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Synthesis and characterization of amphiphilic per-(6-thio-2,3-trimethylsilyl)cyclodextrin: Application to Langmuir film formation

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Abstract

New amphiphilic cyclodextrins are synthesized by selective modification. Two synthetic strategies are investigated. Per-(6-thio-2,3-trimethylsilyl)cyclodextrins can only be obtain by synthesizing first the per-6-thio-cyclodextrin and then silylating the remaining hydroxy functions. Characterizations of the products were achieved by ESI-MS and intramolecular coupling between thiol functions was evidenced. These new compounds are shown to be amphiphilic, and form stable Langmuir–Blodgett films that can be transferred on the upstroke and the downstroke of a substrate with a transfer ratio close to unity.
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Keywords: Amphiphilic compounds; Cyclodextrin; Langmuir–Blodgett films

1. Introduction

A large amount of work has been devoted to the synthesis and applications of α, β and γ cyclodextrins (CD) derivatives (Boger, Corcoran, & Lehn, 1978; Croft & Bartsh, 1983; Li & Purdy, 1992; Wenz, 1994). The versatility of these compounds allows applications in many areas. Bender and Komiyama (1979) extensively promoted the chemistry of CD (Chart 1) as enzyme mimic. Szejtly (1988) and Hinze (1981) focused on the applications of CD in chromatographic separation and purification. Other teams studied their ability to form inclusion complexes by insertion of organic molecules within the hydrophobic cavity of the CD (Rekharsky & Inoue, 1998). The outer surface of the CD being hydrophilic, thanks to the glucopyranose hydroxylic functions, the water-solubility of hydrophobic compounds can be improved. Drug delivery application recently used amphiphilic CD (Lin, Cremi-non, Perly, & Djedaini-Pilard, 1998). Modification of the physico-chemical properties (i.e. water solubility) of these compounds has been successfully achieved by regioselective modification of one side of the cyclodextrins, providing thus amphiphilic compounds. These new molecules were found to form either Langmuir–Blodgett (LB) films (Kawabata et al., 1988) or vesicles (Zhang, Ling, Coleman, Parrot-Lopez, & Galon, 1991). The required hydrophobic moiety for such applications was achieved by the use of aliphatic chains grafted onto the side geometrically corresponding either to the primary hydroxylic functions (Mazzaglia, Donohue, Ravoo, & Darcy, 2001) or to the secondary ones of the CD (Parrot-Lopez et al., 1992). It was suggested that at least 6 methylene groups per chains were necessary to provide stable LB films (Kawabata et al., 1988). However, in many cases, the transfer of the films onto a flat substrate produced results of questionable

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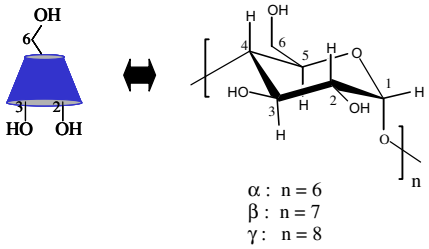


Chart 1.

quality (Greenhall et al., 1995). The influence of the nature of the hydrophobic moieties of the CD has been scarcely studied. Indeed, siloxane-based cyclodextrins have only been studied by Coleman et al. (Eddaoudi, Baszkin, Parrot-Lopez, Boissonnade, & Coleman, 1995) who observed that (heptakis-6-*O*-tert-butyldimethylsilyl)-β-CD was able to form Langmuir monolayers.

A large amount of work was dedicated to the immobilization of cyclodextrin on a flat surface. Such a surface is commonly expected to act as a template for the immobilization of guest molecules with specific recognition (Spinke, Liley, Gunder, Angermaier, & Knoll, 1993). However, to be used in sensor applications, such surfaces must possess a high degree of order and packing (Ulman, 1991). One straightforward way to achieve this task is to self assemble thiolated cyclodextrins on a gold surface (Nelles et al., 1996; Weisser, Nelles, Wohlfart, Wenz, & Mittler-Neher, 1996). However, lateral diffusion of such compound is limited and optimal packing was not achieved. Reinhoudt and co-workers (Beulen et al., 2000; de Jong, Huskens, & Reinhoudt, 2001) improved the adsorption of cyclodextrins derivatives onto a gold surface by changing the thiol functions into thioether groups. They noticed a large improvement of the degree of order and the packing density of the deposited cyclodextrins monolayers. A quasihexagonal lattice could be achieved as shown by AFM characterization.

