



Gemini Surfactants from Alkyl Glucosides.

Mariano J. L. Castro, José Kovensky and Alicia Fernández Cirelli[†]*

Centro de Investigaciones en Hidratos de Carbono (CIHIDECAR, CONICET)
Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina

Abstract: 1,5-Bis-[6-(*O*-(*n*-butyl α -D-glucopyranosid)] glutarate **7** was synthesized starting from D-glucose by a simple procedure. The anomeric mixture of alkyl glucosides was separated by flash chromatography of their peracetates. Detritylation in neutral conditions is described. This is the first example of a non ionic gemini surfactant where alkyl glucosides are linked through a spacer at C-6.
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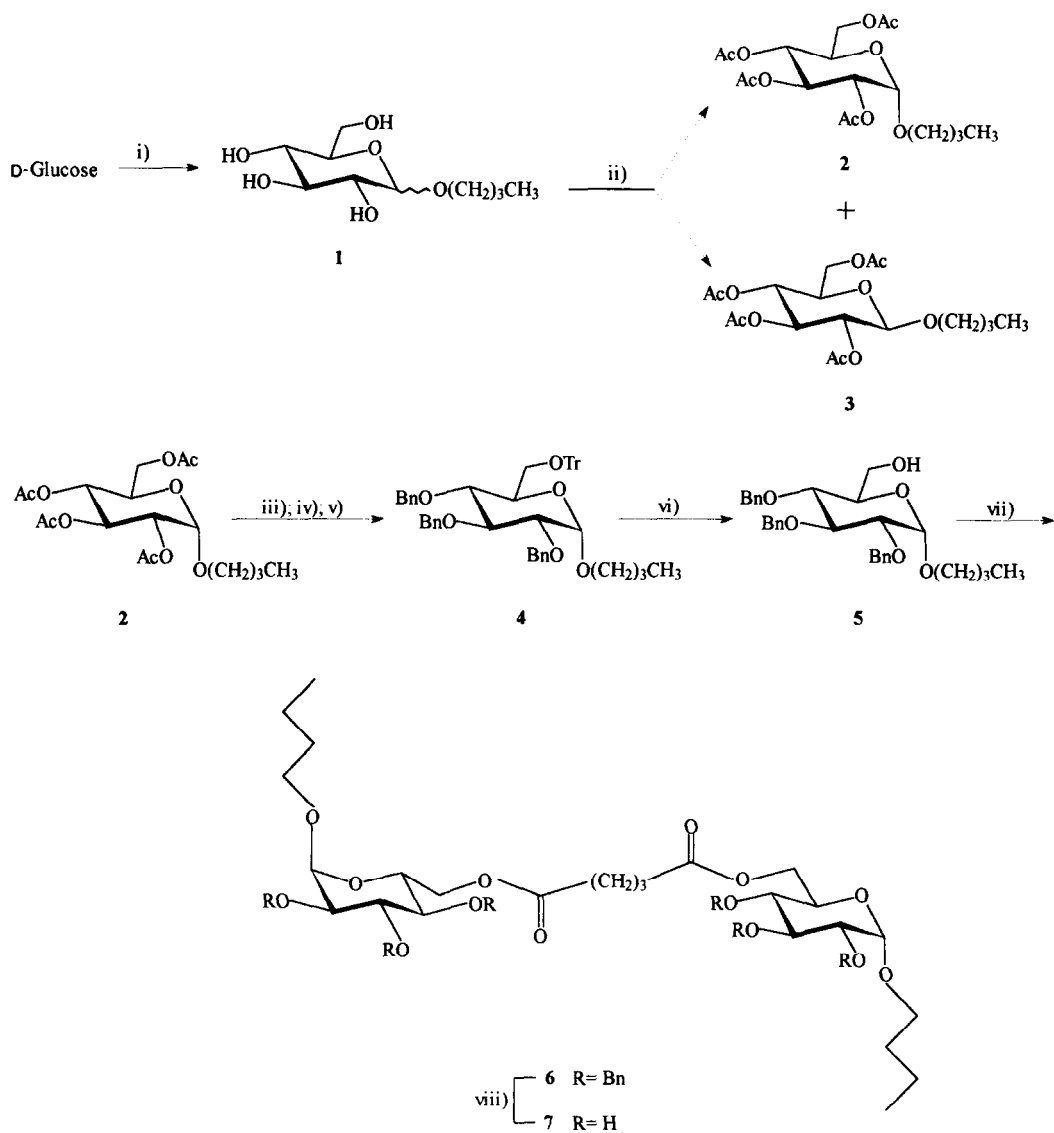
Gemini surfactants are amphiphiles that possess in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail.¹ Molecular dynamics simulations have shown² that these surfactants form structures and have dynamic properties drastically different from those of single-chain surfactants. Single-chain surfactants form spherical micelles whereas gemini surfactants, whose two head groups are coupled by the short hydrophobic spacer, form thread-like micelles. Gemini surfactants have also been studied as liquid crystal generators.³

