NEW GLYCOSIDES OF LIGNIN

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New biodegradable surface active agents were prepared by glycosidation of prehydrolysis lignin with the D-glucose using anhydrous ferric chloride as the catalyst which afforded polymeric alkyl, benzyl and aryl glucofuranoside derivatives of lignin. Moreover, a series of novel lignin-based surface active agents was obtained by subsequent oxidation of the primary alcohol groups of D-glucose into carboxyl groups by 2,2,6,6-tetramethyl-1-piperidine oxoammonium ions with sodium hypochlorite and sodium bromide in an aqueous alkaline solution at pH 11.

Keywords: glycosylation, lignin-glucoside, lignin-glucosiduronic acid, surface tension

Introduction

Lignin sulfonate has long been used as surface-active agent. The application of other industrial lignins as surfactants requires modifications to improve their water solubilization. Lignin, co-product of a prehydrolysis stage of kraft beechwood pulping representing low molecular sulfur-free lignin, was found to be useful for the preparation of composite polypropylene films [1] and dispersing agents [2]. Surface active agents based on carbohydrates were first patented in 1930. Industrial applications were found mainly for sucrose and some alditol esters and owing to their higher water solubility ethoxy derivatives [3]. Glycosidic type surfactants C6-C12-alkyl-β-D-glucopyranosides have been prepared by the Koenigs-Knorr reaction [4].

Ferrieres [5] described O-glycosylation of long chain alcohols with totally unprotected neutral carbohydrates, performed in heterogenous media and promoted by anhydrous ferric chloride, which afforded alkyl D-glycosides in high yields. Application of this method for the synthesis of several alkyl, aryl and benzyl α-D-glucosides as well as their β-anomers was described in our previous paper [6].

The objective of the present paper is the preparation new biodegradable surface active agents by glycosidation of prehydrolysis lignin with D-glucose according to Ferries [5] and subsequent oxidation of the primary alcoholic group of D-glucose into carboxyl groups in the prepared lignin derivatives.

Materials and Methods

Lignin samples. The sulfur-free preparation of average molecular weight 1900 was obtained by fractionation of hardwood prehydrolysate (170°C). It contained 19.1% OCH3 and 0.15% ash. Glycosidation procedure. To a suspension of D-glucose (3.6 g) in dry 1,4-dioxane (50 mL) at room temperature were added 3 g of appropriate lignin and, by small portions (9.72 g) of anhydrous FeCl3. After 24 h at room temperature and removal of the solvent, the residue was partitioned between n-butanol and 5% aqueous HCl. The organic layer was washed with acidic water solution, and the aqueous layers thus obtained were extracted with n-butanol (3x20 mL). The combined organic extracts were concentrated under reduced pressure.

Oxidation procedure. The lignin sample after glycosidation (1 g) was suspended in 200 mL of water containing 2,2,6,6-tetramethyl-1-piperidine
oxoammonium salt (50 mg), 1.6 g of sodium bromide and 95 ml of 5.0% (w/v) sodium hypochlorite solution and stirred for 2 h. The pH was adjusted to 10-11 and kept constant with 0.5 M NaOH. The majority of the reaction was conducted at 0° ± 2 °C. When the oxidation was finished (about 2 h), the reaction was quenched by adding 96% EtOH (10 mL), followed by neutralization with 4 M HCl. The oxidized glucose derivative of lignin was isolated by dialysis and subsequent lyophilization.

**Analytical methods.** The glucose content was determined by GLC analysis of neutral sugars as alditol trifluoroacetates. The amount of the glucuronic acid produced by oxidation of the primary alcohol groups to carboxylate groups was obtained by measuring the amount of sodium hydroxide that was required to maintain the pH at 11. The uronic acid content of the final oxidized lignin sample was determined according to the Dische carbazole method [7] after acid hydrolysis of the oxidized lignin-glycosidic sample.

Infrared spectra were measured on a NICOLET Magna-IR 750 with DTGS detector and OMNIC 3.2 software. The samples were pressed into KBr pellets with sample/KBr ratio of 2/200 mg. 128 scans at a resolution of 4 cm⁻¹ were averaged. Surface tension measurements were performed using tensiometer by Lecompte du Nouy, based on the ring method carried out at 25°C.

