STARFISH SAPONINS, XIII. OCCURRENCE OF NODOSOSIDE IN THE STARFISH *ACANTHASTER PLANCI* AND *LINCKIA LAEVIGATA*[1]

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Starfish have been a rich source for discovery of marine steroidal glycosides with new structures (1). Recently, we have described a novel group of steroidal glycosides that are composed of polyhydroxylated (five to six hydroxyl) sterol aglycones and a carbohydrate portion glycosidally attached at C-24 of the steroid, from the starfish *Protoreaster nodosus* (2) and *Hacelia attenuata* (3,4). In particular, *Protoreaster nodosus* has yielded 24-O-[2-O-methyl-β-*D*-xylopyranosyl-(1→2)-α-*L*-arabinofuranosyl]-5α-cholestane-3β,5,6β,8,15α,24ξ-hexol, which we named nodososide (2).

Continuing with our investigation of biologically active marine steroidal glycosides from echinoderms, we have been working on saponins of the Pacific starfishes, *Acanthaster planci* (L.), whose major asterosaponin, thornasteroside A, was fully characterized a few years ago by Kitagawa and Kobayashi (5), and *Linckia laevigata* (L.), and have isolated from both sources, in small amounts, a steroidal glycoside identical with nodososide.

EXPERIMENTAL

ANIMAL COLLECTION AND EXTRACTION.—*L. laevigata* was collected in March 1981, and *A. planci* in September 1982, off Nouméa, New Caledonia. Starfishes were chopped and extracted (5 h) with H_2O and the extracts lyophilized. *L. laevigata* (5 kg, fresh animals) gave 129 g of crude extract; *A. planci* (5 kg) gave 850 g of crude extract.

ISOLATION OF THE NODOSOSIDE.—*L. laevigata*: The aqueous lyphilized extract was extracted with light petroleum (bp 40-70°), then with $CHCl_3$, followed by MeOH-$CHCl_3$ (1:9), MeOH, and H_2O-MeOH (1:1). The MeOH-$CHCl_3$ extract gave 23 g of residue, which was separated by a silica gel short-column chromatography (300 g SiO_2). Fractions (250 ml) were collected; fractions 1-8 were eluted with MeOH-$CHCl_3$ (1:9), fractions 9-11 with MeOH-$CHCl_3$ (2:8), and fractions 12-13 with MeOH-$CHCl_3$ (3:7). Fraction 9 gave 187 mg of residue that was chromatographed by hplc on a μ-bondapack C-18 column (7.8 mm×30 cm, flow rate 5.5 ml/min^{-1}) using 35% H_2O in MeOH. The major peak collected between 18 and 21 min after injection contained 8 mg of nodososide.

A. planci: The same procedure was used to yield 9 mg of nodososide.

Nodososide, $[\alpha]_D = -20.3°$ (from *L. laevigata*), $-19.5°$ (from *A. planci*) (lit. $[\alpha]_D = -21.3°$, 2), was identified by 270 MHz pmr and authentic sample comparison by hplc and SiO_2-tlc.

Full details of the identification of the compound are available on request to the senior author.

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