

# Decyl Glucoside Synthesized by Direct Glucosidation of D-Glucose Over Zeolite Catalysts and Its Estrogenicity as Non-Endocrine Disruptive Surfactant

Kyong-Hwan Chung<sup>1</sup>, Hangun Kim<sup>2</sup>, Young-Kwon Park<sup>3</sup>, Byung-Hoon Kim<sup>4</sup>,  
Sun-Jae Kim<sup>5</sup>, and Sang-Chul Jung<sup>1,\*</sup>

<sup>1</sup>Department of Environmental Engineering, Suncheon National University, Suncheon 57922, Korea

<sup>2</sup>College of Pharmacy, Suncheon National University, Suncheon 57922, Korea

<sup>3</sup>School of Environmental Engineering, University of Seoul, Seoul 02504, Korea

<sup>4</sup>Department of Dental Materials, Chosun University, Gwanju 61452, Korea

<sup>5</sup>Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Korea

The estrogenicity of decyl glucoside was asserted as a non-endocrine disruptive surfactant with its preparation method using zeolite catalysts. Its estrogenicity was estimated using E-assay method. The decyl glucoside was synthesized by direct glucosidation from D-glucose with 1-decanol. The conversion and yield were improved with increasing of amount of acid sites of the zeolite catalysts. The decyl glucopyranoside is more hydrophilic than nonylphenol and has a high wettability. The decyl glucopyranosides exhibited extremely lower proliferation of estrogenic cell compared with nonylphenol.

**Keywords:** Decyl Glucoside, Estrogenicity, Direct Glucosidation, Zeolite, Surfactant.

## 1. INTRODUCTION

Surfactants are compounds that lower the surface tension between two liquids or between a liquid and a solid.<sup>1</sup> They may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.<sup>2</sup> The two major surfactants had been used a linear alkylbenzene sulfonates and the alkyl phenol ethoxylates. They break down in the aerobic conditions found in sewage treatment plants and in soil to the metabolite nonylphenol, which is thought to be an endocrine disruptor.<sup>3,4</sup> Nonylphenol was first reported to have estrogenic action based on its induction of proliferation and up-regulation of the progesterone receptor I human estrogen-sensitive breast tumor cell.<sup>5,6</sup>

Recently it has also been established that nonylphenol has antiandrogenic activity, i.e., is capable of interfering with the proper functioning of androgens that are essential for the normal development of males and their reproductive systems.<sup>7</sup>

Long-chain alkyl glucosides are non-ionic compounds with excellent surfactant properties, biodegradability, and low toxicity.<sup>8,9</sup> Therefore, alkyl glucosides with an alkyl chain have been concerned as alternative surfactants of alkylphenols recently.<sup>10</sup> They have several applications as cosmetic surfactants, food emulsifiers, and pharmaceutical dispersing agents.<sup>11,12</sup>

Decyl glucoside (DG), as a long-chain alkyl glucoside, has been applied in cosmetic formularies as a mild non-ionic surfactant. It is prepared by the reaction of glucose obtained from corn starch with decanol which is derived from coconut. Studies concerning the use of decyl glucose in antiseptic, sunscreen, and hair products are described in some of the published literature.<sup>13–15</sup>

In this study, the DG from D-glucose with 1-decanol was prepared by direct glucosidation reaction on acid zeolite catalysts. The catalytic activities of the zeolite catalysts were estimated in the glucosidation reaction. The physical properties of DG were analyzed compared with nonylphenol. We also evaluated the estrogenicity of DG compared with that of nonylphenol using E-assay method.

\*Author to whom correspondence should be addressed.

## 2. EXPERIMENTAL DETAILS

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<sup>+</sup> ion. We denote the H<sup>+</sup> ion exchanged zeolites following the zeolite code names, H-FAU and H-MOR.

DGs were prepared from D-glucose (Sigma, 99%) with 1-decanol (Aldrich, 99%) by direct glucosidation over the zeolite catalysts. D-glucose (2.5 g) and 1-decanol (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 DG yields were determined as the percentage of the amount produced with respect to the sum of total products.

Surface tensions were measured using a ring and plate method tensiometer (Kruss K100, Germany) and maximum 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).