The aim of this paper is to describe a new strategy to realize some cyclodextrins-modified gold surface for DNA nanochip applications using an electrochemical molecular beacon approach (Fan, Plaxco, & Heeger, 2003) where a cyclodextrin Langmuir film is transferred onto a gold surface. Thiol functions present in the subphase allow the anchoring of the film on the surface, and removal of the hydrophobic moieties release the cyclodextrin cavity for the complexation of the electroactive functions. A stem loop oligonucleotide possessing a terminal thiol and a ferrocene group could then be immobilized on the gold surface. The ferrocene tag would leave the cavity of the CD upon hybridization of a targeted sequence of the nucleotide. To achieve this task, the synthesis of new amphiphilic cyclodextrins derivatives able to form stable Langmuir–Blodgett films that can be anchored to metal surfaces was investigated. It was decided to convert secondary hydroxyl functions of the CD into siloxane groups in order to create hydrophobic moieties, which can be subsequently removed to release the cavity of the cyclodextrins for complexation purposes. The conversion of the primary hydroxyl groups into thiol functions, which are still hydrophilic, would allow the formation of chemical bonds when transferred onto gold surfaces. Two synthetic strategies will be discussed.

2. Experimental section

Triphenylphosphane (Aldrich) was purified by recrystallisation from methanol before use. DMF (SDS) was cryodistilled from CaH_2. Toluene (SDS) was freshly distilled from metallic sodium. Trimethylsilylimidazol (tMSI), thiourea and iodine were purchased from Aldrich and used without further purification. Cyclodextrins provided by Wacker Chemie were dried under vacuum at 80 °C for 48 h prior use. All reagents were of the best commercial available quality.

NMR spectra were recorded with a Bruker Avance 300 spectrometer (^{1}H. 300 MHz, ^{13}C. 75 MHz and ^{29}Si 59.5 MHz).

ESI-MS experiments were carried out on a Q-star Pulsar (Applied Biosystems, Foster City, CA, USA) tandem quadrupole-time of flight mass spectrometer equipped with a PE SCIEX ionspray source. The Analyst QS software was used for the experiments. Typical optimized values for the source parameters were: capillary voltage 5.5 kV, declustering potentials (DP1/DP2) 60 V, Focusing Potential (FP) 360 V, curtain gas and nebulizer gas: 20–30 psi. In the infusion mode, samples were typically 10^{-5} mol L^{-1} in DMF/MeOH or THF/MeOH mixtures. All solutions were continuously infused by means of a syringe pump at a typical flow rate of 5 μL min^{-1} into the electrospray probe. During our ESI-MS experiments the time of flight analyzer (equipped with a reflectron) was routinely capable of performing mass spectra of 4000–8000 mass resolution on the 500–3000 Da mass range with <50 ppm mass accuracy.

An appropriate amount of cyclodextrin solution in hexane (1–2 mg mL^{-1}) was carefully spread onto the water subphase. The initial molecular area is set at 1000 $Å^2$. Ten minutes prior to compression are allowed for the spreading solvent to evaporate. The Langmuir monolayers were compressed using a constant barrier speed of 20 $Å^2$ $molecule^{-1}$ min^{-1}, at 20 ± 1 °C. At least two measurements were carried out for each experimental condition. Built-up films on CaF_2, quartz, or glass substrates were obtained by the vertical lifting method at a target pressure of 18 mN m^{-1}, with a 10 mm min^{-1} dipping speed. The substrates were soaked in water and ethanol. A final rinsing was carried out with dichloromethane under sonication during 15 min in order to obtain hydrophobic substrates.

All Langmuir and Langmuir–Blodgett experiments were conducted on a 600 cm^2 Teflon Nima trough (611D system). The surface pressure measurements were carried out using the Wilhelmy plate technique. The subphase

water is purified by a Millipore system producing water with a resistivity of 18 MΩ cm.

