antithrombotic drug ginkgolide B was achieved, with optimal simultaneous solubilization, using 6^I-S-α-maltosyl-6^I-thiocyclomaltoheptaose. Water solubility enhancements of the almost insoluble anticancer drug Taxotere® up to 4.5 g L^{-1} were obtained with 6^I-methylthioureido-β-CD.

From a systematic investigation on the role of the chemical modification with regard to the hemolytic character of cyclodextrins, conclusions have been brought about the charge and the geometry of the modification: i) Substitution at primary hydroxyl groups usually decreases the hemolytic character; ii) introduction of an amino group, resulting in a positive charge at physiological pH, decreases the hemolytic character; iii) negative charges are comparatively less effective; iv) zwitterionic groups seems to enhance the hemolytic character of the cyclodextrin molecule. Most of these data probably relate to interactions with erythrocyte membranes which may result in extraction of components. Taking into account the above results, it is anticipated that convenient functionalization with biological markers, oligosaccharides or proteins, may result in site-specific drug delivery systems based on these supramolecular carriers.

Determination of Sugars, and Some Other Compounds in Infant Formulae, Follow-up Milks and Human Milk by HPLC-UV/RI

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Progressive attempts have been made by the industry to bring composition of the infant formulae closer to that of the human milk. Follow-up milks are given to infants after 4–6 months of age to make the transition from human or infant formulae to cow's milk. The composition of these artificial milk formulae, relative to some constituents, namely, the sugars, does not correspond to that of genuine cow's milk from which they are originally prepared. A Regulation (91/5/EC Directive, J.O.E.C., #L 175/35, 4.7.91) establishes the type and limits of carbohydrates which can be added. Other milk endogenous compounds such as uric and orotic acids appear naturally in these formulae and because their levels can be good indicators of the quality of cows' milk used their quantification is also important.

In the present study the composition of sugars, uric and orotic acids in infant formulae and follow-up milks commercially available on the local market is reported. The levels found are compared with Portuguese and European Standards and with human and cows' milk composition. 50 samples including all of these products were analysed, using a rapid and accurate HPLC procedure developed for that purpose, which allowed simultaneous determination of lactose, glucose, galactose, saccharose, maltose, uric and orotic acids by HPLC using refractive index and UV detectors in series.

For the analysed sugars all, except two, infant formulae contained exclusively lactose, as happens with human and cow's milk. The two exceptions were lactose free infant formulae used for lactase-deficient infants and contained maltose and glucose. In follow-up milks the prevailing carbohydrate was lactose but they also contained other sugars such as, maltose, saccharose and traces of glucose and galactose, at the levels allowed by regulation. With respect to uric and orotic acid composition no significant differences between their levels were obtained when determined by ANOVA methodology, followed by Fisher's PLSD test ($p > 0.01$).

Fiber Preparation of N-acylchitosan and its Composite With Cellulose by Spinning Their Sodium Xanthate Solutions

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Chitin, chitosan and cellulose have a structural backbone of (1 → 4)-linked β-D-glucan. Cellulose xanthate is used widely in the global rayon industry, but chitin xanthate is little used in the textile field. The present paper aims to develop a method of generating novel fibres of N-acylchitosan and its composite with cellulose from their aqueous alkaline sodium xanthate solutions.

A sodium N-acylchitosan solution in aq. 14% NaOH was treated with CS_2 to afford the corresponding aq. sodium N-acylchitosan xanthate solution. The xanthate solution and its clear mixed solution with sodium cellulose xanthate were spun at 45–50°C through a viscose-type spinneret into a coagulation bath containing aq. 10% H_2SO_4, 32% Na_2SO_4 and 1.3% $ZnSO_4$.

Eight kinds of novel fibers were prepared from N-acetylchitosan, N-propionylchitosan, N-acetylchitosan-cellulose composites (6:4, 4:6 and 3:7, w/w), and N-Propionylchitosan-cellulose composites (4:6, 5:5 and 3:7, w/w). All the fibers obtained were white and showed absorptions at 1650–1657 and 1550–1554 cm^{-1} (C=O and NH of N-acyl) in FTIR spectra (KBr). N-Propionylchitosan-cellulose composite filament had better mechanical properties than did N-acetylchitosan-cellulose composite filament, because of the relatively firm interaction of N-Propionyl groups. These fibers are usable not only as biomedical materials (e.g., controlled digestible surgical suture, tissue wound-dressing etc.) but also as general functional textile materials.

Modelling Cucrose Crystallization – A Simulator for Operator Training

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Here, we report on the study of the operation of an industrial semi-batch evaporative-crystallizer for cane sugar refining, making use of an in-house developed process simulator with the required capacities for development and training in process control. Today, computer-based supervisory and control systems are routinely employed in plants, running applications on-line and in real-time. A major job for the future, which has already started, will be to incorporate new methodologies into those industrial equipment and thus to bring such methodologies into process operation. A practical difficulty hindering development in this direction is that experiments with real industrial processes, both for the assessment of new strategies and for the required operator training, are difficult to carry out for reasons of economy and safety. Such limitations can be overcome with the available technology and theory, building new laboratory environments and tools, focusing on computer control and on the concepts related to the use of information in real-time.

