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Two new triterpenoid saponins from *Polygala crotalarioides*

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Abstract

Two new oleanane-type saponins, crotalarioside A (**1**) and crotalarioside B (**2**), were isolated from the roots of *Polygala crotalarioides*. Their structures were elucidated on the basis of spectroscopic and chemical evidence.

Keywords: *Polygala crotalarioides*; Chemical constituents; Oleanane-type saponins

Polygala crotalarioides Buch. Ham. (Polygalaceae) is known to be a folk tonic medicine in Yunnan Wa nationality [1]. Its bioactivities attracted us to investigate its chemical constituents. In the previous paper, we reported structural elucidation of five new xanthones [2,3]. Our continuing phytochemical investigation into the constituents of this plant has resulted in the isolation of two new oleanane-type saponins, crotalarioside A and crotalarioside B. Their structures were elucidated on the basis of spectral analysis.

1. Experimental

The dried roots (1 kg) of *P. crotalarioides* were extracted with 75% EtOH four times under reflux. After removal of the solvent *in vacuo*, the aqueous solution was passed through a HPD-100 column and the absorbed materials were eluted with water, 75% aqueous ethanol and ethanol, successively. The 75% ethanol eluate was concentrated *in vacuo* to give a residue (96 g), which was chromatographed on a silica gel (200–300 mesh) column chromatography with $CHCl_3$/MeOH/H_2O (7:4:1) to afford 10 fractions (fraction 1–10). Fractions 1–4 were chromatographed on Si gel with $CHCl_3$/MeOH/H_2O (7:3:0.5) and then resubjected to Sephadex LH-20 with MeOH to give the total saponins (15 g). The total saponins were passaged over RP-18 eluted with MeOH/H_2O (5:5–7:3) to give 4 fractions (fraction A–D). Fraction D was further purified by semi-pre HPLC eluted by CH_3CN/0.1% AcOH–H_2O solution (24:76) to afford compounds **1** (24 mg) and **2** (10 mg).

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2. Results and discussion

Compound **1** was obtained as white powder, and analyzed for $C_{53}H_{82}O_{24}$ by negative-ion HRFABMS (*m/z* 1101.3976 $[M-H]^-$ (calcd. for $C_{53}H_{81}O_{24}$, 1101.3965)). Its IR spectrum exhibited absorption bands for hydroxyl (3424 cm^{-1}), carbonyl (1718 and 1737 cm^{-1}), and olefinic groups (1631 cm^{-1}). The ^1H and ^{13}C NMR spectra showed signals due to 30 aglycone carbon signals, including five singlet methyls [δ_C 33.1 (s), 24.0 (s), 18.4 (s), 17.1 (s), 13.8 (s)], one oxygenated methylene [δ_C 64.4 (t)], one oxygenated methine [δ_C 86.1 (d)], two olefinic carbons [δ_C 139.1 (s), 127.0 (d)], three carboxyl carbons [δ_C 208.0(s), 180.1 (s), 176.8 (s)]. Also observed were signals of four anomeric carbons and their corresponding anomeric protons [δ_C 107.4 (d), 104.0 (d), 101.3 (d), 94.8 (d); δ_H 5.03 (d, 1H, J = 6.8 Hz), 5.13 (d, 1H, J = 7.5 Hz), 6.47 (br s, 1H), 6.06 (d, 1H, J = 8.2 Hz)], indicating a triterpenoid saponin with four sugar moieties. Comparison of the ^1H and ^{13}C NMR data of the aglycone unit with those of polygalasaponinXXIII [4] showed that the structures of the two aglycones were very similar. The only difference was the replacement of a methyl group in polygalasaponinXXIII by an oxygenated methine group in **1**. Both of the two aglycones were oleanane-type triterpenoids with a ketone quaternary carbon at C-2.

