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CHARACTERIZATION OF SOME BOVINE BRAIN OLIGOSACCHARIDES

AND SYNTHESIS OF DEOXY-FLUORO SUGARS

by

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ABSTRACT

CHARACTERIZATION OF SOME BOVINE BRAIN OLIGOSACCHARIDES
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Mannose rich glycopeptides were isolated from bovine brain tissues. They were separated into three groups according to their acidity. The content of phosphorous in the acidic glycopeptides was determined relative to asparagine. The content of hexoses and aminosugars was also determined in all three acidic, basic and neutral fractions. C-13 nuclear magnetic resonance spectra showed that the basic glycopeptide has relatively higher amounts of amino acids than the acidic and neutral glycopeptides.

The neutral glycopeptides yielded three oligosaccharide chains by hydrazinolysis. All three carbohydrate chains were linked to the amide nitrogen atoms of asparagine residues and contained only N-acetyl-glucosamine and mannose. N-acetylglucosamine was the linkage sugar of all three oligosaccharide chains. They contained the chitobiose moiety at their core region, and consisted of three branches, all of which were terminated with α -D-mannose residues. The first branch point of the sugar chains contained a C-3 and C-6 substituted β -mannose residue which was linked to the C-4 hydroxyl group of nonreducing N-acetylglucosamine moiety of chitobiose. A C-3 and C-6 substituted α -mannose residue was responsible for the second branch point.

A new reaction to synthesize fluoro-deoxy sugars was discovered. Diethylaminosulfur trifluoride (DAST) caused the replacement of the C-4 and C-6 hydroxyl groups of methyl- α -D-glycopyranosides by fluorine atoms. A Walden inversion was observed at C-4. In one case, in addition to the described major product, monofluorination at C-6 was also observed. When the C-6 hydroxyl group was blocked the reaction at C-4 with a Walden inversion was still observed.

Methyl- β -D-glycopyranosides react with DAST to give 4,6-dideoxy-4,6-difluoro and 6-deoxy-6-fluoro derivatives as described for methyl- α -D-glycopyranosides. However, in addition to these two products, methyl- β -D-glycopyranoside also yielded 3,6-dideoxy-3,6-difluoro derivatives with a Walden inversion at C-3. Fluorination of oligosaccharides proved to be unsuccessful.