2.1. Per-6-deoxy-iodo-β-CD (2α, 2β and 2γ)

According to the procedure of Gadelle and Defaye (1991) to a mixture of triphenylphosphane (21 g, 80 mmol) and iodine (20.2 g, 80 mmol) in DMF (40 mL) was added either 1α, 1β or 1γ (4.32 g, 26.6 mmol equiv). The mixture was stirred at 80 °C for 18 h and it was then concentrated under vacuum to half volume. The pH was adjusted to 9–10 by addition of sodium methoxide in methanol (3 M, 30 mL), with simultaneous cooling. The solution was kept at room temperature to destroy the formate esters formed in the reaction, after 1 h it was precipitated into methanol. The precipitate was collected by filtration to yield either 2α (78% from 1α), 2β (86% from 1β) or 2γ (76% from 1γ). ^{13}C NMR (75 MHz, DMSO-d_6) of 2α: δ 102.0, 86.5, 72.4, 71.8, 70.8, 9.9, ^{13}C NMR (75 MHz, DMSO-d_6) of 2β: δ 102.4, 86.2, 72.5, 72.2, 71.29, 9.8 and ^{13}C NMR (75 MHz, DMSO-d_6) of 2γ: δ 102.0, 85.3, 72.4, 71.8, 71.2, 9.3.

2.2. Per-(2,3-trimethylsilyl-6-iodo)-CD (3α, 3β and 3γ)

3α, 3β or 3γ (1 g, 0.52 mmol equiv) is dissolved in cryodistilled DMF (16.4 mL) in a three round neck flask under inert atmosphere. tMSI ($N_{tMSI} = 3N_{OH}$) (3.26 mL, 22.1 mmol) is then introduced. Freshly distilled chloroform was added to the solution up to the disappearance of the precipitate that results from modification of the first hydroxyl functions. The solution was stirred at room temperature for 6 days. Water was then added to quench the reaction and the organic phase was washed with water until neutral pH. Then the solvent was removed and the product was dried. The yield was about 96% for either 3α, 3β or 3γ. ^{1}H NMR of 3α (300 MHz, C_6D_6) δ 2.75.2 (m, 42H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of α-CD), −0.40.7 (m, 108H, $Si(CH_3)_3$), ^{1}H NMR of 3β (300 MHz, C_6D_6) δ 2.95.5 (m, 49H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of β-CD), −0.10.6 (m, 126H, $Si(CH_3)_3$), ^{1}H NMR of 3γ (300 MHz, C_6D_6) δ 2.75.2 (m, 56H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of γ-CD), −0.40.5 (m, 144H, $Si(CH_3)_3$).

2.3. Per-6-deoxy-6-thio-CD (4α, 4β and 4γ)

According to the procedure of Rojas, Königer, Stoddart, and Kaifer (1995) to a stirred solution of 2α, 2β or 2γ (2 g, 7.35 mmol equiv) in DMF (20 mL) under N_2 were added thiourea (0.614 g, 8.08 mmol). The mixture was heated to 70 °C. After 19 h the solution was concentrated under vacuum to obtain yellow oil, which was dissolved by addition of a NaOH solution (100 mL, 0.12 M). The mixture was flushed under N_2. After 1 h 30 min, the product was precipitated by addition of $KHSO_4$ solution (1.5 M). The precipitate was collected by filtration to yield either 4α (80% from 2α), 4β (82% from 2β) or 4γ (76% from 2γ). ^{13}C NMR (75 MHz, DMSO-d_6) of 2α: δ 102.5, 86.8, 72.8, 72.5, 72.1, 26.3, ^{13}C NMR (75 MHz, DMSO-d_6) of 2β: δ 102.2, 85.0, 72.6, 72.3, 72.1, 26.0 and ^{13}C NMR (75 MHz, DMSO-d_6) of 2γ: δ 102.2, 85.0, 72.3, 72.5, 72.0, 25.9.

