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Estrogenicity of Octyl Glucoside Synthesized by Direct Glucosidation as Non-Endocrine Disruptive Surfactant

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The estrogenicity of octyl glucoside was studied with its preparation method using microporous zeolites. Its estrogenicity was estimated using E-assay method to confirm the possibility as non-endocrine disruptive surfactant. The octyl glucoside was synthesized from D-glucose with 1-octanol by direct glucosidation. The high conversion of D-glucose was obtained on H-FAU zeolite which has a mild acid strength. The conversion and yield were improved with increasing of acid site amount of the zeolite catalysts. The octyl glucopyranoside is more hydrophilic than nonylphenol and has a high wettability. The octyl glucosides represented extremely lower estrogenic cell proliferation compared with nonylphenol.

Keywords: Estrogenicity, Octyl Glucoside, Direct Glucosidation, Zeolite, Surfactant.

1. INTRODUCTION

Surfactants have been used as emulsifiers, detergents, foaming agents, wetting agents, and dispersants.[1] Some of the surfactants are noted to be toxic to humans and ecosystems. The toxic surfactants have been restricting by proposal or spontaneous restrictions. Alkyl phenol ethoxylates have been used as major surfactants. They break down in the aerobic conditions found in sewage treatment plants and in the metabolite, nonylphenol, which has been found to be an endocrine disruptor.[2] Concerns have been expressed about alkylphenols owing to their environmental prevalence and their potential effect as xenoestrogen and endocrine disruptors.[3] Nonylphenol has been reported to have estrogenic activity based on its proliferation induction and up-regulation of the progesterone receptor I human estrogen-sensitive breast tumor cells.[4] It has been established recently that nonylphenol has antiandrogenic activity, which means that it affects the appropriate functioning of the androgens which are necessary to the normal growth and reproductive organs of males.[5]

Long-chain alkyl glucosides have excellent surfactant properties with biodegradability and low toxicity.[6] Therefore, they have recently been considered as alternative surfactants to alkylphenols. Octyl glucoside (*n*-octyl-*β*-D-glucoside) is a detergent frequently used to solubilise integral membrane proteins for studies in biochemistry. It has become one of the most important detergents for purification of membrane proteins because it generally does not denature the protein and can readily be removed from final protein extracts. Octyl glucoside (OG) been also proposed as a conditioning agent to prevent microbial colonization of contact lenses, due to its ability to lower the hydrophobicity of contact lenses and prevent adhesion of cells.

In this study, the estrogenicity of OG was evaluated compared with that of nonylphenol using E-assay method. The preparation method of OG was also suggested. The OG from D-glucose with 1-octanol was prepared by direct glucosidation reaction on microporous zeolite catalysts. The catalytic activities of the zeolite catalysts were evaluated in the direct glucosidation reaction. The physical properties of octyl glucopyranoside were analyzed compared with nonylphenol. We also estimated the characteristics of cell proliferation of human breast cancer cell line (MCF-7) to the octyl glucopyranosides and nonylphenol to compare their estrogenicities.

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2. EXPERIMENTAL DETAILS

2.1. Catalysts

FAU (zeolite Y, Si/Al = 3) was purchased from Zeobuilder Co. The MOR (Mordenite, Si/Al = 10) zeolite was also purchased from Tosoh Co. The cations of zeolites were exchanged with H^+ ion. We denote the H^+ ion exchanged zeolites following the zeolite code names, H-FAU and H-MOR.

2.2. Direct Glucosidation Reaction

OGs were prepared from D-glucose (Sigma, 99%) with 1-octanol (Aldrich, 99%) by direct glucosidation on the zeolite catalysts. D-glucose (2.5 g) and 1-octanol (50 mL) were introduced as the reactants. The reactants were put into the reactor with the zeolite catalyst. The reaction was carried out directly in the reactor with stirring at 130 °C. The compositions of the products were measured by GC equipped HP-1 capillary column and detected by an FID analyzer. The conversion was determined as the percentage of D-glucose consumed. The OG yields were determined as the percentage of the amount produced with respect to the sum of total products.

2.3. Characterization of the Zeolite Catalysts and Products

NH_3-temperature programmed desorption (NH_3-TPD) profiles were measured using a chemisorption apparatus. Surface tensions were measured using a ring and plate method tensiometer (Kruss K100, Germany) and maxmum bubble pressure tensiometer (Kruss BP2, Germany). Critical micelle concentration (CMC) was determined from the value of surface tension. Contact angles (CA) were measured using pendant drop tensiometer (Kruss DSA 100, Germany).

