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Peruvianoside A, a Novel Migrated Lanostane Trisaccharide from *Scilla peruviana*

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A novel migrated lanostane trisaccharide, named peruvianoside A, was isolated from the bulbs of *Scilla peruviana*. The structure was determined by extensive 2D NMR analysis.

In the course of our screening for new bioactive compounds from plants of the family Liliaceae, a novel migrated lanostane trisaccharide, named peruvianoside A (**1**), was isolated from the methanolic bulb extract of *Scilla peruviana* (4.0 kg). This paper reports the structural elucidation of **1**.

Peruvianoside A (**1**), $C_{49}H_{78}O_{20}$, was obtained as an amorphous powder, 492 mg, $[\alpha]_D$ -23.2° (MeOH).[1] Acid hydrolysis of **1** with 1M HCl (dioxane - H_2O, 1 : 1) afforded D-glucose and L-rhamnose.[2] The aglycone was decomposed during the acidic hydrolysis. The IR and ^1H NMR spectral data, and comparison of the ^{13}C NMR signals of the aglycone moiety[3] with those of lanosterol[4] indicated **1** to be a lanost-8-en-3β-ol trisaccharide with the D-ring and side-chain being modified. The ^1H-^1H COSY spectrum revealed the partial structures formed of the D-ring and side-chain, the connections of which were established by the ^1H-^{13}C long-range correlations (Figs. 1 and 2). The NOEs observed in the phase-sensitive NOESY sepctrum were illustrated in Fig. 3, providing confirmative evidence for the stereostructure.

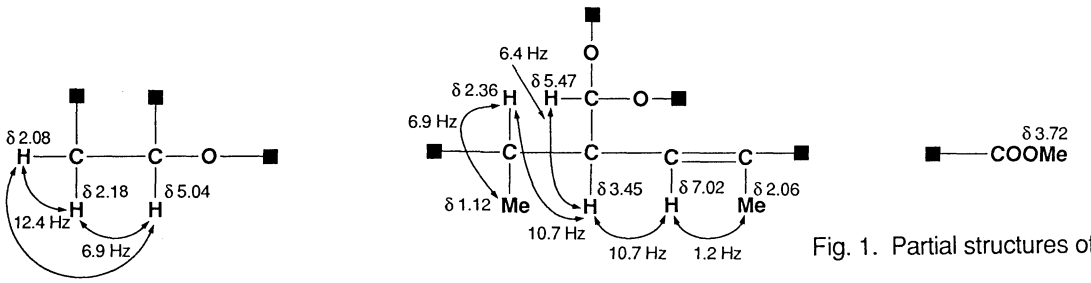


Fig. 1. Partial structures of 1.

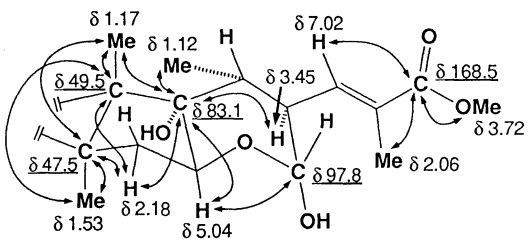


Fig. 2. ^1H-^{13}C long-range correlations of the aglycone moiety of **1** in pyridine-d_5.

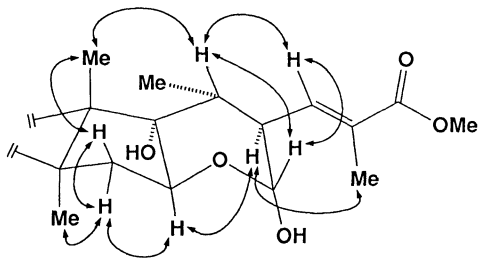


Fig. 3. NOEs of **1** in pyridine-d_5.

The presence of a terminal α-L-rhamnopyranosyl unit and two 2-substituted β-D-glucopyranosyl units in the molecule was shown by comparison of the ^{13}C NMR resonances for each monosaccharide,[5] which were assigned by a combined use of ^{1}H-^{1}H COSY and HMQC spectra, with those of reference methyl glycosides.[6] The ^{1}H-^{13}C long-range correlation from each anomeric proton across the glycosidic bond to the carbon of another substituted monosaccharide or the aglycone confirmed the sugar sequence (Fig. 4). From the data presented above, the structure of **1** was elucidated.