**Results and discussion**

Recently, Ferriers et. al. [3] revealed a new type of O-glycosylation of long chain alcohols (n-octyl, n-decyl, n-dodecyl, 10'-undecenyl) with totally unprotected uronic acids and neutral carbohydrates, performed in aqueous media and promoted by anhydrous ferric chloride, which afforded alkyl D-glycofuranosid uronic acids and alkyl D-glycofuranosides, respectively, in high yields. These alkyl glycofuranosides are becoming increasingly important as surfactants [8] or liquid crystals [9] and can be obtained through a convenient one-pot synthesis. By application of this method on the lignin model monomeric compounds, alkyl and aryl α and β-D glucopyranosides as well as glucopyranosides were prepared. [4]

**Figure1. FTIR spectra of the prehydrolysis lignin (A), glycoside lignin (B) and glycosiduronic acid lignin (C).**
Glycosidation of prehydrolysis lignin with D-glucose in heterogeneous media (1,4-dioxane) using anhydrous ferric chloride as a catalyst afforded new polymeric glucoside of lignin containing approximately 4.2% of D-glucose. The prepared lignin derivatives were examined by IR spectroscopy (Fig. 1). The presence of bound D-glucose is evident from the new absorption bands at 995 and 1092 cm\(^{-1}\) corresponding to C-O and C-C stretching vibrations and at 1160 cm\(^{-1}\) assigned to C-O-C antisymmetric stretching vibrations [10].

Based on our previous results with lignin model compounds, it can be suggested that the reaction product of lignin with D-glucose contains predominantly lignin-glycosidic linkages as illustrated in Figure 2.

In addition, the lignin-glucuronosiduronic acid was obtained by subsequent specific oxidation of the primary alcoholic group of D-glucose to carboxyl groups in the prepared glucoside of lignin with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion with sodium hypochlorite and sodium bromide in an aqueous alkaline solution at pH 11, according to de Nooy [11] and Chang [12]. The new lignin-glycosiduronic acid derivate, prepared this way contains approx. 3.9% of D-glucuronic acid. Under these conditions, other hydroxyl groups of glucose and as well as aliphatic alcohols are resistant towards oxidation (13).

The IR spectrum of this lignin derivative (Fig 1 C) shows that the carboxyl group of glucuronic acid contributes to the increase in intensity in the non-conjugated lignin carbonyl region (1707 cm\(^{-1}\)). Moreover, the new band at 1235 cm\(^{-1}\) corresponding to carboxyl vibration was revealed. This observation indicates the transformation of \(-\text{CH}_2-\) into \text{COOH} groups [10].

The conversion of lignin-glucosides into glucuronic acid lignin derivatives is shown in Figure 3.

An important property of surfactants is their positive adsorption in the water-air phase boundary, the result of which is the decrease of the surface tension of water. Both new sulfur-free lignin derivatives were tested from the viewpoint of their surface activity tension. The values determined, as illustrated in Figure 4, indicate that both types of modifications increase the surface activity of prehydrolysis lignin significantly due to its high hydrophilicity.

It can be assumed that the activity of surfactants depends upon the presence of different types of polar hydroxyl and carboxyl groups. The glycosiduronic acid derivative of lignin contains both hydroxyl and carboxyl groups which increase its hydrophilicity. Therefore, this derivative exhibits high solubility in water and also shows the highest surface activity.
Conclusion

Based on the obtained results, it can be concluded that glycosidation represents a rapid and simple method for increasing solubility and surface activity of lignin. This effect is more significant after subsequent oxidation of primary alcoholic groups of glucose present in the prepared lignin-glucoside. The surface properties of the new D-glycoside and D-glycosiduronic acid derivatives of beech wood prehydrolysis lignin showed that the chemical modification used yielded sulfur-free, modified biopolymers which exhibit properties of biodegradable polymeric surfactants.

Acknowledgment

We are grateful to the Slovak Grant Agency (project 2/506098) for financial support.

References