, **4**, **6**) showed much more potent activity than the 3, 28-*O*-bisdesmoside (**3**).

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10. **1a** : colorless fine crystals, mp 200~202°C, $[\alpha]_D$ +57.3° (MeOH), positive mode FAB-ms : m/z 991 $(M+Na)^+$, $C_{48}H_{72}O_{20}Na$, ir (KBr) : 3474, 1743, 1736, 1076 cm^{-1}, ^{1}H nmr (pyridine-d_5) ; δ 3.28 (dd-like, 3-H), 5.00 (d, J=7.6, 1'-H), 4.72 (m, 3'-H), 5.38 (m, 4'-H), 5.82 (s, 3''-H), 4.63 (s, 2'''-H_2), 6.33 (d, J=7.9, 1''''-H).
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12. The ^{1}H nmr (pyridine-d_5) of **3** and **4**; **3** : δ 3.55 (dd-like, 3-H), 4.98 (d, J=7.6, 1'-H), 4.51 (m, 3'-H), 4.65 (m, 4'-H), 5.34 (br s, 2"-H), 6.31 (br s, 3"-H), 5.06, 5.35 (ABq, J=16.5, 2"'-H_2); **4** : δ 3.37 (dd-like, 3-H), 5.00 (d, J=5.9, 1'-H), 4.52 (m, 3'-H), 4.68 (m, 4'-H), 5.34 (br s, 2"-H), 6.34 (br s, 3"-H), 5.07, 5.38 (ABq, J=16.7, 2"'-H_2).
13. **3a** : colorless fine crystals, mp 191~192°C, $[\alpha]_D$ +13.5° (MeOH), negative mode FAB-ms : m/z 969 $(M-H)^-$, $C_{48}H_{73}O_{20}$, ir (KBr) : 3410, 1740, 1736, 1076 cm^{-1}, ^{1}H nmr (pyridine-d_5) : δ 3.34 (dd-like, 3-H), 4.97 (d, J=7.6, 1'-H), 4.46 (m, 3'-H), 4.60 (m, 4'-H), 5.40 (br s, 2"-H), 6.25 (br s, 3"-H), 4.92, 5.33 (ABq, J=16.5, 2"'-H_2), 6.33 (d, J=7.6, 1""-H).
14. Determination of the configurations of C-2" and 3" positions in **3**, **4**, **5**, and **6** are now in progress.
15. **5a** : colorless fine crystals, mp 211~213°C, $[\alpha]_D$ +26.6° (MeOH), positive mode FAB-ms : m/z 1155 $(M+Na)^+$, $C_{54}H_{84}O_{25}Na$, ir (KBr) : 3473, 1742, 1736, 1076 cm^{-1}, ^{1}H nmr (pyridine-d_5) : δ 3.26 (dd-like, 3-H), 4.99 (d, J=6.9, 1'-H), 4.43 (m, 3'-H), 4.60 (m, 4'-H), 5.41 (br s, 2"-H), 6.36 (br s, 3"-H), 4.77, 5.69 (ABq, J=16.5, 2"'-H_2), 6.33 (d, J=7.9, 1""-H), 5.69 (d, J=7.3, 1"""-H).
16. **5b** : colorless fine crystals, mp 155~157°C, $[\alpha]_D$ +38.2° (MeOH), positive mode FAB-ms : m/z 1197 $(M+Na)^+$, $C_{57}H_{90}O_{25}Na$, ir (KBr) : 3432, 1747, 1736, 1076 cm^{-1}, ^{1}H nmr (pyridine-d_5) : δ 3.21 (dd-like, 3-H), 5.00 (d-like, 1'-H), 4.42 (m, 3'-H), 4.38 (m, 4'-H), 4.80 (br s, 2"-H), 6.10 (br s, 3"-H), 4.76, 5.08 (ABq, J=16.3, 2"'-H_2), 6.35 (d, J=7.6, 1""-H), 5.42 (d, J=7.2, 1"""-H).
17. **6** : colorless fine crystals, mp 174~176°C, $[\alpha]_D$ +30.0° (MeOH), negative mode FAB-ms : m/z 955 $(M-H)^-$, $C_{47}H_{71}O_{20}$, ir (KBr) : 3432, 1748, 1736, 1078 cm^{-1}, ^{1}H nmr (pyridine-d_5) : δ 3.38 (dd-like, 3-H), 4.99 (d, J=7.0, 1'-H), 4.48 (m, 3'-H), 4.52 (m, 4'-H), 5.41 (br s, 2"-H), 6.35 (br s, 3"-H), 4.94, 5.21 (ABq, J=16.2, 2"'-H_2), 5.72 (d, J=7.6, 1"""-H).

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