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To cite this version:

Aurélien Cocq, Cyril Rousseau, Hervé Bricout, Estefanía Oliva, Véronique Bonnet, et al.. Highly Water-Soluble Amphiphilic Cyclodextrins Bearing Branched and Cyclic Oleic Grafts. European Journal of Organic Chemistry, 2019, 2019 (30), pp.4863-4868. 10.1002/ejoc.201900789 . hal-02271385

HAL Id: hal-02271385

https://hal.science/hal-02271385v1

Submitted on 14 Nov 2023

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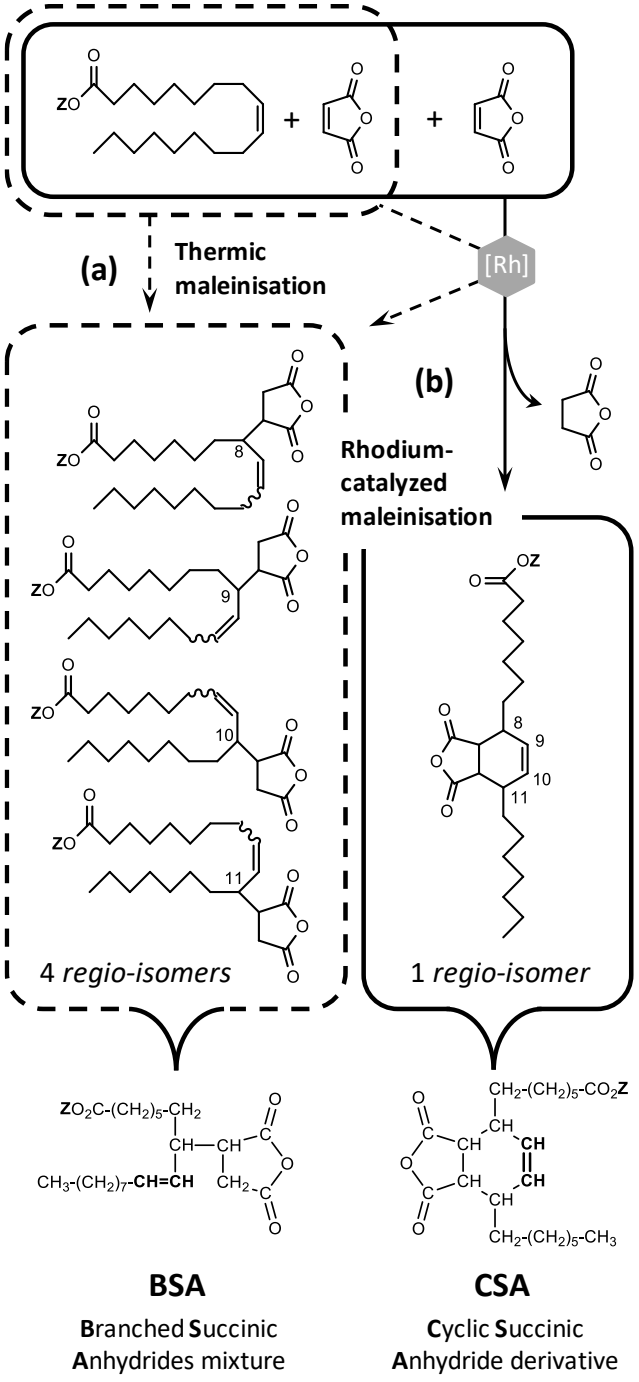
Highly Water-Soluble Amphiphilic Cyclodextrins bearing Branched and Cyclic Oleic Grafts

Aurélien Cocq,[a] Cyril Rousseau,[a] Hervé Bricout,[a] Estefanía Oliva,[b] Véronique Bonnet,[b] Florence Djedaïni-Pilard,[b] Eric Monflier,[a] and Sébastien Tilloy*[a]

Abstract: Amphiphilic β-cyclodextrins bearing various amounts of branched and cyclic oleic grafts are synthetized. The first step of this synthesis is the alkenylation of maleic anhydride by oleic acid derivatives, in the presence of a rhodium catalyst, to produce oleic succinic anhydrides with different ratios of cyclic to branched groups. The second step is the grafting of the oleic succinic anhydrides mixtures on β-cyclodextrin. The obtained cyclodextrins are highly water-soluble and surface active.

