

x-O-*n*-alkyl-itol. Substrate Structure and Alkyl Chain Position Influences on Their Liquid Crystalline Properties

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We prepared the hereafter series of x-O-*n*-alkyl galactitol, glucitol, mannitol and xylitol derivatives by reducing the corresponding x-O-*n*-alkyl-monosaccharide precursors.

Alkyl chain is noted $R = n - C_nH_{2n+1}$ with $n = 6$ to 12. Studied parameters are: length (n) and position (x) of alkyl chain number and orientations of hydroxyle groups.

The liquid crystalline phase studies show, as for their monosaccharidic precursors, that transition phase temperatures increase either with the alkyl chain length or with the OH group number increasing. Nevertheless, the X-position of the alkyl chain and the relative OH group orientations have generally higher influence than those observed for their heterocyclic analogs.

Sugar Nitronates: Versatile Intermediates for the Preparation of Chiral Bicyclic Systems

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Recently we have disclosed an asymmetric variant of the tandem $[4+2]/[3+2]$ cycloaddition of nitroalkenes starting from a carbohydrate-appended heterodiene. Its reaction with ethyl vinyl ether (EVE) gave rise to a single diastereoisomer in 86% yield and whose structure was unequivocally determined by X-ray diffractometry. Our previous attempts, however, to isolate the intermediate nitronates were unsuccessful. We reasoned that such elusive species could be trapped *in situ* in the presence of a second dipolarophile, thereby enabling the preparation of diversely functionalized bicyclic systems. With these premises we have now performed asymmetric cycloadditions with EVE and an electron-withdrawing alkene such as methyl acrylate, acrylonitrile, or methyl vinyl ketone in ethanolic solution. The latter alkenes captured the sugar nitronate releasing the corresponding cycloadducts as crystalline solids in high yields. The reactions are regiospecific, exhibit a pronounced facial diastereoselectivity, and the major products can be obtained as pure diastereoisomers by recrystallization. As expected for an inverse electronic demand cycloaddition, the deficient alkenes alone did not react with the nitroalkene. This ensures that the initial Diels-Alder reaction will always occur with the electron-rich vinyl ether.

Synthesis and Hydrogenolysis of Dioxolane Type Diphenylmethylene and Fluoren-9-ylidene Carbohydrate Acetals Containing a Neighbouring Substituted Hydroxyl Function

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Hydrogenolysis of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals containing a free OH group in the vicinity of the *equatorial* side of the dioxolane ring resulted exclusively in *axial* diphenylmethyl or fluoren-9-yl ethers with chloroalane (AlH_2Cl) as the reagent.

Series of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals of hexoses containing adjacent *O*-alkyl, deoxy or hydroxy functions were prepared and hydrogenolysed with the $LiAlH_4-AlCl_3$ reagent. The hydrogenolysis resulted in all cases a mixture of the corresponding *axial* and *equatorial* ethers.

The observed direction of ring-cleavage was discussed.

Synthesis of α,β -unsaturated Lactones Linked to Sugars. Configurational Determination by N.O.E.

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In this work we present the synthesis of bioactive sugar derivatives containing in their structure an α,β -unsaturated lactone. The spiro lactones were synthesised by a Reformatsky type reaction of the appropriate carbonyl compounds with ethyl bromomethylacrylate and activated zinc.

The configuration of the new stereogenic centre was determined by N.O.E. experiments.

Synthetic Approach to Pyrazole Sugar Derivatives

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In this work we report the synthesis of the pseudo-C-nucleosides by two different procedures. The starting material used was a pentodialdofuranose and the chain elongation was accomplished by Reformatsky and Wittig reactions. Construction of the pyrazole ring was possible by reaction with a hydrazine derivative followed by cyclization or by 1,3-dipolar cycloaddition with diazometane and treatment with chlorine.

The bioactivity of the compounds was tested against *Musca Domestica* and the results obtained show that they produce some effect in their nervous system.

Synthesis of Angucycline Antibiotics Bearing C-glycosidically Linked Oligosaccharides

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The quinoide angucycline antibiotics form an interesting group of natural products due to their broad spectrum of biological activities which include antibacterial, cytostatic, and enzyme inhibiting effects as well as activity in the inhibition of platelet aggregation. A large number of angucyclines bear a C-

glycosidic moiety with only one sugar molecule, e.g. urdamycinone B, or an oligosaccharide chain, for example urdamycin B. The sugar components of such angucycline group antibiotics seem to play an important role with respect to the antiplatelet activities and the mediation of solubility.