The theory on process modelling and simulation plays a key role in the development of such environments and tools. For a significant number of processes, deterministic models can be written which, with appropriate parameters determined by

non-linear parameter estimation, represent well the process behaviour. A process simulator for studies on computer-based operation should have the capacity to represent adequately both intrinsic process characteristics and practical features of process operation. This means, essentially – (i) processing of non-linear dynamical models, including sensors and final control elements, synchronised with real-time; (ii) efficient mathematical treatment of process non-linearities, such as dead-times; (iii) communications through standard analog and/or serial signals; (iv) simulation of noisy measurements; (v) interactivity in real-time with the operation. One such tool has been developed within the research group.

The theoretical non-linear dynamical model of the crystallization process, implemented in the process simulator, includes growth rate dispersion mechanisms and the characterisation of crystal size distribution (CSD) by its first six linear moments. Values of the state variables (internal temperature, brix, vacuum pressure and level), together with those of other key variables (feed and steam properties) are made available as standard analog output signals, as if they came from industrial sensors. Also, standard analog input signals, corresponding in practice to the commands to the control valves, are received and translated as inputs to the integration routines. Noises can be superimposed to the output signals. Process loads and process characteristic parameters can be changed on-line. With such standard communications and working synchronised with real-time, the simulator provides the environment to which any formal industrial control system can be linked. Or, simply, manual operation can be performed. Studies aiming at the development of new strategies for computer-based crystallizer operation and the relevant operator training on the use of new technologies are now possible at low cost and in a safe environment.

New Autocatalytic Oxidations of Primary Alcohols in Cellulose in Phosphoric Acid

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Homogeneous oxidations at 4°C of cellulose dissolved in phosphoric acid with (i) sodium bromate with a small amount of sodium bromide, (ii) sodium chlorate with a small amount of sodium chloride and (iii) sodium chlorite have been studied. With these reaction systems the primary alcohol groups were completely (>95%) oxidised to carboxylic acids. Undesired ketones due to secondary alcohol groups oxidation were reduced with sodium borohydride. The selectivity observed is explained in terms of common autocatalytic oxidation mechanisms involving the positive hypohalous acidium ions, H_2OCl^+ and H_2OBr^+.

New Compounds From Microbiological Products of Sucrose

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A microbial product of sucrose, a high molecular weight levan, is readily made in high yield and high purity from commercial sucrose, sugarcane and sugarbeet juices and molasses.

Several derivatives of this levan have been synthesized. The characteristics and properties of these polymeric derivatives are described. Applications and uses of the compounds are outlined.

New Synthetic Pathways to C-glycosides

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C-glycopyranosyl compounds exhibit antimicrobial, antifungal, and antitumor activities, most probably based on enzyme inhibition, or interference with cell surface recognition and differentiation processes.

C-glycosidic analogues of that component would be metabolically stable, and thus offer enhanced therapeutic value. Synthesis of a configurational variety of e.g. amino (glyco-pyranosyl) methanes is thus an important synthetic goal. The amino group would allow linking the C-glycoside to a variety of scaffolds.

Our first approach has been to C-link a C-N synthon (HCN or CH_3NO_2) to the anomeric carbon of a natural carbohydrate. We have realised this with cyanide on glycal, on per-O-acetyl sugars and on cyclic acetal protected glycosyl fluorides, prepared by a novel method. The catalytic hydrogenation of glycosyl cyanides presented challenges and new synthetic possibilities. With CH_3NO_2, and 4,6-O-alkylidene protected D-glucose or D-mannose derivatives, we obtained very good yields of cyclic Henry condensation products in THF with a novel catalytic procedure.

The novel reduction of the resulting nitro (4,6-O-benzylidene-b-D-glycopyranosyl) methane with Fe°/Ni° in THF/H_2O/CO_2 readily supplied amino (4,6-O-benzylidene-b-D-glycopyranosyl) methane, which was diasterodiversified into D-allo, D-manno, and D-altro C-glycosides. These approaches fail, however, if prerequisite natural carbohydrate precursors are not available in a given case. Thus, a total synthesis scheme was also initiated.

Phtalimido acetaldehyde diethylacetal and 4-penten-2-ol, with $TiCl_4$, form 2-methyl-4-chloro-6-phtalimido-methyl tetrahydropyran, which was functionalized into phtalimido (6-deoxy-b-D,L-hexopyranosyl) methanes. Chiral extensions of this method are possible.

C-"disaccharides" became available from the Ferrier "dimerisation" of glycals, and from the hydrogenation of glycosyl cyanides.

Oxidized and Carboxy-alkylated Carbohydrates and Some Potential Applications

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Converting carbohydrates into carboxylates or polycarboxylates is an obvious way of upgrading renewables. The (poly)carboxylates obtained may display unique properties or may enter the competition with fossil-based materials such as poly-acrylates.

Methods to introduce carboxylate groups include carbohydrate oxidation and carboxy-alkylation.

Progress in oxidation is still substantial. Some old methods are revised (noble metal catalysis, nitrate/nitrite oxidation) and new methods come to the fore. Here, the amazingly selective TEMPO-catalyzed 6-oxidation of low and high molecular mass pyranose systems will be discussed.