2.4. Estimation of Estrogenicities of OGPs and Nonylphenol

MCF-7 (Michigan Cancer Foundation-7) cell line as a human breast cancer cell line was induced in the estimation of estrogenicity. The cell line was cultivated on Dulbecco's modified Eagle's medium (DMEN) including 10% charcoal dextran treated fetal bovine serum (CDT-FBS) for 6 days. The sex hormone in a serum of CDT-FBS was removed by adsorption with a charcoal and dextran. Chemical stock solution dissolved in dimethylsulfoxide (DMSO) was diluted again to 0.1% solvent concentration with DMSO. The cell line was evaluated the MTT (2-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetra zolium bromide, Sigma) assay after cultivation in an incubator for 144 h. MTT was distributed as 0.1 mg/well and then cultivated again for 4 h. After DMSO injection to the cultivation medium, the sample was estimated the absorbance at 540 nm by spectrophotometer. The control was consisted of cultivation medium only. 17β-estradiol (99%, Sigma) and nonylphenol (99%, Sigma) were induced as positive controls and octyl-α-glucopyranoside (99%, Sigma-Aldrich), octyl-β-glucopyranoside (99%, Sigma-Aldrich) were used as the object controls in evaluation of estrogenicity.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activities of the Zeolite Catalysts

The acidities of the zeolites differed considerably according to their framework, as shown in Figure 1. The FAU zeolite has a lot of weak acid sites. On the contrary, the MOR zeolite has strong acid sites. In this glucosidation reaction, two OGs isomers i.e., the (α, β)-octyl glucopyranoside and (α, β)-octyl glucofuranoside isomers, were produced mainly as an anomeric mixture. A small amount of short-chain alcohols and their derivatives were also formed as byproducts through the decomposition of 1-octanol.

The catalytic activities of the zeolite catalysts are listed in Table I. Conversions of D-glucose were obtained above 80% on the two catalysts. The H-FAU catalyst showed a high yield of OGs. The yields of OG on the catalysts exceed 70%, but that on H-MOR zeolite was lower. The yield of OG and OGP selectivity were higher over the H-FAU zeolite catalysts. These results mean that the weak acid sites concentration of the zeolites can induce higher catalytic activity in the reaction.

3.2. Effect of Acidities and Pore Topologies of the Zeolite Catalysts

The FAU zeolite has tri-directional channels and super cavities in the pores. The MOR zeolite has narrow pore entrances and a straight pore channel. The yields of OGP and OGF exceeded 80% on the H-FAU zeolite catalysts.

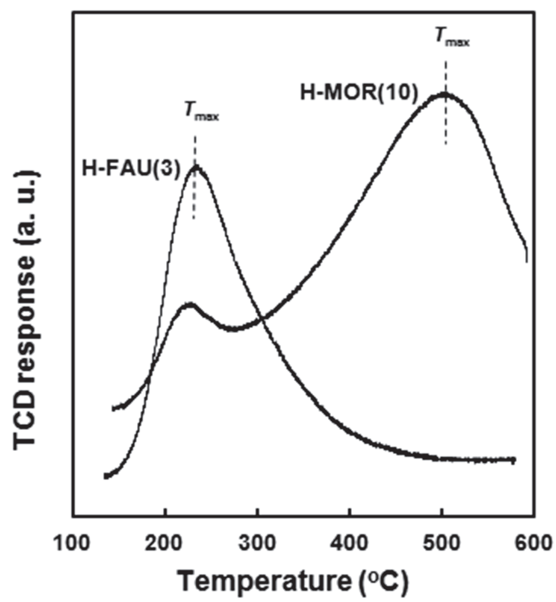

Figure 1. NH_3-TPD profiles of the zeolite catalysts.

Table I. Catalytic activities of the zeolite catalysts in the glucosidation.

Catalyst	Conversion (%)	Yield (%)		Selectivity (%)	
		OGP	OGF	OGP	OGF
H-FAU	93.1	63.2	18.3	77.5	22.5
H-MOR	81.2	20.5	23.1	47.0	53.0

The high catalytic activities were derived from weak acid sites. The yield of OGP was larger than that of OGF on the H-FAU zeolite catalyst. The selectivities of the two isomers depending on the pore structure of the zeolites are insensitive to the activation conditions. The furanosides are formed from the attack of the alcohol on the glucosyl oxonium intermediate. The more stable pyranosides are produced from them through a process of ring opening. In this process, the selectivities of the isomers are affected by the pore topologies. This suggests that the product selectivity may be closely dependent on the pore structure.

The H-FAU catalyst showed a high OGP selectivity. This is attributed to its high pore volume and numerous weak acid sites, leading the production of OGP. Its pore structure provides sufficient space volume to form pyranosides by the isomerization of the furanosides in the pore channels. On the contrary, the yield of OGF was higher than that of OGP on the H-MOR catalyst.

3.3. Physical Properties of OGPs and Nonylphenol

Figure 2 shows the surface tensions and contact angles of OGP and nonylphenol. The CMCs of were determined from the values of concentration at surface tension unchanging despite of increasing of their concentration. From the results, the CMC of OGP was determined as 2.2×10^{-2} mol/L and surface tension at CMC was 31.2 mN/m. The CMC of nonylphenol was measured as 1.2×10^{-4} mol/L, respectively. The CMC of OGP was higher than that of nonylphenol. The contact angle of OGP was lower than those of nonylphenol and water. This indicates that the OGP is more hydrophilic than nonylphenol and has a high wettability.