Introduction

To increase sustainability in chemical transformations, the utilization of renewable resources and catalytic processes has become an important field of research.[1] More precisely, vegetable oils are interesting resources to produce value-added products.[2] In this context, the maleinisation of oleic acid derivatives was described to produce interesting monomers for biobased polymers. More precisely, the addition of maleic anhydride on oleic acid derivatives can be performed either by a thermic way or by a rhodium-catalyzed way. The thermic way produced branched succinic anhydrides (BSA) at high temperature (around 220°C) as published by Candy and coll. (Scheme 1a).[3] The catalytic way enabled low reaction temperatures compared to the thermic way. Behr and coll. were the first to describe the rhodium catalyzed maleinisation of oleic acid derivative[4] followed by Eschig and al. (Scheme 1b).[5] This catalytic way mainly produced cyclic succinic anhydrides (CSA) but also BSA which are similar to the products formed by thermic way. Note that the CSA was not obtained without the use of a catalyst. In this context, we recently published the synthesis of new amphiphilic oleic succinyl-cyclodextrins obtained by esterification of various cyclodextrins (CDs) with branched oleic succinic anhydrides made from oleic acid or its methyl ester by thermic maleinisation.[6] In this publication, the aim was to synthetize oleic succinic anhydrides by using various amounts of rhodium catalyst to access different ratios of cyclic to branched products. These anhydrides were then



Scheme 1: **(a)** Thermic and **(b)** rhodium-catalysed maleinisation of an oleic derivative.

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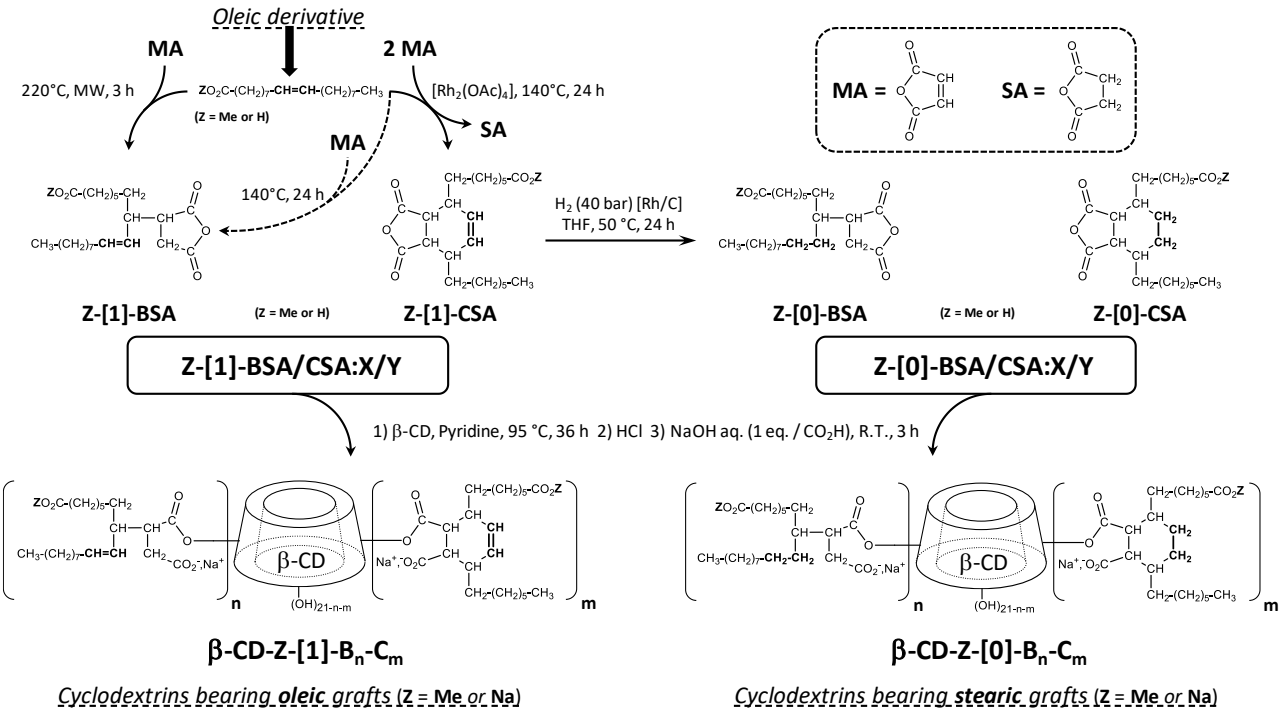


Scheme 2: Synthesis methodology of the modified cyclodextrins (**MA** = maleic anhydride; **SA** = succinic anhydride; **BSA** = branched succinic anhydride; **CSA** = cyclic succinic anhydride; **Z** = moiety bound or associated to the terminal carboxylate group of fatty acid derivatives or of CD grafts; **[1]** or **[0]** = number of C=C double bonds of fatty acid derivatives or of CD grafts; **X/Y** = relative molar proportions of BSA and CSA (%); **B** = branched graft; **C** = cyclic graft; **n** = number of branched grafts per CD; **m** = number of cyclic grafts per CD.

used to esterify β-cyclodextrin producing amphiphilic β-cyclodextrins bearing various amounts of branched and cyclic oleic grafts. The impact of the cyclic to branched ratio on physico-chemical properties (aqueous solubility, critical aggregation concentration and surface tension) was also studied.