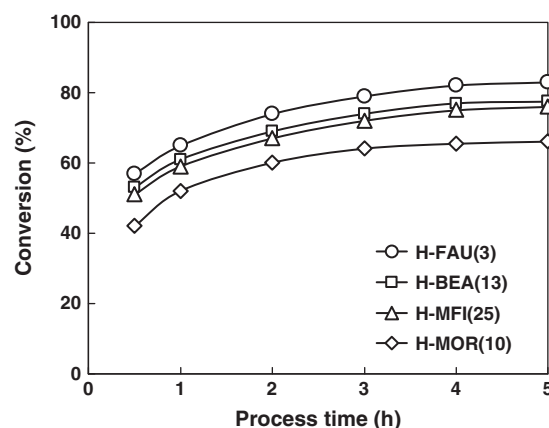
MCF-7 (Michigan Cancer Foundation-7) cell line as a human breast cancer cell line was induced in the estimation of estrogenicity. The cell line was cultivated on Dulbecco's modified Eagle's medium (DMEM). Chemical stock solution dissolved in dimethylsulfoxide (DMSO) was diluted again to 0.1% solvent concentration with DMSO. The cell line was evaluated the MTT (2-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, Sigma) assay after cultivation in an incubator for 144 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. 17 $\beta$ -estradiol (99%, Sigma) and nonylphenol (99%, Sigma) were induced as positive controls and decyl- $\alpha$ -glucopyranoside (99%, Sigma-Aldrich) was used as the object controls.

## 3. RESULTS AND DISCUSSION

### 3.1. Catalytic Activities of the Zeolite Catalysts

In this glucosidation reaction, two DGs isomers i.e., the ( $\alpha$ ,  $\beta$ )-decyl glucopyranoside (DGP) and ( $\alpha$ ,  $\beta$ )-decyl glucofuranoside (DGF) 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-decanol.

Figure 1 presents the variation of D-glucose conversion with process time over various zeolite catalysts. The conversion was increased with increasing process time to 5 h.



**Figure 1.** Variation of conversion of D-glucose with process time on various zeolite catalysts at 130 °C.

The catalytic activities of the zeolite catalysts are listed in Table I. Conversion of D-glucose was obtained above 70% on the H-FAU zeolite catalyst. The H-FAU catalyst showed a high yield of DGs. The selectivity of DG exceeded 70% on the H-FAU zeolite. These results mean that the weak acid sites of the zeolites can induce higher catalytic activity in the reaction.

### 3.2. Physical Properties of DGPs and Nonylphenol

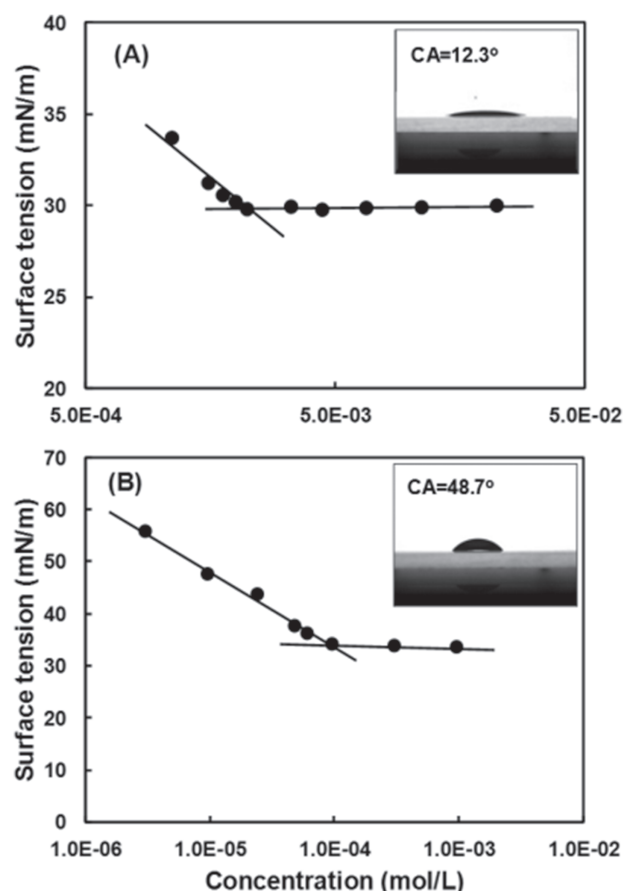
Figure 2 shows the surface tensions and contact angles of DGP and nonylphenol. The CMCs of DGP were determined from the values of concentration at surface tension unchanging despite of increasing of their concentration. From the results, the CMC of DGP was determined as  $2.2 \times 10^{-3}$  mol/L and surface tension at CMC was 30.1 mN/m. The CMC of nonylphenol was measured as  $1.2 \times 10^{-4}$  mol/L, the surface tension at CMC was 34.4 mN/m, respectively. The surface tension at CMC were similar between two materials. The contact angle of DGP was lower than those of nonylphenol and water (CA = 74.8°). This indicates that the DGP is more hydrophilic than nonylphenol and has a high wettability.

