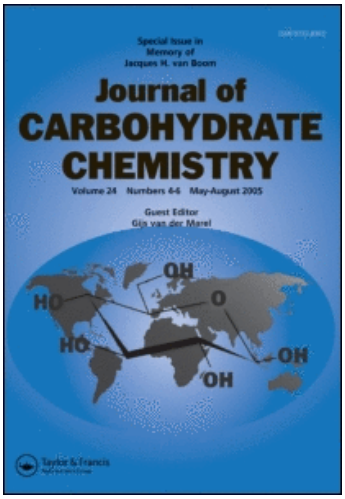


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# ULTRASOUND PROMOTED GLUCOSE OLIGOMERIZATION UNDER FISCHER GLYCOSYLATION CONDITIONS: STRUCTURAL ASPECTS

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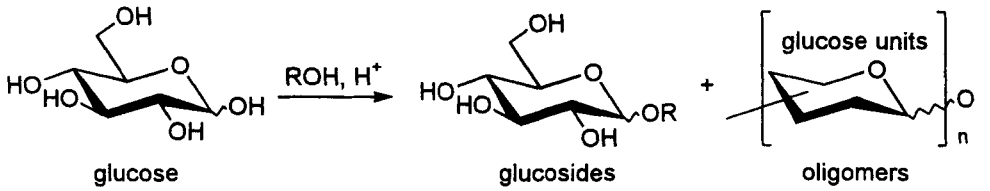
## ABSTRACT

The structure of glucose oligomers obtained by sonochemical glucose polymerization in dodecanol under Fischer glycosylation conditions was investigated. Oligomers having a degree of polymerization up to 23 were observed, with a mean value higher for the sonocatalyzed reaction compared to classical heating, as revealed by mass spectroscopy using the MALDI-TOF technique. The presence of anhydro terminal units was also ascertained by this method. Glycosidic bond types and branching ratios were evaluated after chemical degradation of the oligomers.

## INTRODUCTION

In the context of our studies on the effects of ultrasound in carbohydrate chemistry, we found that under Fischer glycosylation reaction conditions (Scheme 1),




**Scheme 1**

glucose was transformed into oligomeric species when the alcoholic acceptor was poorly reactive. This oligomerization process was shown to occur more easily in the presence of acidic bentonites, such as KSF/O, and was favoured under ultrasonic irradiation.[1]

The formation of such oligomers, based on the polymerization reaction of glucose, has been studied in connection with the success of polydextrose, a low calorie food ingredient which is now produced on the thousand-ton scale. The structural complexity of these polyglucose molecules is due to the various types of glycosidic junction binding monomers to each other, to the branching occurrence, and to the chain length.[2-5] Furthermore, chain termination of the oligomerization process can proceed through an intramolecular glycosylation process leading to anhydro derivatives. In the manufacturing process of polydextrose, developed by Rennhard at Pfizer central Research,[6] sorbitol is added thus limiting the average degree of polymerization (DP) by terminating the chain with this polyol which is not subject to oxonium formation.

The increased occurrence of glucose oligomers was observed in the particular case of dodecanol which, under classical conditions, provided dodecyl glucosides as the major products. The presence of water in the medium appeared to be responsible for the aggregation of the glucose particles in suspension, leading to a gummy hydrated glucose phase in which the autoglycosylation process was favoured (Figure 1).

The competitive hydrolysis of the glucosides, although detected, could not be the unique cause of the observed differences. The effect of ultrasound was shown to be related to an acid transfer from the solid catalyst to the liquid phase, but essentially to the efficiency of the phase mixing in heterogeneous systems allowing the trapping, by the glucose suspension, of the residual water present in the catalyst as well as that produced by the glycosylation reaction. This was confirmed in diglyme, in which only oligomeric