In the last years, non ionic surfactants containing polar moieties instead of ionic groups have been synthesized from carbohydrate derivatives linked as hydrophilic heads.^{4,5}

On the other hand, it is well known that alkyl glycosides prepared starting from renewable raw materials, namely carbohydrates and long hydrocarbon chain alcohols, are ecologically safe non-ionic surfactants.⁶

We performed molecular mechanics simulations to evaluate the possible three-dimensional array of a gemini surfactant constructed with two of these molecules⁷ (Fig. 1). These studies indicated that two molecules of alkyl glucosides linked through their primary hydroxyl groups may adopt a suitable conformation to improve their surfactant properties. The two hydrocarbon chains would be oriented to opposite sides of the molecule, and the hydrophobic spacer would give additional flexibility to the hydrophilic heads.

[†] Research Member of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).



i) *n*-BuOH, PTSA, 100 °C; ii) (AcO)₂O, Py, r. t.; iii) Na, MeOH, r. t.; iv) TrCl, Py, r. t.; v) BnBr, NaH, DMF r. t.; vi) PyH⁺Cl⁻, EtOH, reflux 2 hs.; vii) ClCO(CH₂)₃COCl, Et₃N, toluene, r. t.; viii) H₂ (1 atm) Pd/C, EtOAc.

Scheme 1

On this basis we have synthesized 1,5-Bis-[6-*O*-(*n*-butyl α -D-glucopyranosid)] glutarate **7** as a model compound starting from D-glucose (Scheme 1).

D-Glucose and *n*-butanol were reacted in the presence of an acid catalyst⁸ to give a 4:1 mixture of α and β -D-glucopyranosides **1** in 64% yield. The anomeric mixture could be separated by flash chromatography on silica gel of the peracetates (**2,3**). Compound **2** was differentiated from **3** through ¹H-NMR (**2**: $J_{1,2} = 2.4$ Hz, **3**: $J_{1,2} = 8.0$ Hz). After deacetylation, the major product *n*-butyl α -D-glucoside was converted to *n*-butyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl- α -D-glucopyranoside **4** by conventional procedures. Detritylation was performed in neutral conditions⁹ to give quantitatively *n*-butyl 2,3,4-tri-*O*-benzyl α -D-glucopyranoside **5**. The suitable protected butyl glucoside **5** was reacted with glutaryl dichloride,¹⁰ leading to 1,5-bis-[6-*O*-(*n*-butyl 2,3,4-tri-*O*-benzyl α -D-glucopyranosid)] glutarate **6**,¹¹ a gemini structure where the two carbohydrate molecules are coupled by a short spacer through an ester linkage on their *O*-6. Hydrogenolysis of benzyl substituents afforded the target molecule **7**.¹² All compounds were purified by column chromatography and characterised by spectroscopical methods (¹H-NMR, ¹³C-NMR, FAB-MS).

This is the first example of a non ionic gemini surfactant where alkyl glucosides are linked through a spacer at C-6.

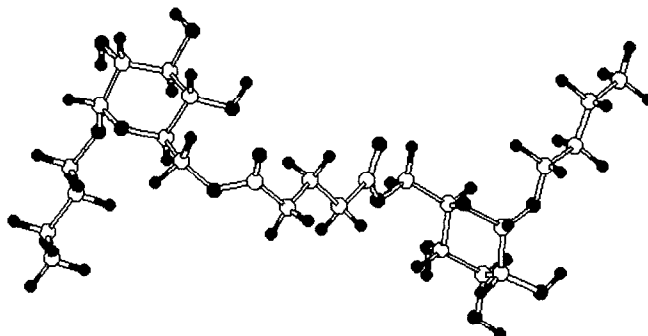


Fig. 1. Optimized structure of 1,5-bis-[6-*O*-(*n*-butyl α -D-glucopyranosid)] glutarate **7**
calculated by AM1 method.