Results and Discussion

The oleic succinyl-β-CDs were synthetized in two steps. The first step of the synthetic pathway is the rhodium catalyzed addition of maleic anhydride (MA) to oleic acid derivative (methyl oleate (MO) or oleic acid (OA)) to produce branched succinic anhydrides and cyclic succinic anhydrides (BSA and CSA, respectively – Scheme 2). The addition reaction of the maleic anhydride (MA) to methyl oleate or oleic acid gave an anhydrides mixture named Z-[1]-BSA/CSA:X/Y. Z is a methyl group or a hydrogen atom, according to the MO or OA nature of the reactant. [1] or [0] is the number of C=C double bonds on the fatty acid derivative. X/Y are relative molar proportions in percentage of BSA and CSA. The BSA products are a mixture of 4 regioisomers[7] (represented as a single compound for simplification) whereas CSA product corresponds to 1 regioisomer (Scheme 1). This mixture of branched and cyclic products was originated from two catalytic mechanisms as described by Behr[4] and Eschig.[5] The mechanisms of thermic and rhodium-catalyzed maleinisations are presented in supporting information (see supporting information; Schemes S1 and S2, respectively). The table 1 summarized the obtained yields and distributions of branched and cyclic succinic anhydrides. From MA and MO in the presence of $Rh_2(OAc)_4$ at 140°C, a mixture of branched and cyclic anhydrides was obtained. The ratio Me-[1]-BSA/Me-[1]-CSA increased when the amount of rhodium catalyst decreased whereas the yields were similar (Table 1; entries 1-2). The same conditions were also applied to the reaction with oleic acid instead of methyl oleate. The ratio H-[1]-BSA/H-[1]-CSA and the yield were equal to 56/44 and 42%, respectively (Table 1; entry 3). In the absence of catalyst and at the same temperature (140°C), only the branched compounds were produced with a low yield (14% - Table 1; entry 4).

Table 1. Catalytic and thermic maleinisation of methyl oleate (MO) and oleic acid (OA) [a]

Entry	Oleic Acid derivative	%Rh[b]	T(°C)	t(h)	Obtained mixture **Z-[x]-BSA/CSA:X/Y**[c]	Yield(%)[d]
1	MO	0.8	140	24	Me-[1]-BSA/CSA:13/87	68
2	MO	0.2	140	24	Me-[1]-BSA/CSA:64/36	60
3	OA	0.2	140	24	H-[1]-BSA/CSA:56/44	42
4	MO	-	140	24	Me-[1]-BSA	14
5	*MO*	-	*220*	*3*	*Me-[1]-BSA*	*40*[e]
6	*OA*	-	*220*	*3*	*H-[1]-BSA*	*27*[e]

[a] Maleic anhydride/oleic acid derivative molar ratio = 2 for entries 1-4 and 1.2 for entries 5 and 6; reaction without solvent; [b] Molar % of rhodium atom with respect to the oleic acid derivative used (catalyst = $Rh_2(OAc)_4$); [c] X/Y = relative molar proportions of BSA and CSA (%); [d] Maleinisation global yield; [e] *Previous works used for comparison in italic*.[6]

Table 2. Hydrogenation of the anhydrides mixtures[a]

Entry	Substrate Z-[1]-BSA/CSA:X/Y[b]	Product Z-[0]-BSA/CSA:X/Y[b]	Yield(%)[c]
1	Me-[1]-BSA/CSA:64/36	Me-[0]-BSA/CSA:64/36	85
2	H-[1]-BSA/CSA:56/44	H-[0]-BSA/CSA:56/44	90
3	*Me-[1]-BSA*	*Me-[0]-BSA*	*90[d]*
4	*H-[1]-BSA*	*H-[0]-BSA*	*85[d]*

