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ISOLATION OF LAEVIUSCOLOSIDE G FROM THE STARFISH *Henricia derjugini* AND CORRECTION OF THE STRUCTURES OF ECHINASTEROSIDES B_1 AND B_2

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Continuing a study of the total polyhydroxysteroids from the Far-eastern starfish *Henricia derjugini*, we have isolated a steroid glycoside by the repeated rechromatography of fractions obtained previously together with henriciosides H_1, H_2, and H_3 [1] and by high-performance liquid chromatography (Du Pont chromatograph, refractometer detector) on Alktex Ultrasphere Si (5 μ, 10.0 × 250 mm) columns with the eluent ethyl acetate–mthanol (18:1), and Zorbax ODS (5 μ, 4.6 × 250 mm) columns with the eluent methanol–water (3:1).

On the acid hydrolysis of (I), mp 221-223°C, $[\alpha]_{Hg}$ −27.6° (*c* 2.0, methanol), L-arabinose and 2,4-di-O-methyl-D-xylose were identified.

PMR spectrum (C_5D_5N, 250 MHz): 0.95 (d, J = 6.4 Hz; CH_3-26.27); 1.03 (d, CH_3-21); 1.25 (s, CH_3-18); 1.25 (m, H-5); 1.54 (d, J = 10.0 Hz, H-14); 1.83 (s, CH_3-19); 1.92 (m, H-25); 2.04 (dd, J_1 = 3.0 Hz, J_2 = 15.0 Hz; H-7a); 2.35 (qd; J_1 = 3.0 Hz; J_2 = 13.0 Hz; H-2a); 3.16 (dd; J_1 = 2.7 Hz, J_2 = 14.9 Hz; H-7e); 3.60 (m, H-24); 3.90 (m, H-3); 4.51 (m, H-4,6); 4.83 (d, J = 7.5 Hz; H-1″); 4.86 (td, H-15), 5.60 (d, J = 2.0 Hz, H-1′).

^{13}C NMR spectrum (C_5D_5N, 62.9 MHz): 40.4 (C-1); 24.8 (C-2); 79.0* (C-3), 73.7 (C-4); 49.9 (C-5); 75.4 (C-6); 45.0 (C-7); 75.7 (C-8); 57.1 (C-9); 36.2 (C-10); 18.9 (C-11); 42.0 (C-12); 44.7 (C-13); 66.3 (C-14); 69.0 (C-15); 41.6 (C-16); 55.1 (C-17); 15.4 (C-18); 18.5 (C-19); 35.3 (C-20); 18.9 (C-21); 32.0 (C-22); 28.4 (C-23); 83.6 (C-24); 31.1 (C-25); 18.5 (C-26); 18.1 (C-27); 109.6 (C-1′); 83.6 (C-2′); 78.9* (C-3′); 85.5 (C-4′); 62.9 (C-5′); 101.5 (C-1″); 84.6 (C-2″); 76.5 (C-3″); 80.7 (C-4″); 64.0 (C-5″); 58.6 (OMe); 60.6 (OMe). The assignments of the signals marked with asterisks are ambiguous.

The positions and configurations of the hydroxy substituents in the aglycon were established by difference spin-decoupling. The signals of the protons and the carbon atoms of the steroid nucleus and of the 2,4-di-O-methylxylopyranose unit of glycoside (I) coincided with the analogous values for henricioside H_1 (II) [(24S)-3-O-(2,4-di-O-methyl-β-D-xylopyranosyl)-5α-cholestane-3β,4β,6β,8,15α,24-hexaol] [1]. Recording the Overhauser effect on the irradiation of the anomeric proton H-1′ (5.60 ppm) revealed an enhancement of the H-24 signal, which showed the attachment of the arabinofuranose residue at C-24.

On the basis of these facts, we determined the structure of (I) as (24S)-3-O-(2,4-di-O-methyl-β-D-xylopyranosyl)-24-O-α-L-arabinofuranosyl-5α-cholestane-3β,4β,6β,8,15α,24-hexaol.

Glycoside (I) proved to be identical with laeviuscoloside G from the the starfish *Henricia laeviuscola* [2]. The ^{13}C NMR spectra of the two compounds were close, although the PMR spectra differed considerably from one another, since they were taken in different solvents (C_5D_5N and CD_3OD).

We have previously described the structure of echinasteroside B_2 (III) from the starfish *Echinaster sepositus* as 24-O-[2-O-methyl-β-D-xylopyranosyl-(1→3)-α-L-arabinofuranosyl]-5α-cholestane-3β,4β,6β,8,15α,24ξ-hexaol, and that of echinasteroside B_1 (IV) as its 15α-acetoxy analogue [3]. A careful repeat analysis of the ^{13}C NMR spectra of glycosides (I-IV) taking the effects of glycosylation into account [2] and a reconsideration of the results of the methylation of (III) showed an error in the assignment of the C-3 and C-4 signals of the aglycon (73.6 and 78.8 ppm) and of the C-2′, C-3′, and C-4′ signals of the arabinofuranose residue (78.8, 85.8, and 83.7 ppm) for echinasteroside B_2 and similar values for echinasteroside B_1. We have come to the conclusion that glycoside (III) is close in structure to glycoside (I) and differs from it by the absence of a methoxy group at C-4″ of the xylopyranose unit. The following assignments of the signals must be considered to be correct for the spectrum of echinasteroside B_2: C-3 (78.8 ppm), C-4 (73.6 ppm), C-2′ (83.7 ppm), C-3′ (78.8 ppm), C-4′ (85.5 ppm).

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As a result, echinasteroside B_2 has been ascribed the structure (24S)-3-O-(2-O-methyl-β-D-xylopyranosyl)-24-O-α-L-arabinofuranosyl-5α-cholestane-3β,4β,6β,8,15α,24-hexaol, and echinasteroside B_1 that of its 15α-acetoxy analogue.

In the light of the corrections given above, the ^{13}C NMR spectrum of echinasteroside B_2 practically coincides with that of granulatoside A from the starfish *Choriaster granulatus* [4], from which we must conclude that they are identical.

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