

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

previously described starting from a semi-defined lactose-rich medium via fermentation by *Rhanelia aquatilis*. Since lactose is the major solid component of whey, production of that high-added value exopolysaccharide may help alleviate the environmental problems raised by whey as the major by-product of the cheesemaking industry

The polysaccharide was produced using five different fermentation media: a synthetic medium, plain whey under aerobic conditions, whey permeate, whey with 2% NaCl, and plain whey under anaerobic conditions. Lactan was recovered, from each medium, by precipitation with 50% ethanol and then lyophilized. Each aliquot of polysaccharide was solubilized in deionized water and solutions with different polysaccharide concentrations, different pH values, and different ionic strengths were analyzed under steady shear flow using a controlled stress rheometer (Carri-Med 50) with cone-and-plate geometry.

All lactan solutions showed a shear-thinning behaviour, and increases in viscosity were observed for increasing concentrations of polysaccharide as expected. The polysaccharide produced from whey with 2% salt and plain whey fermented under anaerobic conditions showed lower viscosity than that obtained from the remaining media. Addition of salts (e.g. KCl and CaCl₂) led to decreases of viscosity, which was virtually the same irrespective of salt concentration. Changes of pH (3–11) affected slightly the viscosity of the polysaccharide solutions, although higher viscosities were obtained at pH 7. The slight effect of pH and ionic strength can be somewhat implicated with the galacturonic acid residues present in the polymer chain. The polysaccharide samples possessed different protein contents, which may have influenced to some extent the rheological behaviour of the gel. The shear-thinning properties of the gum lead to potential applications in several food and non-food products.

Regio- and Stereoselectivity Issues in Allylic Reactivity of Vinylogous Esters/Carbonates Bearing the 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl Auxiliary

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Carbohydrate-based dienes have been shown to exhibit good-to-excellent diastereofacial selectivity in their reactions with cyclic dienophiles and aza-dienophiles. Glucose-bound vinylogous systems have previously been synthesized and shown to undergo diastereoselective addition reactions. In the present study new cyclic and acrylic vinylogous esters/carbonates were synthesized and their diastereofacial reactivity studied. With bromoallylic derivatives the nucleophilic displacement of the bromine atom was performed with oxygen, nitrogen and sulphur nucleophiles affording, in some cases, allylic rearrangement products where a new stereogenic centre was developed with medium-to-good diastereoselectivity. A model of reactivity is advanced on the basis of the absolute stereochemistry established by X-ray analysis.

Quantification of Mercury in Sugar by Cold Vapour Atomic Absorption Spectrometry

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Mercury is a heavy metal which levels in environment are of growing concern due to its biomagnification in certain live systems and consequent human dietary intake. Several studies have been performed to accomplish for the Hg contamination extent, almost all of them being performed in sediments, soils, water and fish. Nevertheless, some studies have also included the monitorization of mercury in agricultural and horticultural crops, namely crowns and leaves of sugar beet, and in the corresponding soils where they were cultivated, to correlate the element contents. Posterior determinations of mercury in crops were performed, which included sugar cane. Recently, additional studies have highlighted the correlation between mercury soil contamination and respective plant contents as is reported for rosemary and mushrooms. As a consequence, some countries have already proposed maximum acceptable levels for mercury in crops and the Joint FAO/WHO Experts Committee on Food Additives established a provisional tolerable weekly intake for total mercury of 0.3 mg of Hg/person.

As saccharose is a purified product from vegetal origin, it is important to control its mercury contamination and this communication presents a method for its quantification. The sample preparation consists of a wet digestion of the matrix with H₂SO₄ and NHO₃ (1:2, v/v) in a closed PTFE container at controlled temperature (80°C) for 2 h; afterwards, saturated KMNO₄ solution is gradually added into the sample solution to complete the mineralization. The measurement of the element is achieved by cold vapour atomic absorption spectrometry after reduction of the oxidized mercury compounds with sodium borohydride solution.

The detection limit is 0.28 μ g/L and the linearity range in the optimized conditions is 0.28–20 μ g/L. The precision is 9.0% and 11.0% for the analytical and over-all procedure, respectively. The validation of the procedure was performed by using a reference material and by the standard additions method (2.5, 5.0 and 10.0 μ g/L), being the recoveries higher than 90%.

Quality Evaluation of Portuguese Honeys

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Honey is the sweet viscous substance elaborated by the honey bee from the nectar of floral plants. It is produced in almost every country of the world and is a very important energy food, used as an ingredient in hundreds of manufactured foods, mainly in cereal based products, for sweetness, colour, flavour, caramelization and viscosity. Several types of honey are produced in Portugal. Sugars represent the largest portion of honey composition (95–99% of the honey solids). Fructose and glucose are the most abundant sugars in it, but others are usually mentioned, namely, saccharose, maltose, melibiose and trealose. Its composition depends highly on the types of flowers used by the bees as well as regional and climatic conditions.

Adulteration of honey is possible, so its quality must be controlled analytically with the aim of guaranteeing the genuinity and preserve consumer from commercial speculations. The present work was conducted to investigate the quality of 25 brands of Portuguese honeys commercially available on the market, in a total of 50 samples. Carbohydrate composition was determined by HPLC-RI to evaluate the monosaccharides, fructose and glucose, the disaccharides, sucrose, maltose, trehalose and melibiose and the trisaccharide melizitose. Sucrose content is important to determine heavy