Acid hydrolysis of **1** with 1 mol/L HCl furnished four monosaccharides, which may be determined to be D-glucose D-fucose, L-rhamnose and D-xylose, by TLC comparison with authentic samples. This was further confirmed by the ^{13}C and ^1H NMR spectral data of these sugar moieties, which were consistent with those reported [4]. Sugar proton and carbon signals in the spectra were assigned by HMQC, HMBC, and HMQC-TOCSY spectra. In the HMBC spectrum, long-range couplings were observed for H-1′ of the glucosyl unit to C-3 of the aglycone, H-1″ of the fucosyl unit to C-28 of the aglycone, H-1‴ of the rhamnosyl unit to C-2″ of the fucosyl unit, H − 1⁗ of the xylosyl unit to C-4‴ of the rhamnosyl unit. The anomeric configurations of D-glucosyl, D-fucosyl, L-rhamnosyl and D-xylosyl were determined to be β, β, α and β, respectively, from the coupling constants of the anomeric proton signals. On the basis of the above evidence, the structure of **1** was elucidated as 2-oxo-olean-12-ene-27-hydroxy-23, 28-dioic acid 3-*O*-β-D-glucopyranosyl-28-*O*-β-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranoside, and was named crotalarioside A (Fig. 1).

Compound **2** was obtained as white powder, and analyzed for $C_{59}H_{92}O_{29}$ by negative-ion HRFABMS (*m/z* 1263.4251 $[M-H]^-$ (calcd. for $C_{59}H_{91}O_{29}$, 1263.4236)). Its IR spectrum exhibited absorption bands for hydroxyl

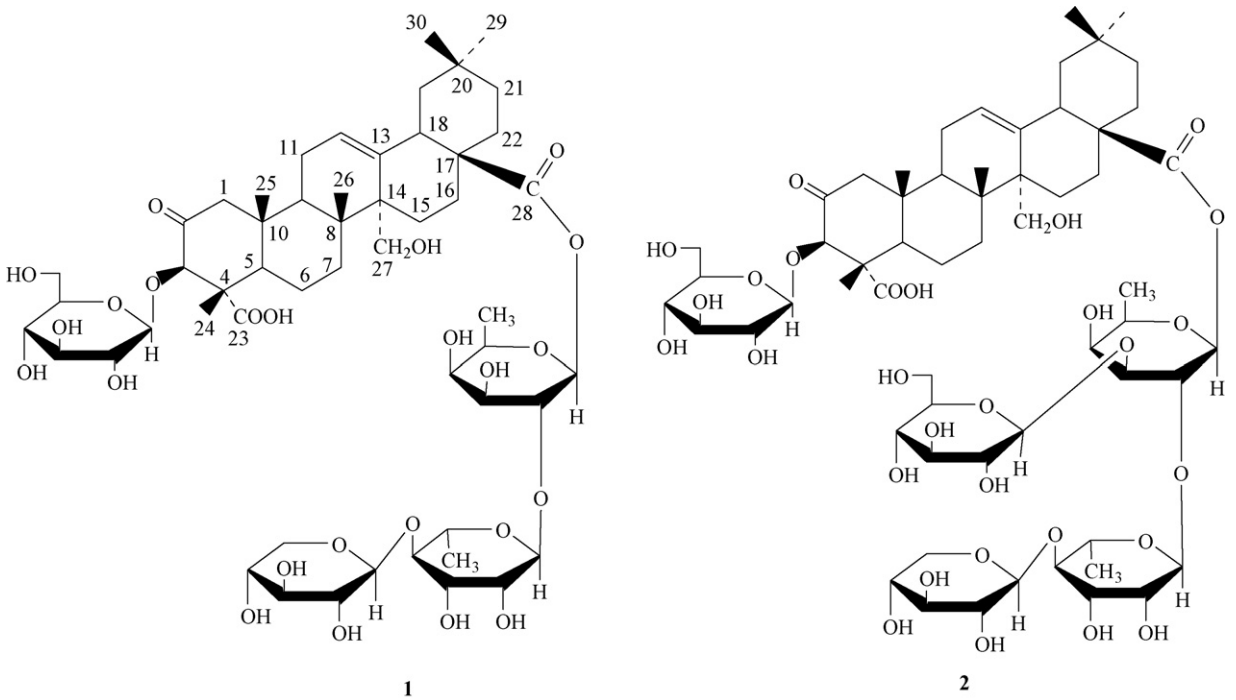

Fig. 1. Structures of compounds **1** and **2**.