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Research Paper

Micellar effect on the direct Fischer synthesis of alkyl glucosides

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ABSTRACT

This manuscript presents results from the investigation on the synthesis of alkyl glucosides by the novel, very efficient and environmentally friendly protocol of the Fischer-type synthesis from unprotected glucose and aliphatic alcohols. The use of the dual functionality catalysts (surfactant + acid catalyst) and micellar reaction system are the main novelty of described method. It has been found, that in developed method of synthesis the reaction of unprotected glucose with aliphatic alcohols carried out with significantly different route, than the normal (classical) route and leads to alkyl glucopyranoside derivatives with high yields. In progress analyses by DLS, HPLC and GC/MS confirm the general postulated pathway of developed method.

1. Introduction

Alkyl glucosides (AGs) are considered as a very important class of biodegradable nonionic surfactants. AGs contain a carbohydrate head group (glucose, galactose, maltose, xylose etc.) and hydrocarbon tail (usually a linear alkyl chain of different length) [1–5]. AGs have numerous important applications as a main components of personal care products, cosmetics, in the preparation of microemulsions (especially in detergents and pesticide formulations) because of their excellent behavior at interfaces and also as agents for extraction of organic dyes and in the membrane protein research [6–8]. The common method of the synthesis of alkyl glucosides is Fischer glycosylation through direct or transacetalization route. In the direct synthesis (one-step protocol), fatty alcohol reacts with glucose or commercial glucose oligomers (e.g. glucose syrup, starch) producing a complex mixture of AGs with various degree of oligomerization ($n \geq 1$, Scheme 1) [9,10].

The main disadvantage of this procedure, however, is poor solubility of carbohydrates in long chain aliphatic alcohols. One of the possible way to eliminate this inconvenience is to conduct this process in biphasic reaction system with phase transfer catalyst (ptc), such as ammonium salts or ammonium ionic liquids [11–15]. A special case of biphasic catalysis is the synthesis in micellar reaction systems [16–18]. Formation of micelles results in a great increase in interfacial surface of two immiscible phases, which makes the reaction proceeding at the interface more effective. Synthesis in micellar reaction systems, such as microemulsion is nowadays one of the most interesting and promising method applied in organic synthesis [19,20]. One of the most spectacular example described in literature of "micellar" effect is esterification reactions [21–23]. Water formed during esterification reaction is not removed from the reaction mixture by conventional methods, but is captured inside the micelles. This phenomenon is the main essence of this method. Synthesis in biphasic systems has been also applied in carbohydrate chemistry, in particular in enzymatic methods of the synthesis of alkyl glucosides. Water in oil microemulsions with reverse micelles provide an interesting alternative to common organic solvents in enzyme catalysis with strong hydrophilic substrates, such as carbohydrates. Several examples of the synthesis of alkyl glycosides in reverse micelles using glycosidases as enzyme catalysts were reported with satisfying results compared to standard aqueous reaction media [24–29].

The use of micelles for separation of reactants was first described by Kobayashi in esterification of carboxylic acids and alcohols [22]. The surfactant-type acid catalyst (dodecylbenzenesulfonic acid, DBSA) and organic substrates in water form microdroplets with hydrophobic interior. For lipophilic substrates (carboxylic acids and alcohols), the equilibrium position between the substrates and the products (esters) lies at the ester side and water molecules would be moved out of the droplets due to hydrophobic nature of their interior.

Application of interfacial phenomena in synthesis of alkyl glucosides is very limited. Only a few reports in this field described the use of micellar reaction systems, but not in the synthesis of alkyl glucosides directly from the unprotected glucose. Although Kobayashi et al. reported stereoselective C-glycosylation in water in microemulsion reaction system with the use of DBSA as a surfactant catalyst, but in this method only fully protected (acetylated) sugars were used [30]. Direct synthesis of alkyl glucosides from peracetylated 1-bromoglucose and aliphatic derivatives of phenols was also described by Kumar [31]. The reaction was carried out in the presence of surfactant ionic liquids,

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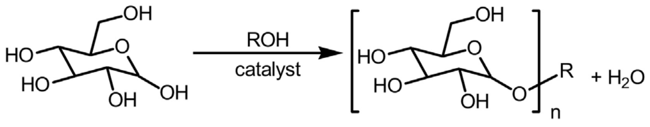


Scheme 1. Synthesis of alkyl glucoside, "classic" route.

which play a dual role both as simple phase transfer catalyst and solvent.

Fischer glycosidation may be considered as a very similar to esterification reaction (acidic catalyst and water as a main by-product). Our idea was based on the methodology successfully applied in the esterification reaction. In contrary to the above described esterification reaction, both reagents (glucose) and products (alkyl glucoside, water) have strong hydrophilic nature. This could suggest, that it will be difficult to remove water from the reaction mixture. Our study, however, clearly showed, that it could be done. We demonstrated, that Fischer glycosidation reaction in micellar system may be carried out according to similar methodology, after some modification.

This paper presents investigation of the synthesis of alkyl glycosides direct from glucose and aliphatic alcohols in microemulsion reaction system. The use of micellar reaction system in the synthesis of alkyl glucosides from alcohols and unprotected glucose has been described for the first time. The proposed reaction pathway is presented below (Scheme 2).

