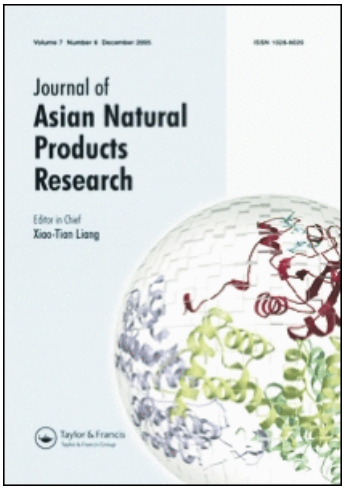

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Note

STUDIES ON DAMMARANE-TYPE SAPONINS IN THE FLOWER-BUDS OF *PANAX GINSENG* C.A. MEYER

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From the dried flower-buds of *Panax ginseng* C.A. Meyer, a new minor dammarane-type triterpene saponin named ginsenoside III together with nine known saponins was isolated. On the basis of spectral and chemical evidence, the structure of the new saponin was elucidated as 3-O-[β-D-glucopyranosyl(1 → 2)-β-D-glucopyranosyl]-20-O-β-D-glucopyranosyl-3β,12β,20(S)-trihydroxy-dammar-25-en-24-one.

Keywords: Ginsenoside III; Flower-buds; *Panax ginseng*; Araliaceae

INTRODUCTION

Panax ginseng C.A. Meyer (Araliaceae) is a famous Chinese herbal medicine, and ginsenosides are generally considered to be its main bioactive constituents. Our study showed that the flower-buds of *Panax ginseng* also contain ginsenosides, and further study resulted in isolation of ten dammarane saponins. The nine known saponins were identified as ginsenoside-Rb_2, Rc, Rd, Re, 20(R)-Rg_2, 20(S)-Rg_2, 2(R)-Rh_1, gypenoide XVII and

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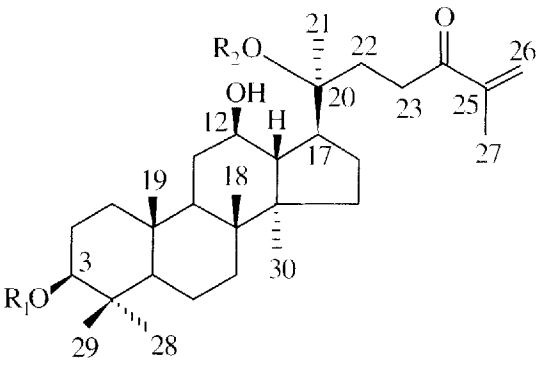

R_1 = -Glc $\overset{2}{-}$ Glc

R_2 = -Glc

FIGURE 1 The structure of ginsenoside III.

notoginsenoside E by comparison with authentic samples or literature data [1–4]. In this paper, we report the structural elucidation of a new dammarane-type triterpene saponin, named ginsenoside III (see Fig. 1).

RESULTS AND DISCUSSION

Ginsenoside III, colorless crystals, m.p. 203–205°C, was positive to both Liebermann–Burchard and Molish reactions. The IR spectrum of ginsenoside III showed absorption bands due to hydroxyl and enone functions at 3400, 1625, and 1070 cm^{-1}. On acid hydrolysis, ginsenoside III gave glucose as the only sugar constituent. Its molecular formula was shown to be $C_{48}H_{80}O_{19}$ from HRFAB and ESI (Electrospray Ionization) mass spectra. The positive ESI mass spectrum exhibited quasimolecular ion peak at *m/z* 983 $[M+Na]^+$ and secondary fragment ion peaks at *m/z* 803 $[M+Na-C_6H_{10}O_5-H_2O]^+$, 641 $[M+Na-2\times C_6H_{10}O_5-H_2O]^+$, 461 $[M+Na-3\times C_6H_{10}O_5-2H_2O]^+$, 365 $[M+Na-3\times C_6H_{10}O_5-2H_2O-C_6H_8O]^+$. The ^{1}H-NMR spectrum of ginsenoside III showed three anomeric protons at δ 4.93 (d, $J=7.6$ Hz), 5.17 (d, $J=7.9$ Hz) and 5.39 (d, $J=7.6$ Hz), which indicated that all the sugars were β-glucopyranosyl units. Comparison of the ^{1}H- and ^{13}C-NMR spectra with those of ginsenoside Rd[4] showed that there

was very good agreement in the sugar moiety and the aglycone except for signals due to the side-chain carbons. This fact suggested that one glucosyl unit was attached to the 20-hydroxyl group and the other sugar chain was a glucosyl^{1}–^{2}glucosyl unit located at C-3 of the aglycone [5]. Furthermore, the sites of all glycosidic linkages were confirmed by the ^{1}H–^{1}H COSY and NOE (NOESY) experiments. In the NOESY spectrum of ginsenoside III, cross-peaks were observed between the anomeric proton of a glucosyl unit (δ 4.93) and H-3 of the aglycone (δ 3.28, dd, $J = 11.7$, 4.4 Hz); and between that of a terminal glucosyl unit (δ 5.39) and the above inner glucose H-2 (δ 4.16), indicating that the sugar chain is a β sophorosyl unit linked to the aglycone via the hydroxyl group at C-3. The remaining glucosyl unit whose anomeric proton and carbon signals appeared at δ_H 5.17 and δ_C 98.1 must therefore be located at C-20.