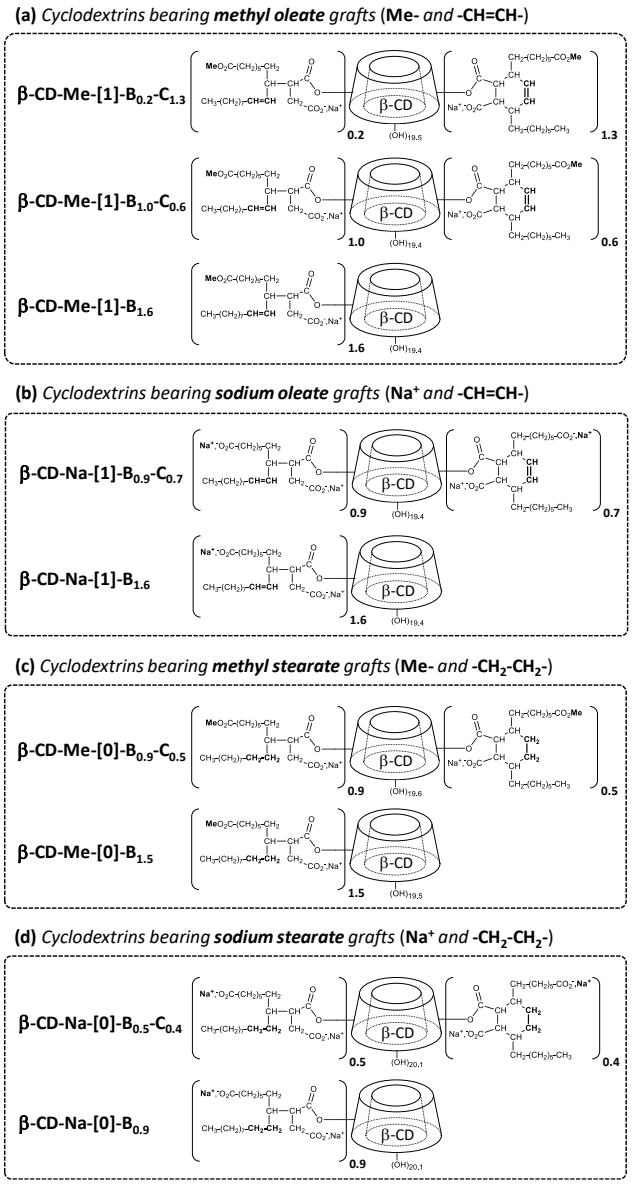
[a] 2 mol. % of [Rh/C; 5% w/w], H_2 (40 bar), THF (10 mL/g of initial mixture), 50°C, 24h; [b] X/Y = relative molar proportions of BSA and CSA (%); [c] Hydrogenation reaction yield; [d] *Previous works used for comparison in italic*.[6]

This result confirmed that a rhodium catalyst was necessary to produce the cyclic anhydrides. For comparison, the entries 5 and 6 recalled our already published branched anhydrides obtained by thermic way.[6] The two results showed that higher temperature (220°C vs 140°C) was necessary to produce a higher quantity of branched products in a shorter time. To evaluate if the carbon-carbon double bond of the branched chain or of the cyclic moiety could influence the physico-chemical properties of the oleic succinyl-β-CDs, hydrogenation of this bond from the anhydrides obtained by maleinisation was also performed in the presence of Rh/C (see supporting information). The hydrogenated mixture Me-[0]-BSA/CSA:64/36 and H-[0]-BSA/CSA:56/44 were obtained with yields of 85% and 90%, respectively (Table 2; entries 1 and 2). For comparison, the entries 3 and 4 recalled the already published results. The linear or cyclic nature of the carbon-carbon double bond did not influence the yields of hydrogenation reaction.

Table 3. Esterification of β-CD by the anhydride mixtures[a]

Entry	Anhydrides mixture used Z-[x]-BSA/CSA:X/Y[b]	Obtained modified cyclodextrin β-CD-Z-[x]-B_n-C_m[c]	n+m[d]	Yield(%)[e]
1	Me-[1]-BSA/CSA:13/87	β-CD-Me-[1]-$B_{0.2}$-$C_{1.3}$	1.5	87
2	Me-[1]-BSA/CSA:64/36	β-CD-Me-[1]-$B_{1.0}$-$C_{0.6}$	1.6	75
3	*Me-[1]-BSA*	*β-CD-Me-[1]-$B_{1.6}$*	*1.6*	*90[f]*
4	H-[1]-BSA/CSA:56/44	β-CD-Na-[1]-$B_{0.9}$-$C_{0.7}$	1.6	55
5	*H-[1]-BSA*	*β-CD-Na-[1]-$B_{1.6}$*	*1.6*	*86[f]*
6	Me-[0]-BSA/CSA:64/36	β-CD-Me-[0]-$B_{0.9}$-$C_{0.5}$	1.4	36
7	*Me-[0]-BSA*	*β-CD-Me-[0]-$B_{1.5}$*	*1.5*	*67[f]*
8	H-[0]-BSA/CSA:56/44	β-CD-Na-[0]-$B_{0.5}$-$C_{0.4}$	0.9	55
9	*H-[0]-BSA*	*β-CD-Na-[0]-$B_{0.9}$*	*0.9*	*75[f]*

