

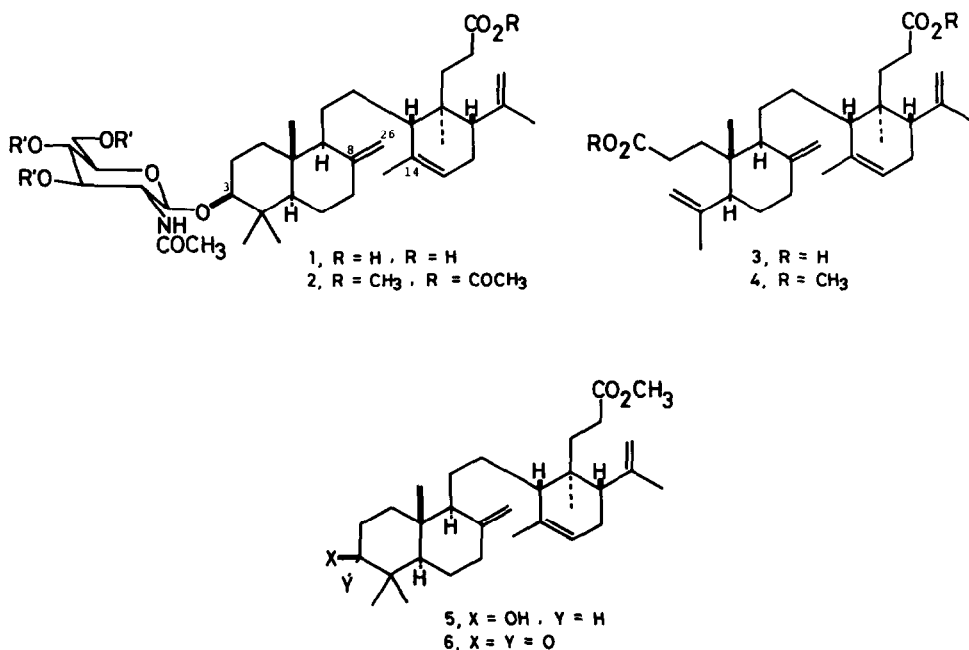
THE STRUCTURE OF LANSIOSIDE A : A NOVEL TRITERPENE GLYCOSIDE WITH AMINO-SUGAR  
FROM LANSIUM DOMESTICUM<sup>1)</sup>

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Summary: Lansioside A, a novel triterpene amino-sugar glycoside, is isolated from Lansium domesticum and its full structure including absolute configuration is established by the chemical derivation and spectral study.

The fruit peel of Lansium domesticum Jack v. duku (Meliaceae) contains a large quantity of latex, and its major constituent has already been shown to be lansic acid (3) through the correlation with  $\alpha$ -onocerin.<sup>2)</sup> Described herein are the isolation and structure determination of a more polar component named lansioside A, which is a novel example of an amino-sugar glycoside.<sup>3)</sup>



Lansioside A (1, mp 174-175 °C,  $[\alpha]_D^{15} +26.2^\circ$  ( $c$  1.06,  $C_2H_5OH$ ), IR (KBr) 3400, 1705, 1640, 1560, 890  $cm^{-1}$ ) was obtained from ethanol extract of the dried peel by means of silica gel column chromatography in 0.2% yield. On esterification ( $CH_2N_2$ ) and following acetylation ( $Ac_2O$ /pyridine), 1 afforded a methyl ester triacetate 2 (mp 149-150 °C,  $[\alpha]_D^{14} +15.1^\circ$  ( $c$  1.10,  $CHCl_3$ )). Methanolysis of 1 ( $H_2SO_4/CH_3OH$ , reflux) provided an aglycon methyl ester 5 ( $[\alpha]_D^{19} +34.9^\circ$  ( $c$  1.36,  $CHCl_3$ )) and an anomeric mixture of methylated sugar derivatives. The latter mixture was acetylated and then fractionated through silica gel column. These were identified with methyl 2-acetamido-2-deoxy- $\alpha$ -D-glucopyranoside triacetate and its  $\beta$ -anomer by the comparison with authentic samples. Lansioside A originally contains an acetyl moiety on the sole nitrogen atom. Therefore, the sugar part was rigidly confirmed to be N-acetyl-D-glucosamine, which is connected to the single hydroxyl group of the triterpene at anomeric position. The stereochemistry of the anomeric carbon of lansioside A was easily established to be  $\beta$ -glycosidyl based on the  $^1H$  and  $^{13}C$  NMR data of 2 (4.67 ppm, d,  $J = 8$  Hz and 104.6 ppm, d respectively).<sup>4)</sup>

The structure of the aglycon methyl ester 5 was deduced from the spectral data. The position of double bonds was assigned by the careful examination of LIS-NMR ( $Eu(fod)_3$ ), in which the signals due to the C-26 methylene protons moved to downfield faster than that of the C-15 proton. The stereochemistry at C-3 was established to be  $\beta$ -hydroxyl based on the coupling pattern of carbonyl proton (3.28 ppm, dd,  $J = 11$  and 4 Hz).

The confirmation of the basic carbon skeleton and the absolute configuration was carried out by the derivation of 5 to lansic acid dimethyl ester (4).<sup>2,5)</sup> Jones oxidation of 5 afforded a ketone 6 (77% yield,  $[\alpha]_D^{18} +35.2^\circ$  ( $c$  0.81,  $CHCl_3$ )). Baeyer-Villiger oxidation of 6 (aq NaOH/30%  $H_2O_2/CH_3OH$ ) followed by esterification provided 4 (7% yield), which was identical with authentic sample derived from lansic acid in all respect including optical rotation.

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#### REFERENCES AND NOTE

- 1) Dedicated to Emeritus Professor Takeo SAKAN on his 70th anniversary of birth.
- 2) A. K. Kiang, E. L. Tan, F. Y. Lim, K. Habaguchi, K. Nakanishi, L. Fachan, and G. Ourisson, Tetrahedron Lett., 3571 (1967). K. Habaguchi, M. Watanabe, Y. Nakadaira, K. Nakanishi, A. K. Kiang, and F. Y. Lim, ibid., 3731 (1968).
- 3) H. Ripperger, A. Preiss, and J. Schmidt, Phytochemistry, 20, 2434 (1981).
- 4) K. Bock and C. Pedersen, J. Chem. Soc. Perkin II, 293 (1974).
- 5) Y. Tsuda and T. Sano, Chem. Pharm. Bull., 28, 3134 (1980).

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