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A Triterpenoid Saponin from *Polycarpon prostratum*

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Abstract: A new triterpenoid saponin, named prostratoside A, was isolated from the whole plants of *Polycarpon prostratum.* Its structure was determined to be 3-O-{ β-D-xylopyranosyl- (1→2)- β-D-glucopyranosyl-(1→4)-[β- D-glucopyranosyl-(1→2)]- α-L-arabinopyranosyl}- 22α- acetoxy - saikogenin G by spectroscopic methods.

Keywords: *Polycarpon prostratum*; caryophyllaceae; triterpenoid saponin; prostratoside A.

From *Polycarpon prostratum* (Forssk.) Aschers. *et* Schwein. Ex Aschers which is said to be toxic and has anti-inflammatory and anodynic activities[1], a new triterpenoid saponin, named prostratoside A, was isolated.

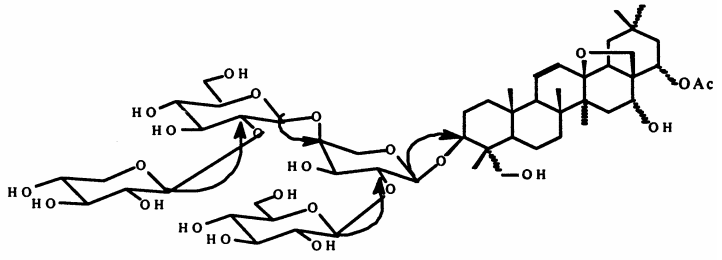
Prostratoside A **1**, mp: 250-252°C, $[\alpha]_D^{24}$ = +4.3 (c 0.88, MeOH), 0.0018% yield. Its HRFAB-MS gave a $[M-1]^-$ ion at m/z 1117.5505, in agreement with the molecular formula $C_{54}H_{86}O_{24}$ (calcd. m/z 1117.5431). The IR spectrum showed absorption bands at 3371, 1717, 1646 and 1046 cm^{-1}. A comparison of **1** with 22α- hydroxy-saikogenin G[2] showed **1** was very similar to 22α- hydroxy-saikogenin G in A-D ring moiety, but its C-22, C-21 and C-17 had changed shifts (+2.8, -3.5, +2.1 ppm respectively), indicating the acetoxy group was placed at C-22. HMBC correlations between C=O and H-22, C-28 and H-22, C-16 and H-22, C-17 and H-22, C-21 and H-22 gave further confirmation. The ^1H NMR signal of H-22 (δ 5.29, dd, J=12.0, 5.5Hz) suggested H-22 may be an axial H (β-position), and the NOE effects observed between H-22 and H-30 (δ 0.98), H-22 and H-28 (δ 3.68, 3.78) gave further confirmation. Therefore, the aglycone was 22α-acetoxy-saikogenin G, and it was a new aglycone.

The sugar moieties was established as arabinose, xylose, glucose by TLC comparison with authentic samples. The negative FAB- MS gave four fragments (m/z 986 $[M\text{-pentose}]^-$, 956 $[M\text{-glc}]^-$, 823 $[M\text{-pentose-glc-H}]^-$, 661 $[M\text{-pentose-glc-glc-H}]^-$), indicated a pentose and a glucose were terminal sugars. By analysis of ^1H-^1H COSY, HMQC-TOCSY, HMBC spectra and comparison with the report[3] for saccharide chain, ^1H and ^{13}C NMR signals (**Table 1**) of sugar moiety could be assigned, and four anomeric proton signals were at δ 5.02 (d, $H\text{-}1_{ara}$), 5.49 (d, $H\text{-}1_{glc1}$), 4.98 (d, $H\text{-}1_{glc2)}$ and 4.92 (d, $H\text{-}1_{xyl}$) respectively. HMBC correlations (**Figure 1**) provided the evidences for determination of sugar sequence. β-Configuration at the anomeric positions may be inferred from the values of the coupling constants for both glucopyranosyl units (8.0 Hz) and xylopyranosyl unit (7.2 Hz). The coupling constant (6.0Hz) may be consistent with an α-L-arabinopyranoside moiety in a conformational equilibrium ($^4C_1$ and $^1C_4$)[4]. Therefore, the structure of prostratoside A **1** is proposed to be 3-O-{β-D-xylopyranosyl-(1→2)- β- D-glucopyranosyl-(1→4)-[β- D-gluco-pyranosyl- (1→2)]- α-L-arabinopyranosyl}- 22α- acetoxy -saikogenin G. It is note-worthy that saikosaponin-like compound was isolated from Caryophyllaceae.

Table 1. ^{13}C NMR Data for Prostratoside A in C_5D_5N (100 MHz)

C	δ	C	δ	C	δ	C	δ	C	δ	C	δ
1	38.7	10	36.4	19	37.6	28	76.8	5	64.4	3	77.7
2	25.9	11	132.6	20	33.3	29	33.4	Glc$_1$C-1	105.1	4	71.2
3	82.4	12	131.5	21	42.2	30	25.2	2	76.3	5	78.4
4	43.9	13	84.9	22	77.1	CO$_{OAc}$	170.7	3	78.5	6	62.5
5	47.9	14	44.2	23	64.8	CH$_{3OAc}$	21.1	4	71.7	XylC-1	107.6
6	17.7	15	35.3	24	13.0	AraC-1	103.9	5	78.4	2	76.1
7	31.7	16	71.0	25	18.9	2	80.4	6	62.9	3	77.9
8	42.2	17	49.6	26	19.7	3	73.5	Glc$_2$C-1	104.2	4	70.9
9	53.1	18	51.1	27	18.2	4	78.2	2	85.3	5	67.6

Figure 1. Structure of Prostratoside A. Arrows Show Selected HMBC Correlations



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References

1 Y. H. Li, *List of Plants in xishuangbanna*, Yunnan Ethnic Press, Kunming, **1996**, 107.

2 Y. H. Gong, "*^{13}C NMR Data of Natural Products*", Yunnan Science and Technology Press, Kunming; **1986**, 135.

3 P. J. Waltho, D. H. Williams, S. B. Mahato, B. C. Pal and J. C. J. Barna, *J. Chem. Soc. Perkin Trans 1*, **1986**, 1531.

4 N. Shoji, A. Umeyama, K. Yoshikawa and S. Arihara, *Chem. Pharm. Bull.*, **1994**, *42*(9), 1750.

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