[a] 1) Anhydride (2 molar eq./β-CD), Pyridine, 95 °C, 36 h, 2) HCl, 3) NaOH aq. (1 eq. / CO_2H), R.T., 3 h; [b] X/Y = relative molar proportions of BSA and CSA (%); [c] n = number of branched grafts (B) per CD; m = number of cyclic grafts (C) per CD; [d] n+m = average total number of grafts per CD; [e] Yield after neutralization with NaOH aq.; [f] *Previous works used for comparison in italic*.[6]



Scheme 3: Names and representations of the synthetized modified cyclodextrins.

The second step of the synthetic pathway is the grafting of the unsaturated or saturated BSA/CSA mixture on β-CD. This step was performed as described for the syntheses of amphiphilic β-CD esters of alkenyl succinic acids published mainly by the group of de Rossi[8] and others groups.[6, 9] The reaction was done in pyridine with 2 molar equivalents of the anhydride functions of the BSA/CSA mixture with respect to β-CD and allowed to produce various oleic succinyl-β-CDs (Scheme 3 and table 3).

These products were named β-CD-Z-[1]-B_n-C_m and β-CD-Z-[0]-B_n-C_m. [1] or [0] is for the number of C=C double bounds on each graft (branched or cyclic). Z is methyl group or a sodium ion. m and n are the average number of branched and cyclic groups per β-CD, respectively. For B and C grafts, only one kind of structure is represented, among the two possible, knowing that each hydroxyl group of the CD can react with one or the other carbonyl group of the succinic anhydride used. Various oleic succinyl-β-CDs were obtained with a degree of substitution (n+m) between

0.9 and 1.6 and with yields from 36% to 87 % (table 3). The ratio branched/cyclic grafts in oleic succinyl-CDs is similar to that of in the anhydrides mixture (for example, for entry 1: Me-[1]-BSA/CSA:13/87 led to β-CD-Me-[1]-$B_{0.2}$-$C_{1.3}$ corresponding to percentages equal to 0.2/(1.3+0.2)x100=13% and 1.3/(1.3+0.2)x100=87%). This result showed that species BSA and CSA have the same reactivity towards β-CD. The yields obtained with mixed anhydrides are lower than those obtained with branched anhydrides (Table 3; compare entries 1-2 and 3; 4 and 5; 6 and 7; 8 and 9). The degrees of substitution are generally comprised between 1.4 and 1.6 (table 3, entries 1-7) except for CD grafted with saturated oleic acid anhydride (table 3, entries 8 and 9).

The aqueous solubility, critical aggregation concentration in water (CAC) and surface tension of aqueous solutions were measured for the synthesized CDs and were gathered in the table 4. The values of aqueous solubility of all CDs (50 – 480 g/L at 20°C) were high compared to CDs possessing pure hydrophobic chains due to the presence of one or two carboxylate functions. At a similar substitution degree, the aqueous solubilities of modified CDs possessing cyclic grafts are higher than those with only branched grafts (table 4; compared entries 1, 2 and 3; 4 and 5; 6 and 7; 8 and 9). More precisely, at similar DS, the presence of cyclic grafts enabled to multiply the water-solubility by a factor 9, 1.6, 5 and 1.7 (table 4; compared entries 1 and 3; 4 and 5; 6 and 7; 8 and 9; respectively). This increase was higher for the CDs bearing the terminal methyl ester functions (table 4; entries 1 and 3; 6 and 7). Indeed, the aqueous solubilities of modified CDs with the terminal methyl ester functions were lower compared with those with the terminal carboxylate functions (table 4; compared entries 2 and 4; 6 and 8). This increase in water-solubility was due to the number of carboxylate functions per graft (one for the first series (Table 4; entries 1, 2, 3, 6 and 7) against two for the second series (Table 4; entries 4, 5, 8 and 9).