Peruvianoside A (**1**) has an unusual migrated carbon skeleton based on lanostanol, and showed medium inhibitory activity on cyclic AMP phosphodiesterase (IC_{50} 23.5 x 10^{-5} M).[7]

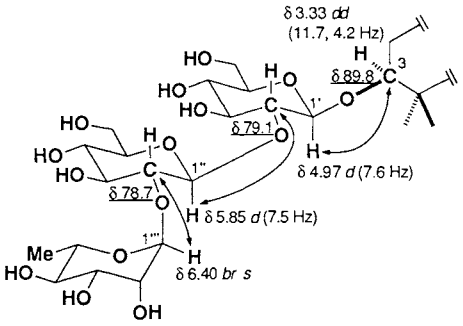
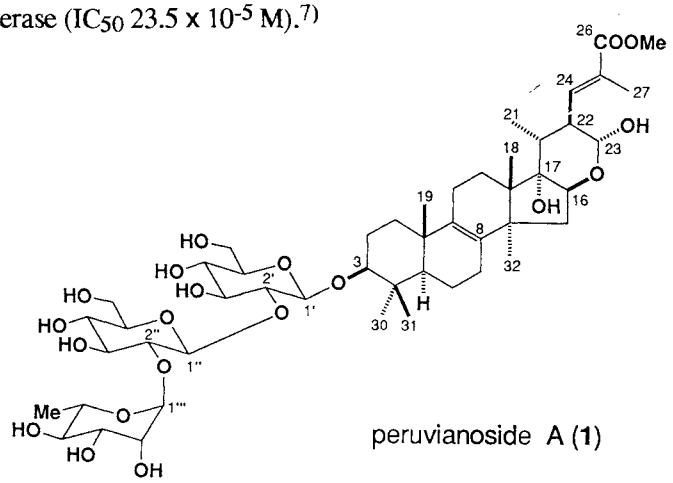


Fig. 4. ^{1}H-^{13}C long-range correlations of the saccharide moiety of **1** in pyridine-d_5.



peruvianoside A (**1**)

References

1) Some spectral data of **1**: negative-ion FABMS *m/z* 985 [M - H]$^-$, 839 [M - Rha]$^-$, and 677 [M - Rha - Glc]$^-$; Anal. Found: C, 58.12; H, 7.95%. Calcd for $C_{49}H_{78}O_{20}\cdot H_2O$: C, 58.55; H, 8.02%. IR ν_{max} (KBr): 3400 (OH) and 1695 (C=O) cm^{-1}; ^{1}H NMR (pyridine-d_5) δ = 6.40 (1H, br s, H-1'''), 5.85 (1H, d, *J* = 7.5 Hz, H-1''), 4.97 (1H, d, *J* = 7.6 Hz, H-1'), 3.72 (3H, s, OMe), 2.06 (3H, d, *J* = 1.2 Hz, H-27), 1.80 (3H, d, *J* = 6.2 Hz, H-6'''), 1.12 (3H, d, *J* = 6.9 Hz, H-21), and 1.53, 1.40, 1.17, 1.16, and 1.01 (each 3H, s, H-32, H-30, H-18, H-31, and H-19).

2) The identifications of the monosaccharides including their absolute configurations were achieved by converting them to the 1-[(*S*)-*N*-acetyl-α-methylbenzylamino]-1-deoxyalditol acetate derivatives followed by HPLC analysis; R. Oshima, Y. Yamauchi, and J. Kumanotani, *Carbohydr. Res.*, **107**, 169 (1982).

3) ^{13}C NMR of the aglycone moiety (pyridine-d_5) δ = 35.9, 27.1, 89.8, 39.8, 51.2, 18.4, 26.6, 135.8, 134.6, 37.1, 21.2, 26.7, 49.5, 47.5, 40.9, 80.7, 83.1, 20.2, 19.2, 36.7, 11.9, 44.5, 97.8, 144.1, 130.1, 168.5, 13.4, 28.3, 16.7, and 27.9 (C-1 - C-32), and 51.6 (OMe).

4) J. -F. Cheng, J. Kobayashi, H. Nakamura, Y. Ohizumi, Y. Hirata, and T. Sasaki, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 2403.

5) P. K. Agrawal, D. C. Jain, R. K. Gupta, and R. S. Thakur, *Phytochemistry*, **24**, 2479 (1985).

6) ^{13}C NMR of the saccharide moiety (pyridine-d_5) δ = 105.2, 79.1, 79.4, 72.0, 77.9, and 61.5 (C-1' - C-6'), 102.1, 78.7, 79.4, 73.0, 77.5, and 62.9 (C-1'' - C-6''), and 102.2, 72.4, 72.7, 74.4, 69.6, and 18.9 (C-1''' - C-6''').

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