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The Structures of Platycodin A and C, Monoacetylated Saponins of the Roots of *Platycodon grandiflorum* A. DC.[1)]

Two monoacetylated saponins named platycodin A (2) and C (3) were isolated from the roots of *Platycodon grandiflorum* A. DC. (Campanulaceae) and the chemical structures of both saponins were established by Mass and ^{13}C NMR spectrometries.

Keywords——platycodin A; platycodin C; oleanane type oligoglycoside; *Platycodon grandiflorum*; Campanulaceae; mass spectrometry; ^{13}C NMR chemical shift; acetylation shift; acyl migration

As we reported in the previous paper,[1)] the structure of platycodin D(**1**), a main saponin of the roots of *Platycodon grandiflorum* A. DC. (Campanulaceae, Japanese name: Kikyo), has been established. The present communication deals with the structural determination of two new saponins named platycodin A (**2**) and C (**3**) of *Platycodon grandiflorum*.

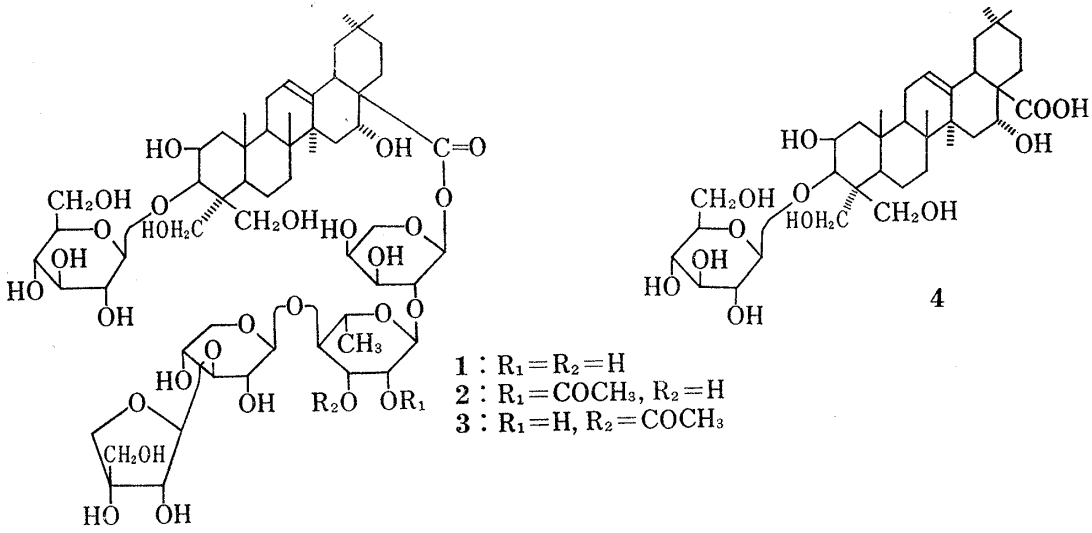

Chart 1

The methanolic solution of the crude glycoside fraction was passed through a column of Sephadex LH-20 and concentrated to dryness. The residue was repeatedly subjected to column chromatography on silica gel and on cellulose powder using $CHCl_3$–MeOH–H_2O or BuOH–AcOEt–H_2O solvent system. Finally, **2**, $C_{59}H_{94}O_{29}\cdot H_2O$, mp 217—220.5° (dec.), $[\alpha]_D^{28}$ −26.6° (c=1.7 MeOH) and **3**, $C_{59}H_{94}O_{29}$, mp 225—227° (dec.), $[\alpha]_D^{28}$ −28.3° (c=1.14 MeOH) were obtained as a white powder from ethanol–ethyl acetate.

The ^1H NMR signals of **2** (δ 2.03 3H) and **3** (δ 2.05 3H) as well as the ^{13}C NMR signals of **2** (δ 20.8, 170.3) and **3** (δ 21.4, 170.7) in C_5D_5N revealed the presence of one acetoxyl group in each saponin.

On hydrolysis with methanolic potassium carbonate at room temperature for 30 min, **2** and **3** afforded the same desacetyl derivative, which was identified as **1** by comparing their general properties and ^{13}C NMR spectra. Further, acetylation of **2** and **3** gave the same acetate, which was identified as per-O-acetate of **1** reported in the previous paper by direct comparisons. These observations indicated that **2** and **3** must be the isomers of monoacetate of **1**.