2.4. Per-(2,3-trimethylsilyl-6-thio)-β-CD (5α, 5β and 5γ)

In a 100 mL three round neck flask containing 4α, 4β or 4γ (0.238 g, 0.19 mmol equiv) and cryodistilled DMF (10 mL) was added trimethylsilylimidazol, ($N_{tMSI} = 4N_{OH}$) (1.6 mL, 0.106 mol) at room temperature under nitrogen. The freshly distilled toluene was added to the reaction mixture when a precipitate appeared keeping homogeneous the reaction medium. After 6 days, the reaction was quenched by distilled water and was extracted by toluene, the organic solution was thoroughly washed with distilled water until pH 7 then the solvent was removed by vacuum evaporation. The products (5α, 5β and 5γ) were obtained in 84% yield. ^{1}H NMR of 5α (300 MHz, C_6D_6) δ 2.75.8 (m, 42H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of α-CD), 1.8 (m, ∼ 6H), −0.20.9 (m, 108H, $Si(CH_3)_3$), ^{1}H NMR of 5β (300 MHz, C_6D_6) δ 2.75.9 (m, 49H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of β-CD), 1.7 (m, ∼7H), −0.20.9 (m, 126H, $Si(CH_3)_3$), ^{1}H NMR of 5γ (300 MHz, C_6D_6) δ 2.65.5 (m, 56H, H1, 2, 3, 4, 5, 6*a*, 6*b* protons of γ-CD), 1.8 (m, ∼8H) , −0.31 (m, 144H, $Si(CH_3)_3$).

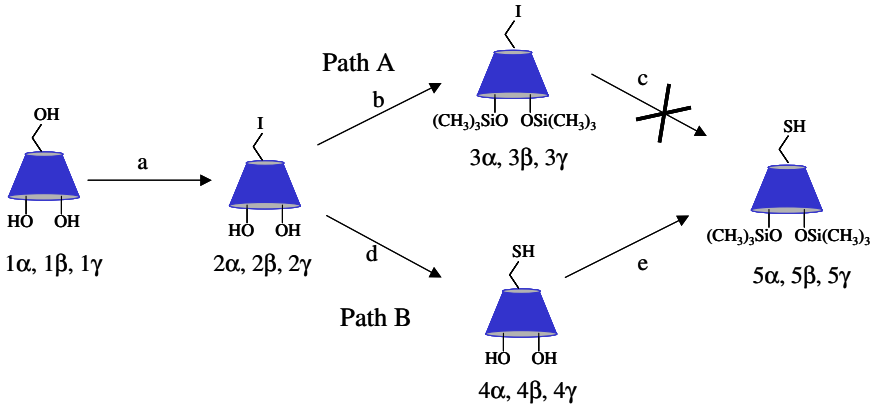
3. Results and discussion

The synthesis of 5α, 5β and 5γ was attempted through two paths, as described in Scheme 1. Both steps require the synthesis of per-6-deoxy-6-iodo-CD (2α, 2β and 2γ) as first precursor.

3.1. Path A

In path A, a precursor 2α, 2β or 2γ already described in the literature (Gadelle & Defaye, 1991) reacts with trimethylsilylimidazole (tMSI) to persubstitute the secondary hydroxyl functions of the CD. We already reported the difficulties of CD silylation, especially on the 3rd position (Harabagiu et al., 2003). As the reaction proceeds, the silylated CD becomes insoluble in DMF. The addition of an organic solvent such as toluene or chloroform ensures the complete dissolution of the modified CD and allows the reaction to proceed to completion.

By ^{1}H NMR spectroscopy, it was observed that the double peak for secondary hydroxyl groups $OH_{(2)}$ and $OH_{(3)}$ of the new CD derivative 3 has totally disappeared and a new peak between −0.4 and 0.6 ppm attributed to the $Si(CH_3)_3$ protons was observed. The integral ratio between the methyl-silicon and the glucopyranose signals was 18/7, as expected. The peaks corresponding to the anomeric protons $H_{(1)}$ were spread in a large signal between 4.5 and 5.5 ppm, that suggests the loss of the seven fold symmetry of the CD ring, as discussed by other authors on cyclodextrins bearing large substituents (Jullien, Canceill, Lacombe,



[a] Reagents: (a) $P(Ph)_3$, I_2, DMF. (b) $C_3H_3N_2Si(CH_3)_3$, DMF, $CHCl_3$. (c) CSN_2H_4, DMF; NaOH; $KHSO_4$. (d) CSN_2H_4, DMF; NaOH; $KHSO_4$. (e) $C_3H_3N_2Si(CH_3)_3$, DMF, Toluene.

Scheme 1. Strategies for the selective modification of cyclodextrins. Reagents: (a) $P(Ph)_3$, I_2, DMF; (b) $C_3H_3N_2Si(CH_3)_3$, DMF, $CHCl_3$; (c) CSN_2H_4, DMF; NaOH; $KHSO_4$; (d) CSN_2H_4, DMF; NaOH; $KHSO_4$; (e) $C_3H_3N_2Si(CH_3)_3$, DMF, Toluene.