2. Experimental

2.1. Materials

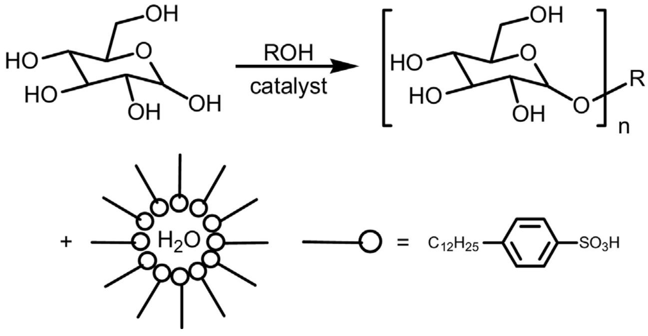
D-glucose (Sigma-Aldrich), 1-octanol, 1-decanol and 1-dodecanol (Alfa Aesar), dodecylbenzenesulfonic acid (DBSA) 95% (Sigma-Aldrich), methanesulfonic acid 99% (Sigma-Aldrich) and octyl-β-glucopyranoside (Sigma-Aldrich) were used as received. Glucopon 225 DK (C_8-C_{10} alkyl polyglucoside, BASF) was used as commercial alkyl glucoside surfactant for comparative synthesis.

2.2. Synthesis procedure

A typical reaction was carried out by adding 3.6 g (0.02 mol) glucose to a 100 ml glass reactor containing 0.2 mol of corresponding alcohol and 0.33 g (0.01 mol) dodecylbenzenesulfonic acid. The resulting suspension was agitated intensively (700 rpm) at desired temperature for 24 h. After that the reaction mixture (clear liquid) was cooled down to room temperature and analysed (GPC and GC/MS).

2.3. Analytical methods

High performance liquid chromatography (HPLC) analyses were carried out on Dionex UltiMate 3000 chromatograph (Thermo Fisher Sci.) and RP-18 Purospher HPLC column 250 × 4.6 mm, 5 µm. The system was fitted with ELSD 2000 UV detector (Alltech, 50 °C, 1.5 ml/min N_2) and methanol/water was used as the mobile phase (0.5 ml/min flow rate). Data were collected and processed using CHROMELEON (version 6.80) software. Analyses were performed at 30 °C and chromatograms of synthesized alkyl glucosides are presented in Fig. S1–S3 (Supporting information).



Scheme 2. Synthesis of alkyl glucosides, "microemulsion" route.

GC/MS analyses were carried out on the head-space system using HP 5890 Series II chromatograph equipped with flame ionization detector, capillary column, Ultra-high-2 (5HT), l = 15 m, d = 0,32 mm. All samples were transformed into silane derivatives with BSA (*N*,*O*-bis(trimethylsilyl)acetamide). Instrument settings: injector temp. − 360 °C, detector temp. − 380 °C. Temperature programming: initial isotherm 100 °C – 1 min, 100–380 °C – gradient 15 °C/min., final isotherm 380 °C − 3 min. Carrier gas: argon − 1.8 ml/min. GC/MS chromatograms and corresponding MS spectra are presented in Figs. S4–S13 (Supporting information).

Dynamic Light Scattering (DLS) analyses were performed with Zetasizer Nano ZS (Malvern) equipped with vertically polarized incident light of wavelength = 633 nm, supplied by a He-Ne laser. Measurements were carried out at angle 173° at 25 or 50 °C. The apparent hydrodynamic diameter of aggregates formed in studied materials, Dh, was calculated using the Stokes-Einstein equation from data derived by cumulants analysis and was given as average from 4 measurements. All samples were filtered before measurements through Pureland PVDF syringe filters of the nominal pore size 0.22 µm. Size distributions of micelles for synthesized alkyl glucosides are presented in Fig. S14 and in Table S1 (Supporting information).

3. Results and discussion

3.1. Synthesis of alkyl glucosides

To demonstrate our assumptions reactions of D-glucose with selected aliphatic alcohols have been conducted under biphasic (micellar) reaction conditions in the presence of dodecybenzenesulfonic acid (DBSA) as surfactant catalyst (Table 1). It has been examined in terms of alcohol used, effect on additional amount of water and reaction temperature. The results clearly demonstrate, that DBSA effectively catalysed this reaction. Firstly, the reaction of glucose with 1-octanol (the molar ratio of glucose to alcohol = 1:10) has been investigated in the presence of dodecylbenzenesulfonic acid (5 mol% in relation to glucose) as surfactant-type Brønsted acid for 24 h at 60 °C, 70 °C and 80 °C, with addition of water (10 wt% in relation to glucose). In the presence of water the conversion of glucose (determined by HPLC analysis) decreased from 96.1% at 60 °C to 55.2% at 80 °C (Table 1, entries 1–3). It has been observed, that increasing reaction temperature had a negative impact on glucose conversion. In the absence of additional amounts of water the situation has significantly changed. At 60 °C conversion of glucose was 79.7%, but after increasing the temperature to 80 °C conversion was also increased and reached 99%.

Table 1
Results of Fischer synthesis of alkyl glucosides in presence of surfactant- type Brønsted catalysts.

Entry	Alcohol	Catalyst	Reaction temp. °C	Water wt%	Conversion %
1	1-octanol	DBSA	60	10	96.1
2	1-octanol	DBSA	70	10	66,3
3	1-octanol	DBSA	80	10	55.2
4	1-octanol	DBSA	60	–	79.7
5	1-octanol	DBSA	70	–	80.5
6	1-octanol	DBSA	80	–	99
7	1-decanol	DBSA	80	–	98.2
8	1-dodecanol	DBSA	80	–	97.5
9	1-octanol	APG + KMS	80	–	45.7

(reaction conditions: glucose: alcohol molar ratio − 1:10; DBSA − 5 mol%; 24hr; 700 rpm).