### 3.3. Estrogenicities of DGP and Nonylphenol

To test the estrogenic effect of DGP, we performed the E-assay on MCF-7 cells using 17 $\beta$ -estradiol and nonylphenol as positive controls. Compared to DMSO-treated cells, 17 $\beta$ -estradiol and nonylphenol promoted MCF-7 cell proliferation most potently by 3.08 and 2.60 fold, respectively,

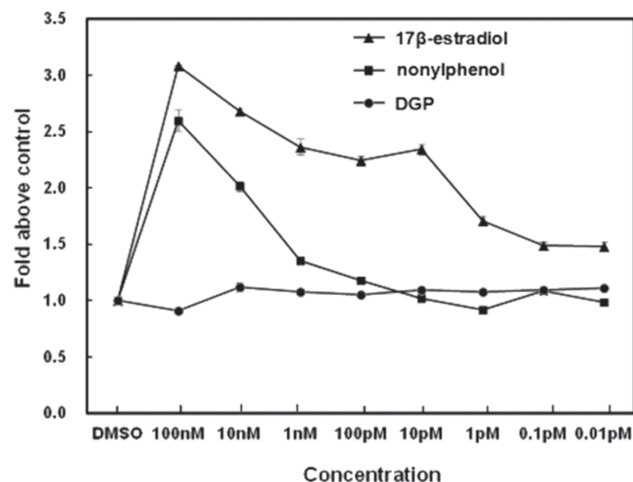
**Table I.** Catalytic activities of the zeolite catalysts in the glucosidation.

Catalyst	Conversion (%)	Yield (%)		Selectivity (%)	
		DGP	DGF	DGP	DGF
H-FAU (3)	83.1	55.1	20.2	73.2	26.8
H-BEA (23)	77.5	38.3	32.9	53.8	46.2
H-MFI (25)	75.8	35.2	27.3	56.3	43.7
H-MOR (10)	63.0	15.4	40.0	27.8	72.2



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

at 100 nM (Fig. 3). In contrast, DGP showed maximally 1.12 times increase in MCF-7 cell proliferation at 10 nM. These results demonstrated that DGP seldom stimulate MCF-7 cell proliferation at tested concentrations and has



**Figure 3.** Estrogenicities of 17β-estradiol, nonyl phenol, and DGP compared with that of control.

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

Compounds	Concentration (nM)	RPE (%)	RPP (%)
17β-estradiol	100	100	100
Nonylphenol	100	84.4	100
DGP	10	36.4	0.001

little estrogenic effect than those observed in same concentration of 17β-estradiol or nonylphenol.

Figure 3 shows the cell proliferation of MCF-7 in 17β-estradiol, nonylphenol, and DGP 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 DGP are nothing but ca. 1.7 fold, respectively.

Table II lists relative proliferation effect (RPE) and relative proliferation potency (RPP) to the DGP and nonylphenol compared with those of 17β-estradiol as a relative basis. In Table II, relative proliferation effect (RPE) and relative proliferation potency (RPP) of the compounds were shown, and DGP has 36.4% of RPE compared to 17β-estradiol and 0.001% of RPP compared to nonylphenol. DGP has lower estrogenic effect than 17β-estradiol or nonylphenol.

In this result, RPE and RPP of DGP were represented lower than those of nonylphenol. The DGP did not influence to the cell proliferation effect above 10 pM concentration compared with 17β-estradiol and nonylphenol. It means that the DGP show low estrogen cell proliferation compared with 17β-estradiol and nonylphenol.

#### 4. CONCLUSION

The high conversion of D-glucose was obtained on H-FAU zeolite catalyst. It seems that the result arises from the relatively a large pore volume and a high concentration of mild acid sites of the zeolite. The pore structure of H-FAU zeolite would provide an enough space time to form pyranoside by isomerization of furanoside in its wide pore channels. The DGP exhibited similar physical properties with nonylphenol. However, it showed an apparently lower estrogenic effect than nonylphenol which confirmed from the result of MCF-7 cell proliferation.

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