For each compound, the critical aggregation concentration (CAC) and the surface tension value obtained at this concentration were determined by the Wilhelmy method. It should be noted that the lowest CAC values were obtained with CDs exhibiting cyclic grafts (Table 4; entries 1, 6 and 8). The values of surface tension at the CAC at 20°C were situated between 29 and 48 mN/m. These values indicated that these modified cyclodextrins possessed a good surface activity compared to the native CDs which are not surface active.[10]

Conclusions

Amphiphilic β-cyclodextrins bearing various amounts of branched and cyclic oleic grafts were synthetized. These compounds were produced by esterification of β-cyclodextrin by oleic succinic anhydride derivatives obtained from oleic acid derivatives and maleic anhydride in the presence of a rhodium catalyst. These amphiphilic β-cyclodextrins are highly soluble in water (50-480 g/L). It is important to underline than modified CDs possessing cyclic grafts are more soluble in water than those with only branched grafts. In addition, these CDs possess low critical aggregation concentrations in water and aqueous solutions of these CDs exhibit low surface tensions. These properties could allow these new compounds to find applications in the field of surfactants and pharmaceuticals.

Table 4. Physico-chemical properties of the modified cyclodextrins

Entry	β-CD-Z-[x]-B_n-C_m[a]	n+m[b]	B/C(%)[c]	Solubility at 20°C (g/L)	CAC at 20°C (mg/L)	Surface Tension (mN/m)[d]
1	β-CD-Me-[1]-$B_{0.2}$-$C_{1.3}$	1.5	13/87	450	6	48
2	β-CD-Me-[1]-$B_{1.0}$-$C_{0.6}$	1.6	64/36	220	31	40
3	*β-CD-Me-[1]-$B_{1.6}$*	*1.6*	*100/0*	*50*	*20*	*42[e]*
4	β-CD-Na-[1]-$B_{0.9}$-$C_{0.7}$	1.6	56/44	450	195	37
5	*β-CD-Na-[1]-$B_{1.6}$*	*1.6*	*100/0*	*286*	*170*	*38[e]*
6	β-CD-Me-[0]-$B_{0.9}$-$C_{0.5}$	1.4	64/36	250	4	38
7	*β-CD-Me-[0]-$B_{1.5}$*	*1.5*	*100/0*	*50*	*48*	*29[e]*
8	β-CD-Na-[0]-$B_{0.5}$-$C_{0.4}$	0.9	56/44	480	6	47
9	*β-CD-Na-[0]-$B_{0.9}$*	*0.9*	*100/0*	*280*	*170*	*38[e]*

[a] n = number of branched grafts (B) per CD; m = number of cyclic grafts (C) per CD; [b] n+m = average total number of grafts per CD; [c] Relative amounts of branched and cyclic grafts on the CD (%); [d] Surface tension value determined at 20°C at the CAC (critical aggregation concentration); [e] *Previous works used for comparison*.[6]

Experimental Section

All chemicals were purchased from Fisher Scientific and Aldrich Chemicals in their highest purity. All solvents were used as supplied without further purification. Distilled water was used in all experiments. Analytical thin-layer chromatography (TLC) was performed on E. Merck aluminium-backed silica gel (Silica Gel F254). Compounds were identified by using UV fluorescence and/or staining with a solution of phosphomolybdic acid in aqueous sulfuric acid and ethanol. NMR spectra were recorded with a Bruker DRX300 spectrometer operating at 300 MHz for ^{1}H nuclei and at 75 MHz for ^{13}C nuclei. $CDCl_3$ (99.50% isotopic purity), [D_6]DMSO (99.80% isotopic purity) and D_2O (99.92% isotopic purity) were purchased from Euriso-Top.

Syntheses of the **Z-[1]-BSA/CSA:X/Y** anhydrides (Z=Me or H)

Me-[1]-BSA/CSA:13/87: 6 g of methyl oleate (74 % of purity) (4.44 g, 15.0 mmol), 2.94 g of maleic anhydride (29.9 mmol, 2 eq.), 26.5 mg of $Rh_2(OAc)_4$ (0.060 mmol, 0.4 mol%, so 0.8 mol% of Rh with respect to the methyl oleate) were mixed and heated in a schlenk tube under nitrogen at 140°C during 24 h. The brown oil obtained was purified by distillation with a Kugelrohr apparatus under reduced pressure. At P = 2.5 mbar, Me-[1]-BSA/CSA:13/87 was isolated at 275 °C. A yellow oil was obtained with a yield of 68 %.