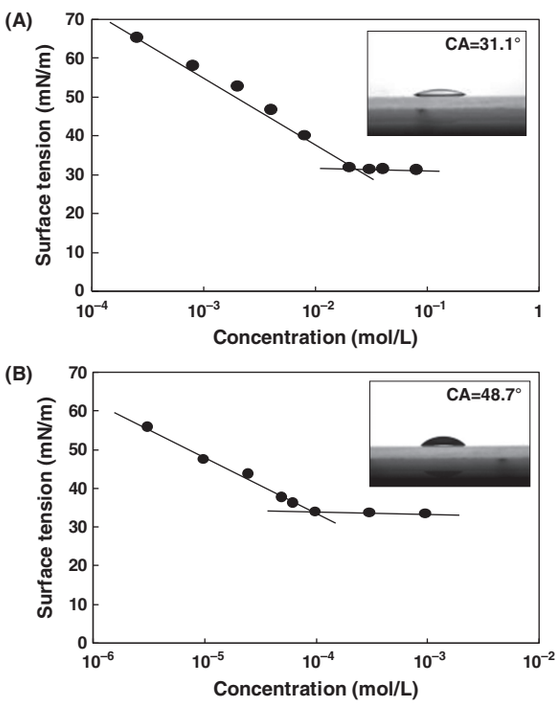

Figure 2. Surface tensions and contact angles of OGP (A) and nonylphenol (B).

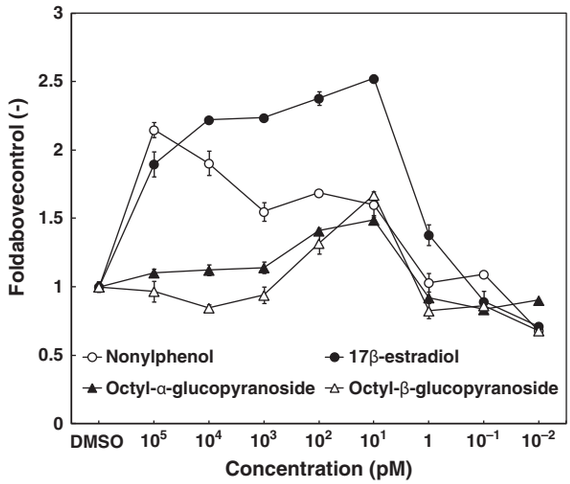

Figure 3. Estrogenicities of 17β-estradiol, nonylphenol, and OGPs compared with that of control.

3.4. Estrogenicities of OGPs and Nonylphenol

Figure 3 shows the cell proliferation of MCF-7 in 17β-estradiol, nonylphenol, and OGPs compared to the control. The cell proliferation rate of 17β-estradiol at 10 pM was increased 2.5 fold and that of nonylphenol was increased to 2.1 fold at 100 nM compared with that of control. Hence, those of OGPs are nothing but ca. 1.7 fold, respectively.

Table II lists relative proliferation effect (RPE) and relative proliferation potency (RPP) of OGPs and nonylphenol compared with those of 17β-estradiol as a relative basis. In this result, RPE and RPP of OGPs were represented lower than those of nonylphenol. The OGPs did not influence to the cell proliferation effect above 10 pM concentration compared with 17β-estradiol and nonylphenol. It means that the OGPs show low estrogen cell proliferation compared with 17β-estradiol and nonylphenol.

Table II. RPE and RPP of 17β-estradiol, nonylphenol, and OGPs.

Compounds	Concentration (nM)	RPE (%)	RPP (%)
17β-estradiol	10	100	100
Nonylphenol	10^5	85.3	20
Octyl-α-glucopyranoside	10	59.1	10
Octyl-β-glucopyranoside	10	66.3	10

4. CONCLUSION

The H-FAU catalyst has shown a high catalytic activity and OGP selectivity in the glucosidation. The conversion and yield were improved with increasing of acid sites of the catalysts. The catalytic activities are depended on the amount of weak acid sites of the zeolite catalysts. The OGP was more hydrophilic than nonylphenol and has a high wettability. The OGPs did not influence to the cell proliferation effect even a high concentration. The OGP show extremely low estrogenicity compared with nonylphenol.

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References and Notes

1. R. S. Boogar, R. Gheshlaghi, and M. A. Mahdavi, *Korean J. Chem. Eng.* 30, 45 **(2013)**.
2. M. Scott and M. N. Jones, *Biochimica et Biophysica Acta* 1508, 235 **(2000)**.
3. R. Thiruvenkatachari, S. Vigneswaran, and I. S. Moon, *Korean J. Chem. Eng.* 25, 64 **(2008)**.
4. A. M. Soto, H. Justicia, J. Wray, and C. Sonnenschein, *Environ. Health Perspect.* 92, 167 **(1991)**.
5. S. Kim and J. Kim, *Korean J. Chem. Eng.* 23, 747 **(2006)**.
6. N. Ferlin, L. Duchet, J. Kovensky, and E. Grand, *E. Carbohydrate Research* 343, 2819 **(2008)**.

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