

Advances in biology and in structural carbohydrate chemistry and emerging knowledge of structure-activity relationships have made necessary access to these structures and to analogues of them. Considerable progress has been made in the last few years in the chemical synthesis of oligosaccharides and glycoconjugates. Examples will be given of ongoing research in methodology as well as of recent syntheses of oligosaccharides of biomedical relevance.

Synthesis of Potential Inhibitors of Carbohydrate Processing Enzymes

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The interest in "glycomimetics" is growing with the knowledge of the multifarious roles that carbohydrates play in the biological events. It is now well proved that glycoconjugates are the main structures responsible for cell-cell and cell-molecule recognition events and host-pathogen interactions. Glycomimetics can, in principle, replace the normal substrate in interactions with receptors and active sites of enzymes, so inhibiting these processes.

We have developed innovative procedures for the synthesis of different glycomimetics of biological relevance. Among them we have synthesized isosteric phosphono analogues of some glycosyl phosphates, looking for inhibitors of glycosyltransferases. The phosphono analogues of α -L-rhamnose 1-phosphate, N-acetyl- α -D-glucosamine 1-phosphate, N-acetyl- α -D-mannosamine 1-phosphate and its GDP-derivative, have been stereoselectively synthesized. Furthermore, C-glycosidic analogues of glycosyl aminoacids, glyceroglycolipids and spacer-connected C-disaccharides, have been synthesized through innovative procedures that exploits ionic and radical chemistry.

The Reductive Cleavage Method for Polysaccharide Structural Analysis

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My lecture will describe a new procedure for establishing the primary structure of polysaccharides. The salient feature of the method, reductive cleavage of the glycosidic carbon-oxygen bonds in fully methylated polysaccharides, gives rise to partially methylated *anhydroalditols* that are subsequently analyzed as their acetyl derivatives by gas-liquid chromatography combined with mass spectrometry. Comparison of the GLC retention indices and mass spectra of these products with those of authentic standards establishes the composition of the polysaccharide and the ring form and position(s) of linkage of each of its glycosyl residues in a single step. The method has already been shown to be applicable to the analysis of polysaccharides containing pentoses, hexoses, deoxyhexoses, hexuloses, 2-acetamido-2-deoxyhexoses, uronic acids, and sialic acids. In addition, the method is applicable to the analysis of polysaccharides containing a wide variety of covalently-attached, non-carbohydrate substituents such as carboxylic acid esters, ethers (methyl, ethyl, carbox-

ymethyl, hydroxypropyl), and pyruvic acid acetals. Furthermore, through proper choice of reagents, the reductive cleavage of glycosidic linkages can be accomplished *selectively* to generate small oligomers that can be characterized and used to deduce the *sequence* of glycosyl residues in polysaccharides. The current status of development of the method will be illustrated by its application to a variety of polysaccharides of biological and industrial importance.

Utilization of Planar Chromatography in the Sugar Industry

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Analysis of sugar mixture by modern liquid chromatography technique, both column and planar, has gained much prominence. As far as planar chromatography is concerned, the introduction of high performance bounded phases layer and of instrumental development technique has opened new perspectives in TLC analysis of sugars, particularly for samples which need cumbersome clean-up processes. In chromatography, gradient elution is the technique of choice whenever the mixture components span a wide range of polarity (or molecular structure). Also in planar chromatography gradient development is possible using an automated technique (AMD), recently introduced. This technique allows large spot capacities because of the reconcentration effect caused by the multiple development and the accommodation of many spots on the same chromatographic plate because of the gradient development. Thus, complex samples, as beet or cane molasses, can be analyzed (or at least screened) on high performance thin layers using modern scanners which allow much information to be obtained both on underivatized and derivatized analysis.

In the analysis of molasses it is interesting also the Over Pressure Liquid Chromatography (OPLC); although it does not allow to utilize the effect of spot reconcentration constituents.

Details concerning the analysis of both beet and cane molasses are reported and a comparison between the two techniques mentioned above is discussed.

What Is The News in Sucrochemistry

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After the presentation of some economical informations on the wealth and European productions and the non-food applications of sucrose, the recent studies in sucrochemistry mainly developed in France will be presented.

New activation processes (microwaves, ultrasound, thermolysis) were used in reactions of acetylation, etherification, esterification and oxidation of sucrose. Using specific reagents (heterogeneous and homogeneous catalysts, TEMPO) regioselective transformations can be controlled.

Substitutions reactions were also studied in relationship, with the concentrations of sucrose and the subsequent hydrophobic effects of the introduced groups on the sucrose moiety. The applications of sucroethers, sucroesters, sucroacetals in polymer chemistry and detergency will be evoked.