Me-[1]-BSA/CSA:64/36: 6 g of methyl oleate (74 % of purity) (4.44 g, 15.0 mmol), 2.94 g of maleic anhydride (29.9 mmol, 2 eq.), 6.6 mg of $Rh_2(OAc)_4$ (0.015 mmol, 0.1 mol%, so 0.2 mol% of Rh with respect to the methyl oleate) were mixed and heated in a schlenk tube under nitrogen at 140°C during 24 h. The brown oil obtained was purified by distillation with a Kugelrohr apparatus under reduced pressure. At P = 2.5 mbar, Me-[1]-BSA/CSA:64/36 was isolated at 275 °C. A yellow oil was obtained with a yield of 60 %.

H-[1]-BSA/CSA:56/44: 6 g of oleic acid (87 % of purity) (5.22 g, 18.5 mmol), 3.62 g of maleic anhydride (37.0 mmol, 2 eq.), 8.2 mg of $Rh_2(OAc)_4$ (0.018 mmol, 0.1 mol%, so 0.2 mol% of Rh with respect to the oleic acid) were mixed and heated in a schlenk tube under nitrogen at 140°C during 24 h. The brown oil obtained was purified by distillation with a Kugelrohr apparatus under reduced pressure. At P = 2.5 mbar, H-[1]-BSA/CSA:56/44 was isolated at 300 °C. A yellow oil was obtained with a yield of 42 %.

Me-[1]-BSA: 28 g of methyl oleate (74 % of purity) (20.72 g, 69.9 mmol) and 8.22 g of maleic anhydride (83.9 mmol, 1.2 eq.) were mixed and heated under microwaves at 220°C during 3 h. The brown oil obtained was purified by distillation with a Kugelrohr apparatus under reduced pressure. At P = 2.5 mbar, Me-[1]-BSA was isolated at 275 °C. Me-[1]-BSA was purified by chromatography on silica gel with hexane/dichloromethane. A yellow oil was obtained with a yield of 40 %.

H-[1]-BSA: 27 g of oleic acid (87 % of purity) (23.49 g, 83.2 mmol) and 9.79 g of maleic anhydride (99.8 mmol, 1.2 eq.) were mixed and heated under microwaves at 220 °C during 3 h. The brown oil obtained was purified by distillation with a Kugelrohr apparatus under reduced pressure. At P = 2.5 mbar, H-[1]-BSA was isolated at 300 °C. H-[1]-BSA was purified by chromatography on silica gel with hexane/acetone. A yellow oil was obtained with a yield of 27 %.

Hydrogenation of the **Z-[1]-BSA/CSA:X/Y** anhydrides into **Z-[0]-BSA/CSA:X/Y** (Z=Me or H)

Me-[0]-BSA/CSA:64/36: 1 g of Me-[1]-BSA/CSA:64/36 (2.5 mmol) in 10 mL of THF was mixed with 106 mg of Rhodium on carbon 5% (51 µmol, 0.02 eq.) at 50°C under 40 bar of dihydrogen during 24 h. The crude product was filtered on celite and the THF was evaporated. A yellow oil was obtained with a yield of 85 %.

H-[0]-BSA/CSA:56/44: 1 g of H-[1]-BSA/CSA:56/44 (2.5 mmol) in 10 mL of THF was mixed with 106 mg of Rhodium on carbon 5% (51 µmol, 0.02 eq.) at 50°C under 40 bar of dihydrogen during 24 h. The crude product was filtered on celite and the THF was evaporated. A yellow oil was obtained with a yield of 90 %.

Me-[0]-BSA: 1 g of Me-[1]-BSA (2.5 mmol) in 10 mL of THF was mixed with 106 mg of Rhodium on carbon 5% (51 µmol, 0.02 eq.) at 50°C under 40 bar of dihydrogen during 24 h. The crude product was filtered on celite and the THF was evaporated. A yellow oil was obtained with a yield of 90 %.

H-[0]-BSA: 1g of H-[1]-BSA (2.6 mmol) in 10 mL of THF was mixed with 108 mg of Rhodium on carbon 5% (53 µmol, 0.02 eq.) at 50°C under 40 bar of dihydrogen during 24 h. The crude product was filtered on celite and THF was evaporated. A yellow oil was obtained with a yield of 85 %.