ACKNOWLEDGEMENTS: This work was carried out with the financial contribution of UBA (Universidad de Buenos Aires) and CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas). M. Castro thanks Universidad de Buenos Aires for a fellowship. Elemental analyses were performed by UMYMFOR (CONICET).

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- Pyridinium chloride (0.75 eq.) in refluxing ethanol was found to be a mild method of detritylation, yielding quantitatively the deprotected product. These neutral conditions may be useful for detritylation of carbohydrate derivatives having acid-sensitive protecting groups and have been successfully tested in our lab on mono- and ditrityl derivatives.
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- $[\alpha]_D^{20} +123.8^\circ$ (*c* 1.06, CHCl₃). IR (film, cm⁻¹) 2927 (CH), and 1735 (C=O). ¹H-NMR (200 MHz, CDCl₃) δ 7.38-7.27 (m, 30 H, Ph), 5.05-4.54 (m, 14 H, $J_{gem} = 12.1$, $J_{1,2} = 3.7$ Hz, CH₂Ph, H-1 and H-1'), 4.26 (m, 4 H, H-6a and H-6'a, H-6b and H-6'b), 4.02 (t, 2 H, $J_{3,4} = 9.4$ Hz, H-4 and H-4'), 3.86 (m, 2 H, H-5 and H-5'), 3.65-3.39, (m, 8 H, H-2 and H-2', H-3 and H-3', 2CH₂O), 2.34 (t, 4 H, $J = 7.2$ Hz, 2 CH₂COO-), 1.93 (m, 2H, CH₂CH₂COO-), 1.62 (m, 4 H, 2 CH₂), 1.40 (m, 4 H, 2 CH₂), 0.94 (t, 6 H, $J = 7.2$ Hz, 2 CH₃). ¹³C-NMR (200 MHz, CDCl₃) δ 173.14 (COO-), 128.53-127.71 (C_{arom}), 96.84 (C-1 and C-1'), 82.11 (C-3 and C-3'), 80.33 (C-2 and C-2'), 77.68 (C-4 and C-4'), 75.79, 75.16, 73.21 (6 CH₂Ph), 68.72 (C-5 and C-5'), 68.13 (2CH₂O), 63.25 (C-6 and C-6'), 33.09 (2CH₂COO-), 31.56 (2CH₂), 20.40 (CH₂CH₂COO-), 19.50 (2CH₂), 13.94 (2CH₃).
Anal. Calc. for C₆₇H₈₀O₁₄: C 72.53, H 7.27. Found C 72.20, H 7.04.
- ¹H-NMR (200 MHz, CDCl₃) δ 4.83 (d, 2 H, $J_{1,2} = 3.3$ Hz, H-1 and H-1'), 4.38 (s, 6 H, OH), 3.70 (m, 8 H, H-4 and H-4', H-5 and H-5', H-6a and H-6'a, H-6b and H-6'b), 3.47 (m, 8 H, H-2 and H-2', H-3 and H-3', 2 CH₂O), 2.44 (t, 4 H, $J = 7.0$ Hz, 2 CH₂COO-), 1.99 (m, 2 H, CH₂CH₂COO-), 1.59 (m, 4 H, 2 CH₂), 1.39 (m, 4 H, 2 CH₂), 0.90 (t, 6 H, $J = 7.3$ Hz, 2 CH₃). ¹³C-NMR (200 MHz, CDCl₃) δ 173.24 (-COO-) 98.59 (C-1 and C-1'), 74.18 (C-3 and C-3'), 72.05 (C-5 and C-5'), 70.01 (C-2 and C-2'), 69.84 (C-4 and C-4'), 68.36 (2CH₂O), 63.02 (C-6 and C-6'), 33.21 (2CH₂COO-), 31.54 (2CH₂), 20.36 (CH₂CH₂COO-), 19.34 (2CH₂), 13.93 (2CH₃).

(Received in USA 22 January 1997; revised 14 April 1997; accepted 15 April 1997)