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## Unusual Structures of Gangliosides from Starfishes

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Gangliosides containing unusual oligiosaccharide chains were isolated from starfish *Asterias rathbuni* and *Leptychaster anomalus* belonging to different orders. Their structures were elucidated by chemical and physico-chemical methods. The main ganglioside from *A. rathbuni* was found to contain pentasaccharide chain with two 8-*O*-methyl-*N*-glycolylneuraminic acid residues bound to one *N*-acetylgalactosamine residue in positions 3 and 6: 8-*O*-Me-NeuGcα2-3 (8-*O*-Me-NeuGcα2-6)GalNAcβ1-3Galβ1-4Glcβ1-1Cer. The ganglioside from *L. anomalus* contained tetrasaccharide chain where *N*-glycolylneuraminic acid residue accupied the subterminal position and is glycosylated at 0-4 by the terminal galactopyranose residue: Galβ1-4NeuGc2-3Galβ1-4Glcβ1-1Cer.

The lipid moieties of both gangliosides were shown to contain normal and α-hydroxy fatty acids at a ratio of about 1:1. Sphingosines were detected in the *L. anomalus* ganglioside, whereas approximately equal amounts of sphingosines and phytosphingosines were found in the *A. rathbuni* ganglioside. Quantitative analysis of long-chain bases and fatty acids was carried out.

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## Glycosphingolipids of *Echinococcus multilocularis* Metacestodes

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*Echinococcus multilocularis* is a cestode parasite responsible for the human alveolar hydatid disease. The metacestodes, state found in rodent and accidentally in man, contain neutral and acid glycosphingolipids, 95 and 5%, respectively. Gangliosides were identified as $GM_3$, $GM_2$, $GM_1$, $GD_{1a}$. Neutral glycosphingolipids were resolved by high performance thin layer chromatography into 12 fractions which were submitted to methylation analysis, mass spectrometry and exoglycosidase degradation. Galactosylceramides (1), di-, tri- and tetragalactosyceramide having Galβ1-6Gal internal linkages were characterized (2). In addition 2 novel fucolipids were found with a Fucα1-3Galβ linkage. Each neutral glycosphingolipid was resolved by thin layer chromatography into 2 or 3 bands, because of the large heterogeneity of their ceramide : neutral glycolipids contain sphinganine linked either to nonhydroxy fatty acids with 16, 18, 26 and 28 carbon atoms, or to hydroxy fatty acids with 16 and 18 carbon atoms. Antibodies directed against di-, tri- and tetragalactosylceramide of *Echinococcus multilocularis* were found in the serum of patients with echinococcoses.

1) Persat, F. *et al.* (1990) *Mol. Biochem. Parasitol.*, **41**, 1 – 6.
2) Persat, F. *et al.* (1992) *J. Biol. Chem.*, **267**, 8764 – 8769

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## Glycosphingolipids of Plerocercoids of Parasite, *Spirometra erinacei*

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Glycosphingolipids are participants in many important events occurring at the cell surface including the binding of pericellular adhesive proteins, bacterial toxins, and viruses to the plasma membrane. In this context, we studied glycosphingolipids of parasite to elucidate underlying biochemical mechanisms of host-parasite relationship. Glycolipids were extracted from the plerocercoids of tapeworm, *Spirometra erinacei*, and chromatographed on a DEAE-Toyopearl column. All glycolipids were eluted in the neutral fraction. The glycolipid migrating closely to authentic globoside, which was the most abundant component of the plerocecoids, was investigated in detail. GLC analysis of TMS sugars showed that this glycolipids is composed of Glc, Gal and Fuc in a molar ratio of 1:2:1. From methylation analysis, exoglycosidase hydrolysis, FAB/MS and NMR analysis, this fucosylated glycosphingolipid was found to consist of a unique carbohydrate structure.

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## Acidic Glycosphingolipids from the Gill of the Salmon (*Oncorhynchus keta*) Presence of Unique Hybrid-Type Gangliosides with the Isoglobo Core

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Previously we have characterized fucosyl-GalNAc derivatives of GM1a, GD1b and its 4-*O*-acetyl NeuAc analog from the kidney of the salmon.

Monosialosyl gangliosides and sulfoglycolipids were extracted from the gill of the pacific salmon, *Oncorhynchus keta*, and separated on a DEAE-Sephadex column. Acidic glycolipids (M1-M15) were purified on a silica bead column and characterized by $^1$H NMR, chemical analysis, enzymatic degradation, TLC-immunostaining, and negative FAB-MS.

In addition to the acidic glycolipids with known structures (galactosyl and lactosyl sulfatides, GM3, LM1, GM1b) and $V^3$αFuc,$IV^3$βGalNAc,$II^3$αNeuAc-$Gg_4$Cer, each two molecular species of the two major monosialosyl gangliosides (M11-M15) with TLC mobilities slower than GM1 were characterized as below:

M11 and M13: NeuAcα2-3Galβ-4GlcNAcβ-3Galα-3Galβ-4Glcβ-Cer
3
Fucα

M14 and M15: NeuAcα2-3Galβ-4GlcNAcβ-3Galα-3Galβ-4Glcβ-Cer

3 4
Fucα GalNAcβ

Thus, the oligosaccharides in these gangliosides are of novel hybrid types of the neolactoisoglobo- and neolacto-isoglobo-ganglio series.

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## Molecular Species Analysis of Glycosphingolipids by HPLC/FAB-MS

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Intestinal tissue of Japanese quail, *Coturnix coturnix japonica*, has $Le^x$ type glycosphingolipids as the normal major glycosphingolipid components (1). Besides the major components and monoglycosylceramide (2), following structures were identified by composition analysis, methylation, and degradation using exoglycosidases: