Supporting Information

Synthesis of 2-Hydroxydodecyl Starch Ethers: Importance of the Purification Process

Alexandre Gilet,[‡,†], Claude Quettier,[※] Vincent Wiatz,[※] Hervé Bricout,[‡] Michel Ferreira,[‡] Cyril Rousseau,[‡] Eric Monflier,[,‡] Sébastien Tilloy,[‡]*

[‡]Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS), 62300 Lens, France

[※]Roquette Frères, 1 rue de la Haute Loge, 62136 Lestrem, France

[†]Institut Français des Matériaux Agro-Sourcés, Parc Scientifique de la Haute Borne, 60 avenue Halley, 59650 Villeneuve d'Ascq, France

* eric.monflier@univ-artois.fr

I) Characterizations

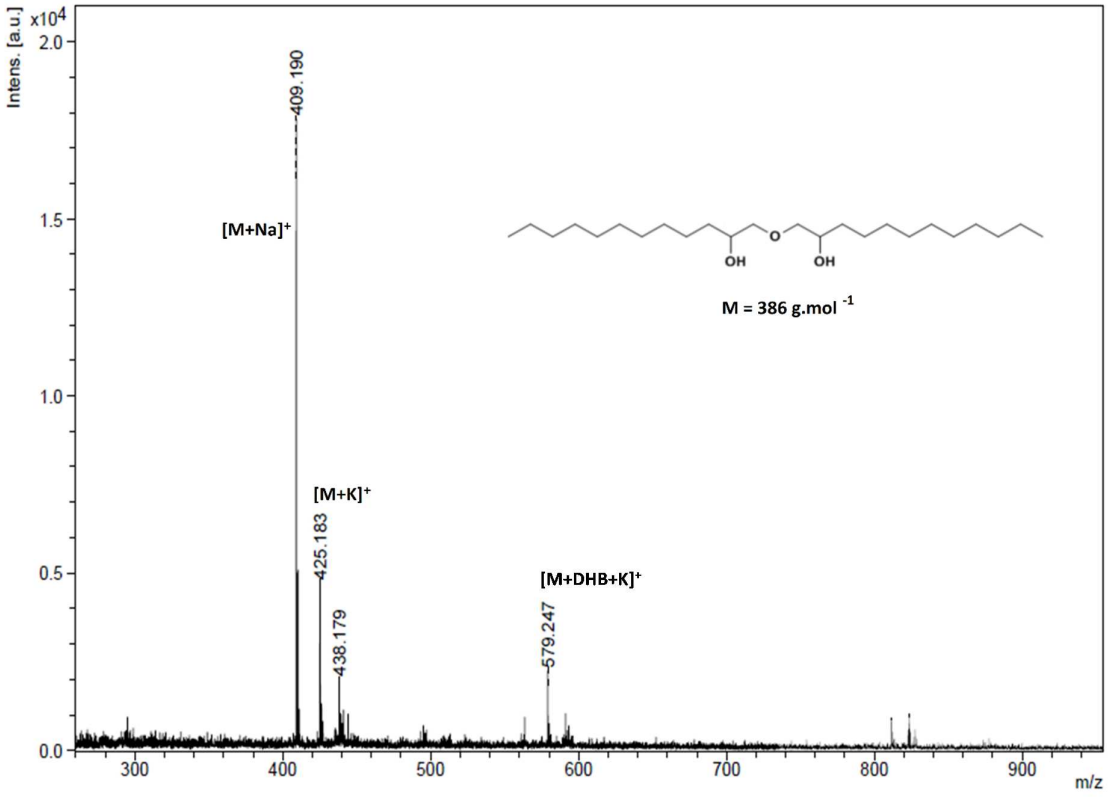

Figure S1: MALDI-TOF spectra of bis-(2-hydroxydodecyl)oxide (positive mode, DHB matrix; DHB=2,5-dihydroxybenzoic acid (154 $g.mol^{-1}$))

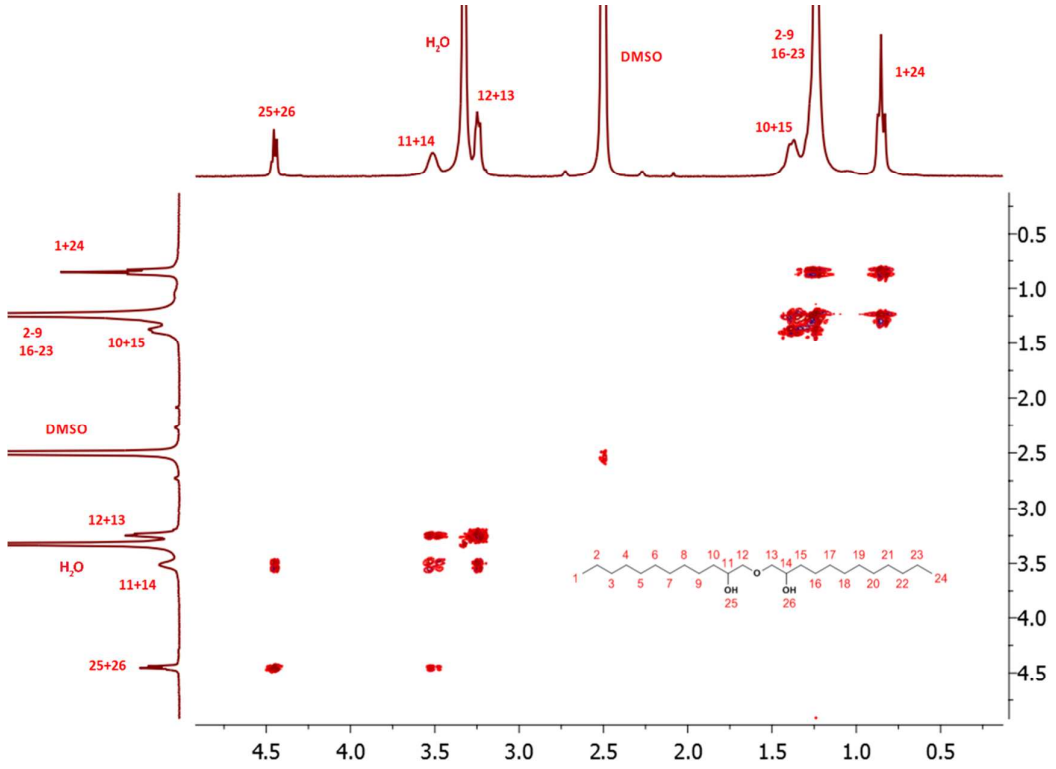

Figure S2: COSY spectrum of bis-(2-hydroxydodecyl)oxide (300 MHz, DMSO, 25°C)

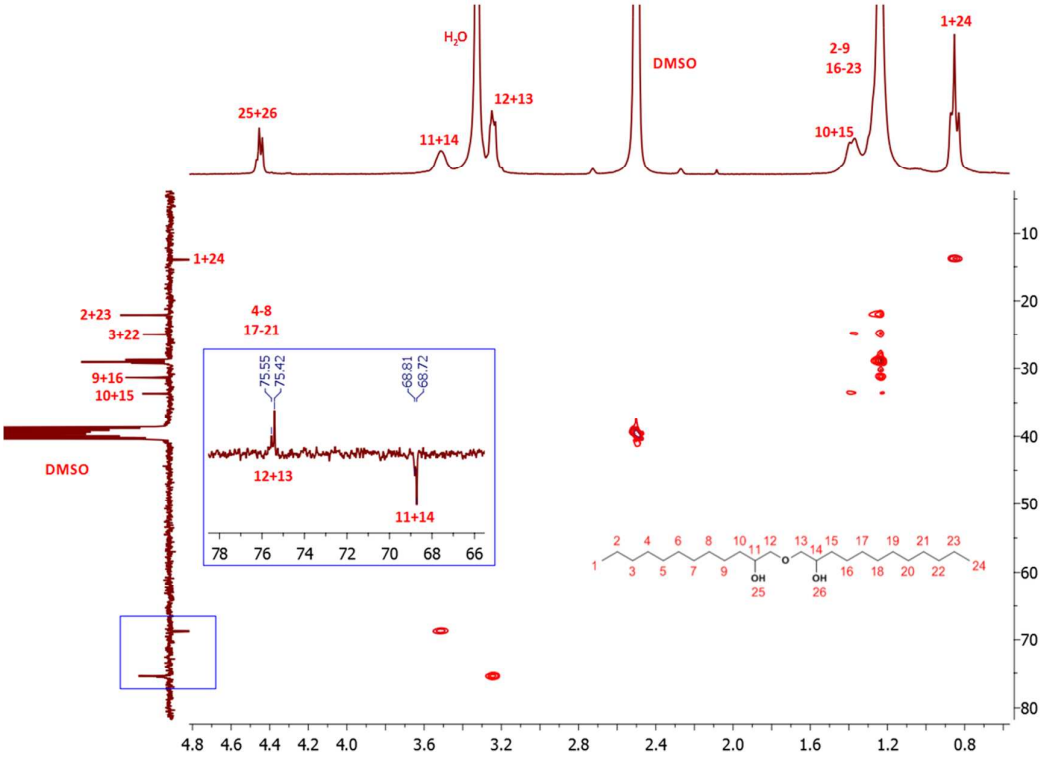

Figure S3: HSQC spectrum of bis-(2-hydroxydodecyl)oxide (300 MHz, DMSO, 25°C)

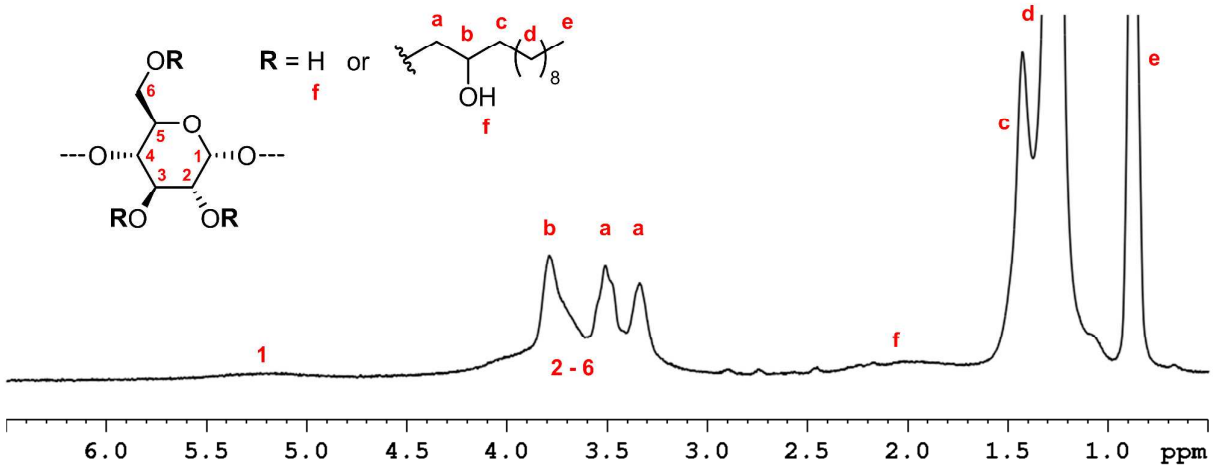

Figure S4: ^{1}H-NMR analysis of the product obtained after evaporation of the filtrate resulting from the Soxhlet extractions done on the **SE-G** sample (300 MHz, $CDCl_3$, 25°C)

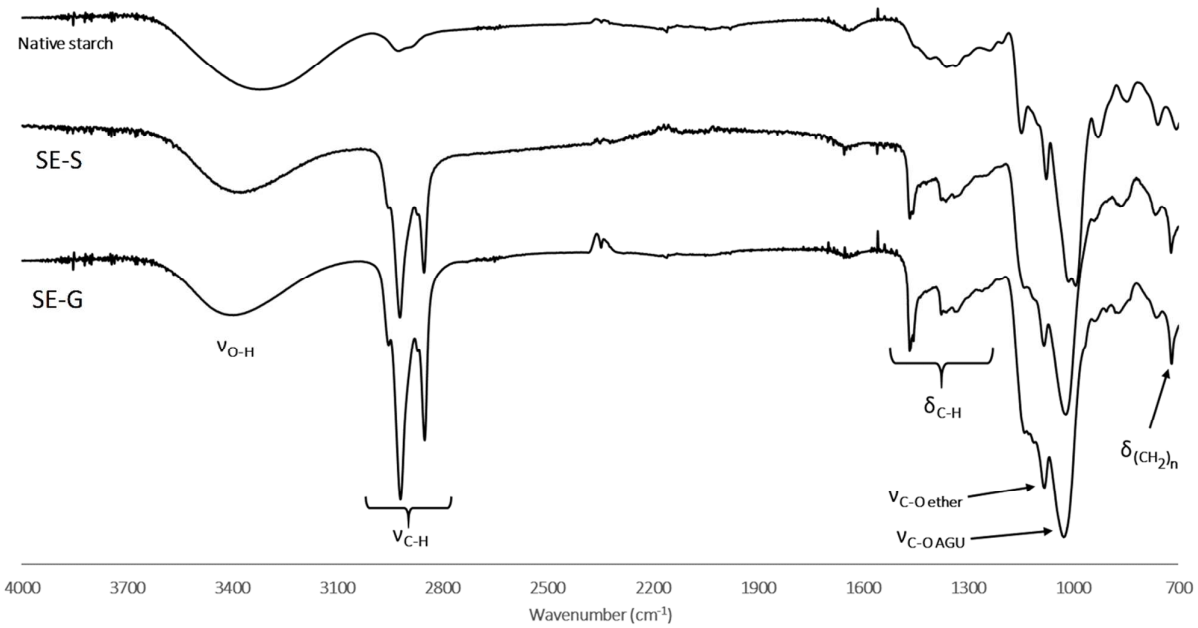

Figure S5: FTIR spectra of native starch and modified starch purified by Soxhlet (SE-S) and purified by grinding (SE-G)

II) Determination of the molar substitution (MS) of the 2-hydroxydodecyl potato starches by elemental analysis

The molar substitution of the 2-hydroxydodecyl potato starches (**MS**) was defined as the average number of 2-hydroxydodecyl groups per anhydroglucose unit in the modified starches.

1) Determination of the molar substitution deducted from the %C in the 2-hydroxydodecyl starches: $MS_{(c)}$

The expression of the $MS_{(c)}$, i.e. the number of 2-hydroxydodecyl groups (HDo) per AGU determined by elemental analysis from wt% of C (%C) in the 2-hydroxydodecyl starches, can be easily demonstrated:

$$\%C = \frac{\text{Mass of C in a modified AGU (g.mol}^{-1})}{\text{Mass of a modified AGU (g.mol}^{-1})} \times 100$$

$$\%C = \frac{\text{Mass of C in an unmodified AGU (g.mol}^{-1}) + \text{Mass of C due to the HDo graft presence (g.mol}^{-1})}{\text{Mass of a unmodified AGU (g.mol}^{-1}) + \text{Mass coming from the HDo graft presence (g.mol}^{-1})} \times 100$$

$$\%C = \frac{6\,M_C + MS \times 12\,M_C}{M_{AGU} + MS \times (M_{HDo} - M_H)} \times 100$$

M_C, M_H, M_{AGU} and M_{HDo} = Molecular mass (g.mol^{-1}) of C, H, AGU ($C_6H_{10}O_5$) and 2-hydroxydodecyl graft ($C_{12}H_{25}O$)

M_C = 12.010736 g.mol^{-1}
M_H = 1.007941 g.mol^{-1}
M_{AGU} = 162.140600 g.mol^{-1}
M_{HDo} = 185.326300 g.mol^{-1}

$$\%C = \frac{600\,M_C + MS \times 1200\,M_C}{M_{AGU} + MS \times (M_{HDo} - M_H)}$$

$$MS \times [(M_{HDo} - M_H) \times \%C - 1200\,M_C] = 600\,M_C - \%C \times M_{AGU}$$

and finally

$$MS_{(C)} = \frac{\%C \times M_{AGU} - 600\,M_C}{1\,200\,M_C - \%C \times (M_{HDo} - M_H)}$$

2) Determination of the molar substitution deducted from the %H in the 2-hydroxydodecyl starches: $MS_{(H)}$

The expression of the $MS_{(H)}$, i.e. the number of 2-hydroxydodecyl (HDo) groups per AGU determined by elemental analysis from wt% of H (%H) in the 2-hydroxydodecyl starches, can be easily demonstrated:

$$\%H = \frac{\text{Mass of H in a modified AGU (g.mol}^{-1})}{\text{Mass of a modified AGU (g.mol}^{-1})} \times 100$$

$$\%H = \frac{\text{Mass of H in an unmodified AGU (g.mol}^{-1}) + \text{Mass of H due to the HDo graft presence (g.mol}^{-1})}{\text{Mass of a unmodified AGU (g.mol}^{-1}) + \text{Mass coming from the HDo graft presence (g.mol}^{-1})} \times 100$$

$$\%H = \frac{10\ M_H + MS \times 24\ M_H}{M_{AGU} + MS \times (M_{HDo} - M_H)} \times 100$$

$$\%H = \frac{1000\ M_H + MS \times 2400\ M_H}{M_{AGU} + MS \times (M_{HDo} - M_H)}$$

$$MS \times [(M_{HDo} - M_H) \times \%H - 2400\ M_H] = 1000\ M_H - \%H \times M_{AGU}$$

and finally

$$MS_{(H)} = \frac{\%H \times M_{AGU} - 1\,000\ M_H}{2\,400\ M_H - \%H \times (M_{HDo} - M_H)}$$