

Synthesis of New Extended Surfactants Containing a Xylitol Polar Group

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ABSTRACT: A new class of extended surfactants was prepared in which the spacer arm between the polar portion and the hydrophobic alkyl chain was a polymer of propylene glycol with an average length of six propylene oxide units. The polar head was a single or double xylitol moiety or a xylitol molecule with carboxylic acid functionality. Surfactants containing double xylitol polar head groups showed a much higher critical micelle concentration value than surfactants with a single polar head.

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Carbohydrates are hydrophilic biodegradable substances with a very low level of toxicity. As such, they are good candidates as polar groups for surfactants for use in pharmaceutical and cosmetic formulations or other environmentally friendly products (1–9). On the other hand, the so-called extended surfactant structure, which exhibits an intermediate polarity spacer, e.g., a polypropylene glycol link, between the conventional hydrophilic and hydrophobic groups, allows a smooth change from polar to apolar media and provides an enhanced solubilization of hydrocarbons and even naturally polar oils (10–13). Previous publications have dealt with extended surfactants with a variety of polar head groups, including some C₆ carbohydrates (12,13). The present paper reports the synthesis and amphiphilic properties of new extended surfactants containing a C₅ carbohydrate, either as a single/double xylitol hydrophile or as the combination of xylitol with a sodium carboxylate for enhanced hydrophilicity.

The lipophilic tail of these compounds is an *n*-dodecyl chain attached to a polypropylene glycol spacer arm, which is a commercial polymer with an average length of six propylene oxide (PO) units. The hydrophilic head group contains one or two xylitol units, which gives a low toxicity (14). The key synthetic step to obtaining these mono-alkyl-

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Abbreviations: CMC, critical micelle concentration; DMSO, dimethyl sulfoxide; EO, ethylene oxide; HLB, hydrophilic-lipophilic balance; m.p., melting point; NMR, nuclear magnetic resonance; PO, propylene oxide.

ated compounds consists of protecting four out of the five free hydroxyl groups in the xylitol molecule by forming diisopropylidene derivatives. Hence, only one hydroxyl group remains to bind with the spacer moiety (15). The protection reaction produces a mixture of isomers in which the main product is the symmetrical isomer in a proportion of 2:1 [as calculated from ¹H nuclear magnetic resonance (NMR) spectra] in comparison with the other isomer, which shows a free hydroxyl at either end of the molecule.

EXPERIMENTAL PROCEDURES

Materials. Melting points (m.p.) were determined on an automatic electrothermal apparatus and are uncorrected. NMR spectra were recorded with a Bruker Avance 400 MHz instrument (Bruker, Karlsruhe, Germany) for solutions in CDCl₃, D₂O, or dimethyl sulfoxide-d₆ (DMSO-d₆). Proton spectra were recorded at 400 MHz and ¹³C spectra at 100 MHz with broadband proton decoupling. Carbon spectra were assigned with the help of distortionless enhancement by polarization transfer experiments. Column chromatography was performed on silica gel (60 mesh; Merck, Darmstadt, Germany) by gradient elution with hexane/acetone or hexane/ethyl acetate. D,L-Xylitol (1) and poly- α -propylene glycol (average molecular weight $\bar{M}_n = 425$) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Epichlorhydrin was obtained from Merck. Other reagents and solvents were of commercial grade and were not purified before use.

Synthesis of 2,3:4,5-di-O-isopropylidene-D,L-xylitol (2). To a stirred solution of xylitol (20.0 g, 131.6 mmol) in anhydrous acetone (300 mL) at 0°C, H₂SO₄ (25.9 g, 263.2 mmol) was added dropwise. After 5 h, the reaction mixture was neutralized by addition of a 30% (w/w) NaOH aqueous solution. The reaction product was extracted with hexane. The organic phase was separated, washed twice with water, and concentrated under reduced pressure to give 2 as white crystals (30 g, 98% yield), m.p. 35°C; ¹H NMR: δ 1.27, 1.33 (6H, s, CH₃ isopropylidene), 3.54 (1H, *dd*, *J* = 4.0, 11.4 Hz, H-1a), 3.71 (1H, *dd*, *J* = 3.5, 12.1 Hz, H-1b), 3.76 (1H, *t*, *J* = 8.0 Hz, H-3), 3.87 (1H, *dd*, *J* = 4.5, 8.0 Hz, H-4), 3.94 (1H, *m*, H-5a), 3.96 (1H, *m*, H-2), 4.09 (1H, *m*, H-5b); ¹³C (CDCl₃): ppm 110.1, 109.9 (O–C–O, isopropylidene), 77.65