During the last few years several papers presenting different methods for the formation of the C-glycosidic bond have been published as well as total syntheses of angucycline antibiotics with D-olivose as the C-glycosidic residue. Therefore, we concentrated on the preparation of precursors for the synthesis of angucyclines with C-glycosidic linked oligosaccharides. In this connection we want to present our investigations towards the synthesis of precursors bearing the framed disaccharide fraction. This building block is an excellent intermediate for several angucyclines, since in most cases D-olivose, which usually is the first sugar attached to the quinone, is followed by an α -linked L-rhodinose at 3'-OH.

Synthesis of Amphiphilic X-O-*n*-alkylmonosaccharides. Substrate Structure and Alkyl Chain Position Influences on Their Liquid Crystalline Properties

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We synthesized the hereafter series of D-galactose, D-glucose, D-mannose and D-Xylose X-O-*n*-alkyl derivatives in which the *n*-alkyl chain R, with 6 to 12 carbon atoms, was regiospecifically introduced at the different positions X in the glucidic substrate—X-O-R-D-galactose, X-O-R-D-Glucose, X-O-R-D-mannose, X-O-R-D-xylose (Me-xyloside).

It is shown, as well in the thermotropic than in the lyotropic liquid crystalline studies, that the phase transition temperatures increase either with the alkyl chain length or with the OH group number increasing. Meanwhile, both the X-position of the alkyl chain and the relative OH group orientations in the heterocycle, have a significant influence on these temperatures.

Vibrational Assignments of Cyclodextrins

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Cyclodextrins (CDs) are macrocyclic carbohydrates composed of six (α -CD), seven (β -CD), eight (γ -CD), or more, D-glucose units linked by 1,4- α -glycosidic bonds, with the overall shape of a short, hollow, truncated cone. Since all the glucose rings have the same orientation, the narrow rim of the cone is formed by the primary O(6)-H hydroxyl groups while the wider rim is composed by the secondary O(2)-H and O(3)-H hydroxyl groups. The internal cavity is relatively hydrophobic because it is lined by the methylene C-H groups and by the ether-like O(4) and O(5) oxygen atoms.

The vibrational spectroscopy, in particular Raman spectroscopy, has become an important tool for the study of cyclodextrins and their complexes. However, the reports concerning the vibrational assignments of such large systems are scarce and controversial.

In this work, a full vibrational assignment of the CDs spec-

tra is proposed based on the comparison with the vibrational spectra of simpler carbohydrates (eg., glucose, maltose and maltotriose) and isotopic substitution. In addition, the Raman spectra of several methyl and hydroxypropyl substituted cyclodextrins were also recorded and analysed.

Ultrasound-mediated Extraction of the Immunologically Active Xylan Component of Corn Cobs

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Corn cobs represent an abundant source of two xylan-type polysaccharides, the water-insoluble arabinoglucuronoxylan and the water-soluble heteroxylan. The last mentioned xylan was shown to exhibit significant biological activities comparable to those of the commercial immunomodulator Zymosan. With regard to the demand for ecologically feasible technologies, various conditions of ultrasound-assisted extraction procedures of corn cobs have been investigated. The water soluble xylans isolated by classical and ultrasound-mediated extractions were compared from the viewpoint of yield, composition, structural features, molecular properties, and biological activity in mitogenic and comitogenic thymocyte tests. The results indicate a higher efficiency of ultrasonic methods as well as a higher biological response of the obtained xylans.

Stereoselective Radical Cyclisations Involving Substrates Bearing the 2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl Auxiliary

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The control of stereochemistry in free radical reactions has been substantially advanced in recent years. In this work acetylated D-glucose was used as a chiral auxiliary to provide good stereocontrol in radical reactions. This strategy, which was modeled on a successful approach developed for Diels-Alder reactions, worked well for intramolecular 5-*exo*-cyclisations. Related intermolecular reactions were not as selective.

The generality of the reaction was established and the removal of the chiral auxiliary was achieved with HCl/ROH to give enantiomerically pure trisubstituted tetrahydrofurans with structures analogous to furanlignans. The stereostructures attributed to the cyclic compounds were based on the Beckwith-Houk transition state model.

Rheological Characterization, Under Steady Shear, of a Polysaccharide (Lactan) Obtained Via Fermentation of Whey-related Media

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Production of lactan, a polysaccharide composed of mannose, galactose, and galacturonic acid at the molar ratios 5:3:2, was