1) A. Tada, Y. Kaneiwa, J. Shoji, and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **23**, 2965 (1975).

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In ^{13}C NMR spectrum of **1**, the signals due to the anomeric carbons were assigned by comparing with that of prosapogenin(**4**), application of partially relaxed Fourier transform (PRFT) procedure,[2] and observations on glycosylation shift[3] as follows: δ 111.1 (ppm) (β-D-apiofuranoside), 106.6 (β-D-xylopyranoside), 106.0 (β-D-glucopyranoside), 101.1 (α-L-rhamnopyranoside), 93.5(L-arabinopyranoside) (see Table I).

TABLE I. ^{13}C Chemical Shifts of Anomeric Carbons (in Pyridine-d_5, 25°)

	glu	ara	xyl	rham	api
1	106.0	93.5	106.6	101.1	111.1
2	106.0	93.3	106.3	97.9	111.1
3	106.1	93.3	105.8	101.2	111.1
4	105.9				

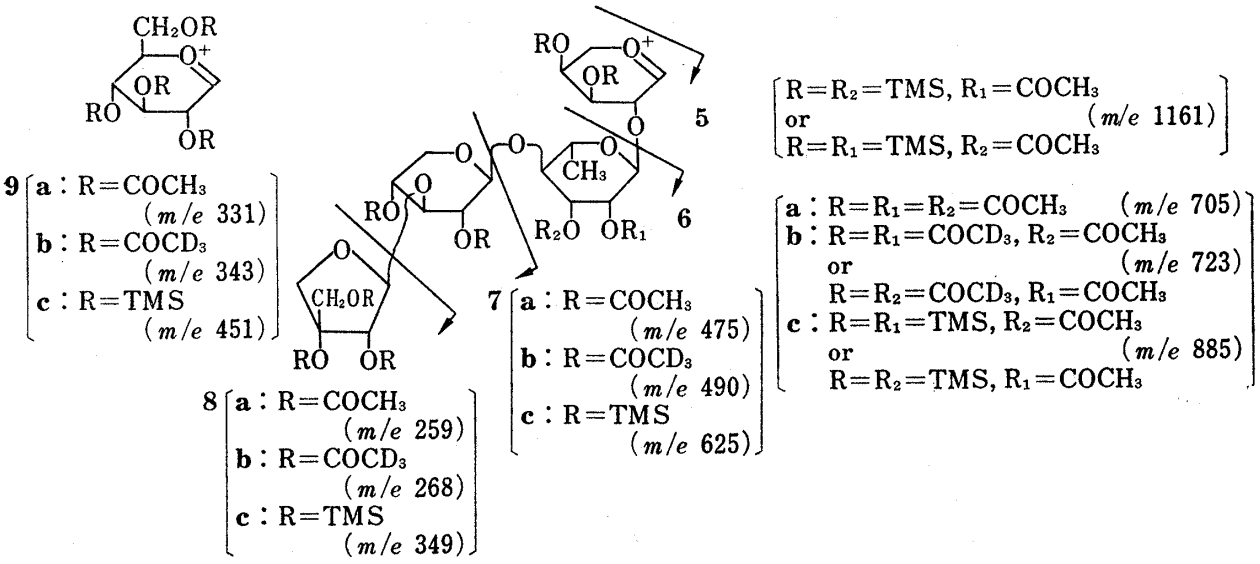

Chart 2

The anomeric configuration of arabinopyranosyl moiety of **1** has been left unidentified. $^1J_{C_1-H_1}$ (166 Hz) of the esteric anomeric carbon signal of L-arabinopyranoside appearing at the most high field indicates the anomeric configuration is equatorial.[4] In other words, the configuration of L-arabinopyranoside is α. Appearance of the anomeric carbon signal of this L-arabinopyranosyl ester at relatively high field(δ 93.5) can be reasonably explained in terms of substitution effect by another glycosyl linkage at its C-2 position. The similar high field displacement was also observed in the spectra of the synthetic glucosyl ester of *ent*-kaur-16-en-19-oic acid; on going from its β-glucosyl ester to its β-sophorosyl ester, the esteric anomeric carbon signal was displaced from δ 95.5 to δ 93.7 ($^1J_{C_1-H_1}$=164 Hz).[5]

The mass fragment peak(*m/e* 1161) due to the oligosaccharide portion of trimethylsilyl derivatives of **2** and **3** corresponds to (apiofuranosyl-xylopyranosyl-rhamnopyranosyl-arabino-