In the side chain of ginsenoside III, the ^{13}C-NMR spectrum showed the presence of two methylene signals at δ 32.8 and 29.9, one keto-carbonyl signal at δ 202.4, two olefinic carbon signals at δ 144.4 and 124.9, and one methyl signal at δ 17.8 which could be assigned as C-22, C-23, C-24, C-25, C-26 and C-27, respectively, by comparison with those of notoginsenoside-B [6] and further confirmed by the HMBC experiment of ginsenoside III in which long-range correlations were observed between the following protons and carbons: H-26 and C-24, 27; H-27 and C-24, 25, 26.

S-configuration of C-20 was determined on the basis of coincidence of chemical shifts in C-17, C-20, C-21, C-22 with those of ginsenoside Rd [4].

Thus, the structure of ginsenoside III was characterized as 3-O-[β-D-glucopyranosyl(1 → 2)-β-D-glucopyranosyl]-20-O-β-D-glucopyranosyl-3β, 12β,20(S)-trihydroxy-dammar-25-en-24-one.

EXPERIMENTAL SECTION

General experimental procedures Melting points were measured on a X6 micro-melting point apparatus (hot-stage type) and are uncorrected; IR spectra were taken on a Perkin Elmer 983 spectrometer; NMR spectra were recorded on a G8X-400 spectrometer in C_5D_5N using tetramethylsilane (TMS) as an internal standard, including ^{1}H-NMR, ^{13}C-NMR, DEPT, ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY, NOESY and HMBC; ESIMS were obtained on a PCQ mass spectrometer.

Plant material The flower-buds of *Panax ginseng* C.A. Meyer were collected in Huairen of Liaoning Province, China and identified by Prof. Z.R. Jiang of Shenyang Pharmaceutical University, where a voucher specimen is deposited.

Extraction and isolation The powdered flower-buds were extracted (×3) with 70% EtOH under reflux. The extract was concentrated *in vacuo* to yield a residue (350 g) which was subjected to macroporous resin chromatography eluting with H_2O; 25%, 50% and 95% EtOH. The 50% EtOH fraction was further chromatographed on silica gel (200–300 mesh) using $CHCl_3$–MeOH (5 : 1, 3 : 1, 2 : 1, 1 : 1) as an eluent. The fraction containing ginsenoside III was subjected to reversed phase HPLC (ODS, eluting with MeOH–H_2O 7 : 3) to afford ginsenoside III (15 mg).

Ginsenoside III: white powder; m.p. 203–205°C. Molecular formula $C_{48}H_{80}O_{19}$ (negative HRFABMS 959.5193 calcd. 959.5215); IR (KBr) ν_{max} 3400 (OH), 2940 (CH), 1625 (C=O), 1070 and 1040 (C–O) cm^{-1}; Positive ESI-MS *m/z* 983 $[M+Na]^+$, 803 $[M+Na-C_6H_{10}O_5-H_2O]^+$, 641 $[M+Na-2\times C_6H_{10}O_5-H_2O]^+$, 461 $[M+Na-3\times C_6H_{10}O_5-2H_2O]^+$, 365 $[M+Na-3\times C_6H_{10}O_5-2H_2O-C_6H_8O]^+$; ^{1}H-NMR δ: 0.80 (3H, s, 18-H), 0.92 (3H, s, 19-H), 0.96 (3H, s, 30-H), 1.11 (3H, s, 29-H), 1.28 (3H, s, 28-H), 1.57 (3H, s, 21-H), 1.85 (3H, s, 27-H), 2.14, 2.71 (each 1H, both m, 22-H), 3.08, 3.34 (each 1H, both m, 23-H), 3.28 (1H, dd, $J=4.4$, 11.7 Hz, 3-H), 4.15 (1H, m, 12-H), 4.93 (1H, d, $J=7.6$ Hz, C-1′-H of Glc), 5.17 (1H, d, $J=7.9$ Hz, C-1‴-H of Glc), 5.39 (1H, d, $J=7.6$ Hz, C-1″-H of Glc), 5.67, 6.22 (each 1H, both s, 26-H); ^{13}C-NMR data, see Table I.

TABLE I ^{13}C-NMR data of ginsenoside III (δ ppm, C_5D_5N)

Carbon	δ	*Carbon*	δ	*Sugars*			
				3-*O*-*sugar*		20-*O*-*sugar*	
				Carbon	δ	*Carbon*	δ
1	39.2	16	26.8				
2	26.9	17	51.5	Glc-1′	105.1	Glc-1‴	98.1
3	89.0	18	16.3	2′	83.5	2‴	75.1
4	39.7	19	16.0	3′	78.3[a]	3‴	79.4[a]
5	56.4	20	83.1	4′	71.7	4‴	71.7
6	18.4	21	22.0	5′	78.1[a]	5‴	78.0[a]
7	35.1	22	32.8	6′	62.9[b]	6‴	62.7[b]
8	40.3	23	29.9	Glc-1″	106.1		
9	50.2	24	202.4	2″	77.2		
10	36.9	25	144.4	3″	78.3[a]		
11	30.8	26	124.9	4″	71.7		
12	70.2	27	17.8	5″	78.3[a]		
13	49.5	28	28.1	6″	63.0[b]		
14	52.	29	16.6				
15	31.0	30	17.4				

[a,b]These assignments may be interchangeable.

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