& Lehn, 1994) and by some of us (Harabagiu et al., 2003). A large peak between 16 ppm and 21 ppm was observed in ^{29}Si NMR spectrum of 3β. No further investigation was conducted to discriminate the trimethylsilyl functions signals corresponding to the 2nd or 3rd position of the glucopyranose ring. ESI-MS spectrum of 3β which formula is $7(C_{12}H_{25}O_4ISi_2)$ and $M = 2912$ g/mol is presented in Fig. 1. Sodium adducts ($M + Na^+$) and ($M + 2Na^{2+}$) were the main ions detected at *m/z* 2936.88 and *m/z* 1476.93, respectively. An inset in the range [2920–2960] shows isotopic distributions of $M + NH_4^+$ (monoisotopic ion at *m/z* 2929.83) and $M + K^+$ (*m/z* 2950.76) adducts beside $M + Na^+$ (*m/z* 2934.68). As reported by Gèze et al. (2002) NMR does not allow an unambiguous quantification of CD derivatization and we observe in the MS spectra a signal (2899.02 uma) attributed to a molecule having the formula $[6(C_{12}H_{25}O_4ISi_2) + (C_{15}H_{34}O_5Si_3)]$.

Synthesis of 5α, 5β and 5γ via reaction of thiourea with corresponding derivatives (3α, 3β or 3γ) according to Rojas's procedure (Rojas et al., 1995) was not possible. Unfortunately the conversion of the iodine function into the thiol function was accompanied by an unexpected desilylation of the secondary face of CD.

3.2. Path B

In this path, either precursor 2α, 2β or 2γ was first converted into the thiol derivative (4α, 4β or 4γ) as already

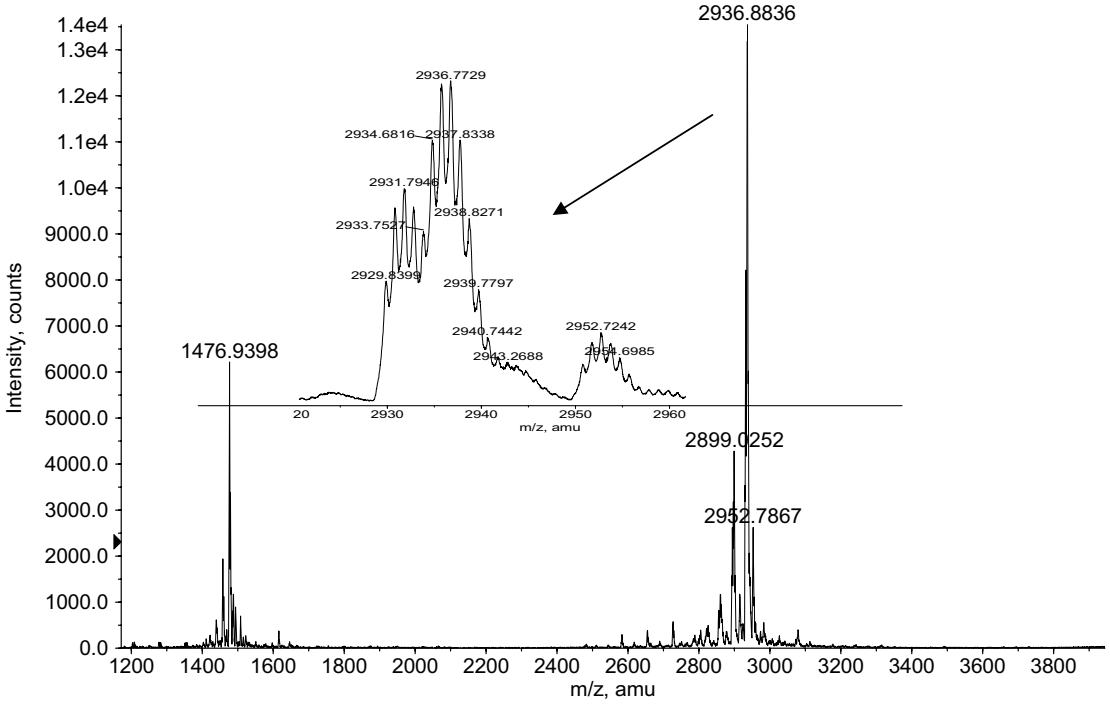


Fig. 1. ESI/MS spectrum of 3β in THF/MeOH.