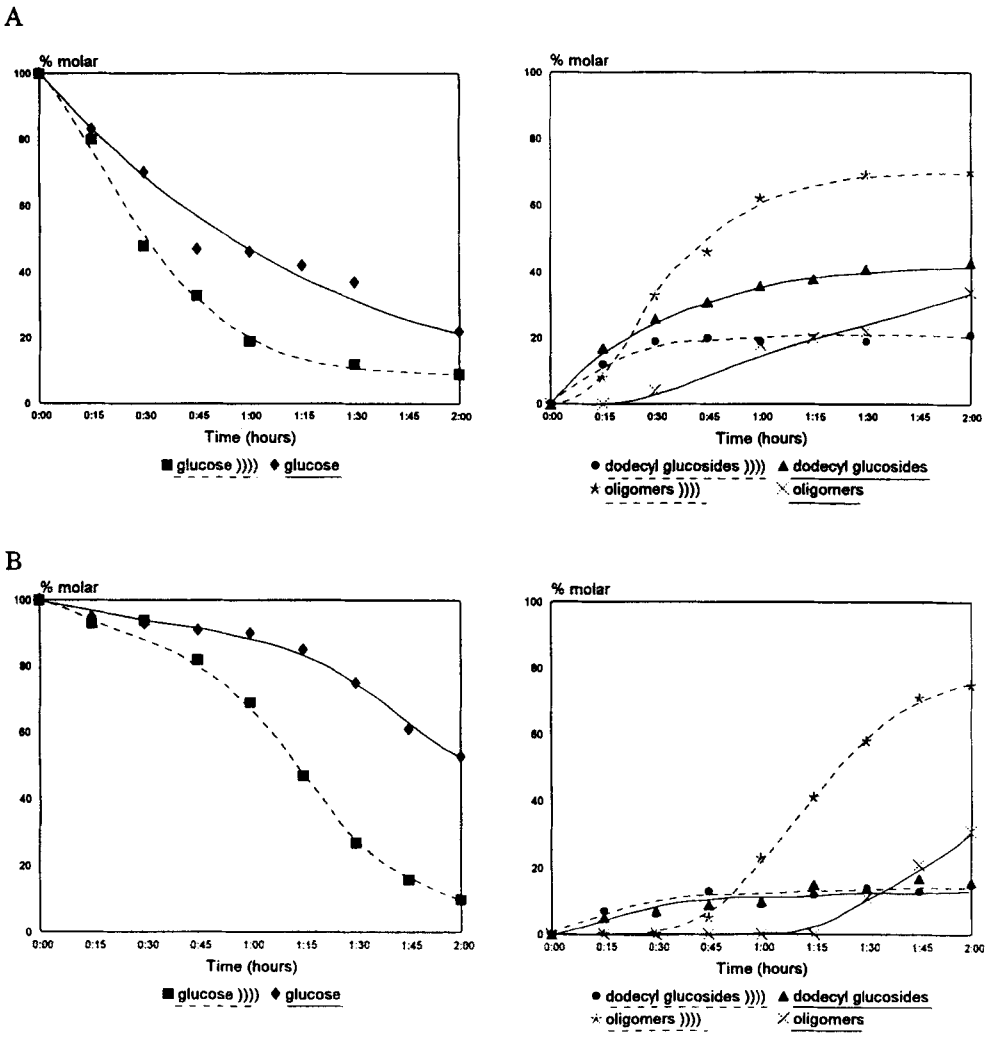



**Figure 1**. Evolution of the reaction of glucose in dodecanol at 115 °C under silent (—) and ultrasound (--) conditions (A: 1% (w/w) *p*-TsOH; B: 5% (w/w) KSF/O).

species (mixed with unreacted glucose) were formed. We now report on the structure of these oligomers obtained under sonochemical conditions.

## RESULTS AND DISCUSSION

The solid residues obtained under ultrasonic irradiation from the dodecanol suspension were first analyzed by $^{1}H$ and $^{13}C$ NMR spectroscopy in $D_2O$ and $d_6$-DMSO, showing that no alkyl chain was present. In the obviously complex mixture of compounds, typical $^{13}C$ NMR patterns corresponding to a polyglucose structure could be assigned, as compared to those observed for the polyglucose structure obtained via an HF based methodology developed by one of us.[7] Distinctive peaks were observed at *ca.* 92 ppm and 96 ppm, respectively, typical of C-1α and C-1β from residual glucose and terminal reducing glucose units, and at 96-100 ppm and 102-104 ppm, respectively, of C-1α and C-1β from non reducing glucose units. At *ca.* 66-68 ppm are found signals corresponding to C-6 atoms involved in a 1→6 glycosidic bond, whereas other C-6s are seen at *ca.* 61 ppm or below. Typical shifts for C-2, 3 and 4 atoms involved in glycosidic bonds were representative of minor components in the mixture.[8]

Quantification of the remaining free glucose by enzymatic assay revealed a 12 % (by weight) glucose content in the solid arising from the sonochemical reaction, and 17 to 40 % in the solid arising from the classical reaction, which was much less reproducible. Acidic hydrolysis (1 M $H_2SO_4$, 1 h, 120 °C) yielded only glucose, as measured by the same enzymatic method, in an amount consistent with a polyglucose structure for the oligomers, therefore establishing unambiguously their composition.

Liquid chromatography analysis using an $NH_2$-bound column and acetonitrile-water elution (65:35) permitted estimatation of the weight proportions of low-mass oligomers (up to DP 4) in the mixture. For the sonocatalyzed reaction, the following proportions were measured: 12 % (remaining glucose, consistent with the enzymatic assay), 12 % (dimers), 11 % (trimers), whereas in the silent reaction, the amounts were respectively 40, 6 and 6 %. Peaks were integrated on the basis of samples containing glucose, maltose and maltotriose for which the same area/weight ratio was measured. For higher DPs, quantification was less accurate, but from the comparison between the two