2) A. Allerhand and D. Doddrell, *J. Am. Chem. Soc.*, **93**, 2777 (1971).
3) T.E. Walker, R.E. Lomdon, T.W. Whaley, R. Barker, and N.A. Matwiyoff, *J. Am. Chem. Soc.*, **98**, 5807 (1976); T. Usui, N. Yamaoka, K. Matsuda, K. Tsuzimura, H. Sugiyama, and S. Seto, *J. Chem. Soc. Perkin I*, **1973**, 2425; R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175; K. Tori, Y. Yoshimura, S. Seo, K. Sakurawi, Y. Tomita, and H. Ishii, *Tetrahedron Lett.*, **1976**, 4163; K. Tori, S. Seo, Y. Yoshimura, M. Nakamura, Y. Tomita, and H. Ishii, *ibid.*, **1976**, 4167; K. Tori, S. Seo, Y. Yoshimura, H. Arita, and Y. Tomita, *ibid.*, **1977**, 179; R. Kasai, J. Asakawa, M. Okihara, K. Mizutani, and O. Tanaka, to be published.
4) K. Bock, I. Lundt, and C. Pedersen, *Tetrahedron Lett.*, **1973**, 1037.
5) I. Sakamoto, K. Yamasaki, and O. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **25**, 3437 (1977).

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pyranose)-(Ac)-$(TMSi)_8$(**5**) indicating that the acetoxyl group must be located not on the aglycone moiety but on any monosaccharide. Further, the mass spectrum of per-O-acetate of **1** shows the fragment peaks at *m/e* 705(**6a**), 475(**7a**), 259(**8a**), and 331(**9a**), which are corresponding to the fragment ions ascribed to splitting of each sugar, while the mass spectra of deuteroacetates of **2** and **3** show the fragment peaks arising from the oligosaccharide portion at *m/e* 723(**6b**), 490(**7b**), and 268(**8b**), respectively. Based on the increase of mass number corresponding to **6a**, **7a**, **8a**, and **9a**, the acetoxyl group of **2** and **3** must be located on the rhamnosyl moiety of each glycoside. Since the xylosyl moiety links to the C-4 hydroxyl group of the rhamnose, the location of the acetoxyl group is restricted to the hydroxyl group of C-2 or C-3 of the rhamnosyl moiety.

Recently, the method for determination of the position of the acetoxyl group in partially acetylated glycosides by analysis of ^{13}C NMR spectrum has been reported.[6a-c] On acetylation of alcohols, the signal of carbinyl carbon(α-C) bearing a hydroxyl group is, in general, somewhat deshielded, while that of β-carbon resonance is displaced upfield. In ^{13}C NMR spectra, the signals of each anomeric carbon of **1** and **3** are superimposable, but the anomeric carbon signal due to the rhamnose of **2** is observed at δ 97.9 shifting to upfield by 3.2 ppm in comparison with that of **1**. Consequently, the location of the acetoxyl group in **2** can be assigned to C-2 of the rhamnosyl moiety, while that of **3** is concluded to be C-3 of the rhamnose.

In addition, a solution of **2** in C_5D_5N was heated at 80° and the time dependence of the reaction was checked by TLC and ^{13}C NMR spectrum. The formation of **3** from **2** was gradually observed and, after about 70 hr, **2** was transformed into the mixture of nearly equal amount of **2** and **3**. The similar acyl migration was also observed in the case of **3**. It has been reported that the acyl group on C-2 or C-3 of rhamnosides readily undergoes acyl migration.[6b,7] This observation supports the above formulation of **2** and **3**, and it must be noted that the measurement of ^{13}C NMR of partially acylated glycosides in C_5D_5N under heating causes the acyl migration and sometimes leads to a erroneous conclusion.

In comparison of ^{13}C NMR spectra of **1** and **3**, the upfield shift of the carbon signal of C-4 of the rhamnosyl moiety from δ 83.8(**1**) to δ 77.6(**3**) seems to be evidently larger than that expected only by the normal acetylation shift. This fact would be explainable by the change of the β-xylosylation shift due to the acetylation of the C-3 hydroxyl group.

Since both **2** and **3** are unstable and a methanolic solution of **2** or **3**, on long standing, gave a mixture of **1**, **2**, and **3**, further investigation for determining whether all of these saponins are genuine is under progress.

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7) S. Asen and R.M. Horowitz, *Phytochemistry*, **16**, 147 (1977).

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