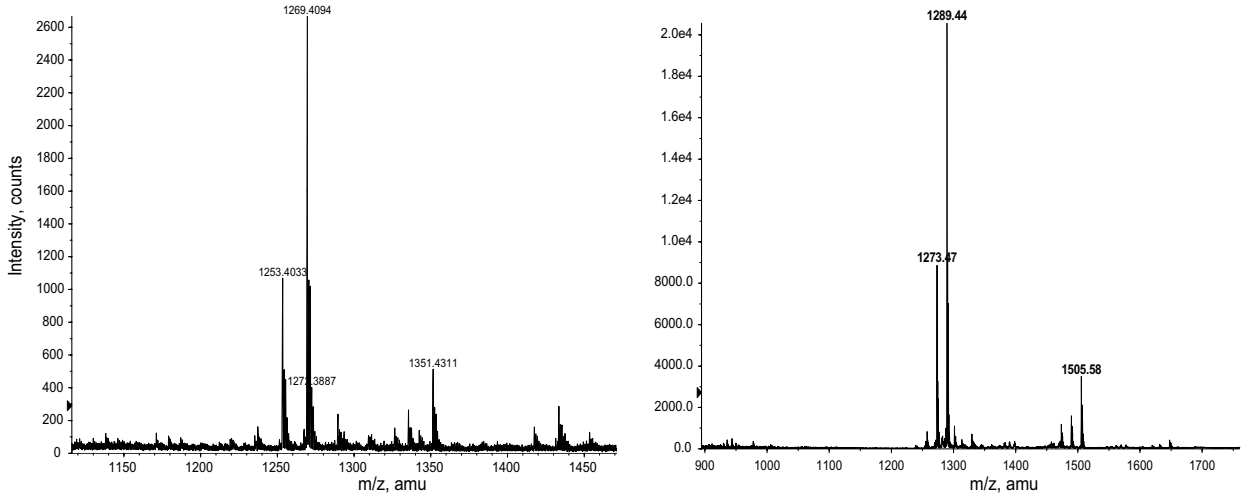
reported by Rojas et al. (1995). Naud, Calas, Blancou, and Commeyras (2000) demonstrated that this reaction is very efficient on semifluorinated *n*-alkane iodide or bromide. Indeed, 93% yield is reported and a formation of a small amount of disulfide is observed.

In our case, iodine function derivatization of 2α, 2β or 2γ-CD was never complete, and strongly depended upon the acid hydrolysis step. ^{13}C NMR analysis of all these samples showed a maximum yield of thiol formation of 87%. To elucidate the side reactions, ESI-MS mass spectra of 4β derivative, whose formula is $7(C_6H_{10}O_4S)$ and $M = 1246.21$ g/mol were recorded in the solvent mixture DMF/MeOH in the presence, then in the absence of CH_3COONa (Fig. 2).

Thus, when sodium acetate was added to the solvent mixture an adduct at *m/z* 1269.4 corresponding to $M + Na^+$ was detected, as well as an ion at *m/z* 1253.40 corresponding to a sodium adduct having six thiol functions rather than seven and one hydroxyl function instead of a thiol function (Fig. 2(a)). However, when no sodium salt was added to the analysis (Fig. 2(b)), other protonic species were detected at *m/z* 1289.44, *m/z* 1273.47 and *m/z* 1505.58. The two ESI-MS experiments allow the identification of different species. These molecular weights, respectively, correspond to β-CD bearing, on primary face, (1 $SCN_2H_3 + 6$ SH), (1 $SCN_2H_3 + 5$ SH + 1OH) and (6 $SCONH_2 + 1$ SH). These derivatives of 4β are depicted in Chart 2 and were attributed to an incomplete hydrolysis of isothiouronium salt formed by the reaction of thiourea with 2β as depicted in Scheme 2. Isolation of the pure thiolated cyclodextrins derivatives via standard technique remained unsuccessful. It must be kept in mind that ESI-QqTOF mass spectrometry is not a quantitative method, and the abundance of the side products is much lower than witnessed by this analysis. In the presence of the sodium salt, the species with a high cationic affinity are ionized preferentially whereas in the absence of sodium salt, the more basic species are ionized first.