Syntheses of the **β-CD-Z-[x]-B_n-C_m** cyclodextrins

The β-cyclodextrin to be esterified was firstly dried by heating 2 h at 80 °C, 2 h at 100 °C, and 2 h at 120 °C under reduced pressure. Then, 2.50 g of dried β-cyclodextrin were dissolved in 75 mL of anhydrous pyridine under nitrogen and 2 eq. of the Z-[x]-BSA/CSA:X/Y anhydride were added. The mixture was stirred 36 h at 95 °C under nitrogen. At the end of the reaction, 15 mL of water were added and solvents were evaporated under reduced pressure. The lightly brown solid obtained was acidified with aqueous HCl until pH = 2 (approximately 2 mL of a solution at 35 %), filtered, washed with water until pH = 5-6, dried and then washed with diethyl ether. The β-CD-Z-[x]-B_n-C_m(CO_2H form) was obtained as a white solid. Then, β-CD-Z-[x]-B_n-C_m(CO_2H form) was dispersed in water (20 mL/g). Then, 1 equivalent of Na^+OH^- per CO_2H group was added and the mixture was then stirred during 3 h at 20 °C up to a total solubilisation. Water was then evaporated under reduced pressure. β-CD-Z-[x]-B_n-C_m(CO_2Na form) was obtained as a white solid.

Acknowledgments

This work was performed, in partnership with the SAS PIVERT, within the frame of the French Institute for the Energy Transition (Institut pour la Transition Energétique (ITE) P.I.V.E.R.T.) (http://www.institut-pivert.com) selected as an Investment for the Future (Investissements d'Avenir). This work was supported, as part of the Investments for the Future, by the French Government under the reference ANR-001-01. Jérémy Ternel, Nicolas Kania, and Dominique Prévost are acknowledged for NMR analysis and technical assistance. PIVERT is acknowledged for the financial support of AC thesis.

Keywords: Cyclodextrin • Maleinisation • Oleic acid • Rhodium • Succinic anhydride

[1] R. Palkovits, I. Delidovich, *Philos. Trans. R. Soc. A-Math. Phys. Eng. Sci.* **2018**, *376*, 12.
[2] J. Y. Jeon, Y. Han, Y.-W. Kim, Y.-W. Lee, S. Hong, I. T. Hwang, *Biofuels Bioproducts & Biorefining-Biofpr* **2019**, *13*, 690-722.
[3] L. Candy, C. Vaca-Garcia, E. Borredon, *J. Am. Oil Chem. Soc.* **2005**, *82*, 271-277.
[4] A. Behr, H. P. Handwerk, *Fett Wiss. Technol.-Fat Sci. Technol.* **1992**, *94*, 204-208.

[5] a) S. Eschig, C. Philipp, T. Salthammer, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 101-110; b) S. Eschig, C. Schirp, *Eur. J. Lipid Sci. Technol.* **2016**, *118*, 117-123; c) S. Eschig, C. Schirp, T. Salthammer, *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 943-951.

[6] A. Cocq, C. Rousseau, H. Bricout, E. Oliva, V. Bonnet, F. Djedaini-Pilard, E. Monflier, S. Tilloy, *Eur. J. Org. Chem.* **2019**, 1236-1241.

[7] J. Ross, A. I. Gebhart, J. F. Gerecht, *J. Am. Chem. Soc.* **1946**, *68*, 1373-1376.

[8] a) C. J. Gonzalez, R. H. de Rossi, *Arkivoc* **2001**, *2*, U76-U85; b) O. F. Silva, J. J. Silber, R. H. de Rossi, N. M. Correa, M. A. Fernandez, *J. Phys. Chem. B* **2007**, *111*, 10703-10712; c) R. H. de Rossi, O. F. Silva, R. V. Vico, C. J. Gonzalez, *Pure Appl. Chem.* **2009**, *81*, 755-765; d) O. F. Silva, M. A. Fernandez, S. L. Pennie, R. R. Gil, R. H. de Rossi, *Langmuir* **2008**, *24*, 3718-3726; e) O. F. Silva, N. M. Correa, J. J. Silber, R. H. de Rossi, M. A. Fernandez, *Langmuir* **2014**, *30*, 3354-3362.

[9] a) J. K. Choi, T. Girek, D. H. Shin, S. T. Lim, *Carbohydr. Polym.* **2002**, *49*, 289-296; b) Y. K. Xi, Z. G. Luo, X. X. Lu, X. C. Peng, *J. Agric. Food Chem.* **2018**, *66*, 228-237; c) J. H. Cheng, Y. N. Hu, Z. G. Luo, W. J. Chen, H. M. Chen, X. C. Peng, *Food Chemistry* **2017**, *218*, 116-121.

[10] L. Leclercq, H. Bricout, S. Tilloy, E. Monflier, *J. Colloid Interface Sci.* **2007**, *307*, 481-487.