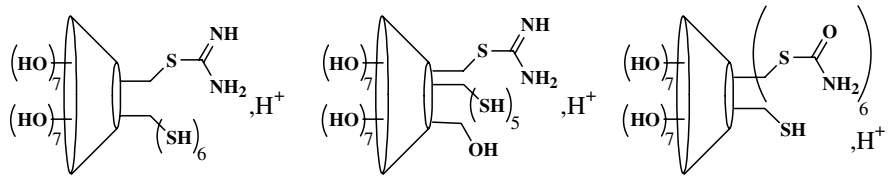
4α, 4β or 4γ were then reacted with tMSI in order to obtain their corresponding 5α, 5β or 5γ (Scheme 1). Table 1 reports the yield of these products (5α, 5β or 5γ) versus reaction time. We can observe that the silylation of the β derivative was easier than for the α and γ cyclodextrins. ^1H NMR analysis of 5β showed that only 14 out of 21 reactive sites were silylated. ^{29}Si NMR spectrum of 5β derivative gave two broad peaks between 15 and 20 ppm, typical of a silylation of the secondary alcohol of the cyclodextrin. However, the discrimination between persilylation of all hydroxyl functions and a side reaction between the thiol functions and tMSI had to be investigated.

ESI/MS analysis of 5β (molecular formula: $C_{84}H_{182}O_{28}S_7Si_{14}$; monoisotopic mass: 2254.74 g mol^{-1})



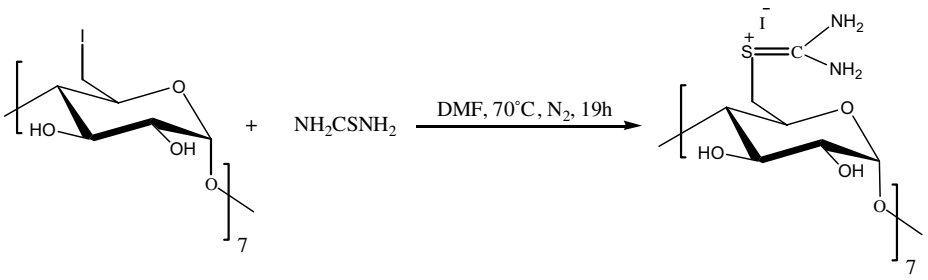
(a) product analyzed in DMF/MeOH (CH_3COONa added) (b) product analyzed in DMF/MeOH

Fig. 2. ESI/MS spectra of 4β.



m/z 1289.44 m/z 1273.47 m/z 1505.0

Chart 2. *m/z* 1289.44 *m/z* 1273.47 *m/z* 1505.0.



Scheme 2. Isothiouronium salt formation.

Table 1
Silylation of per-6-deoxy-6-thio-CD in DMF/Toluene at 25 °C with $N_{tMSI}/N_{OH} = 3$ and under nitrogen

Entry	CD	[tMSI] (mol L)	Times (days)	Yield (%)	Modification yield (%)
1	α	0.93	1	68	72
2	α	0.93	6	89	95
3	β	1.05	1	81	100
4	β	1.05	6	87	100
5	γ	1.2	1	89	84
6	γ	1.2	4	80	100

evidenced an intense sodium adduct as shown in Fig. 3. As previously discussed some primary hydroxyl functions might remain after iodine derivatization. Thus, a peak at *m/z* 2335.76 corresponds to CD derivatization witnessing molecules containing $15OSi(CH_3)_3$ and 6 sulfur atoms. The signal at *m/z* 2205.65 corresponds to CD derivatives with $13(OSi(CH_3)_3)$ and 7 sulfur atoms. Given the fair agreement between theoretical and analytical NMR characterization, it is difficult to distinguish incomplete silylation from a degradation of the product during ESI/MS analysis.

The first observation which can be done is the high intensity of the population attributed to sodium adduct corresponding to β-CD molecule containing fourteen $Si(CH_3)_3$ functions, seven sulfur atoms and a defect of two atomic mass units (amu). Indeed, the monoisotopic ion showed in the inset depicted in Fig. 3 corresponds to $(M-2\ amu + Na)^+$. This species results from the loss of two protons explained by the formation of an intramolecular disulfide bridge. The persilylation of the secondary hydroxyl groups induces a twist of the molecule that widens the larger side of the CD torus. The retraction of the narrower side allows then the formation of bond between two thiol functions. No intermolecular coupling was evidenced by electrospray analysis. However, simulation of the isotopic distribution suggested that in the range

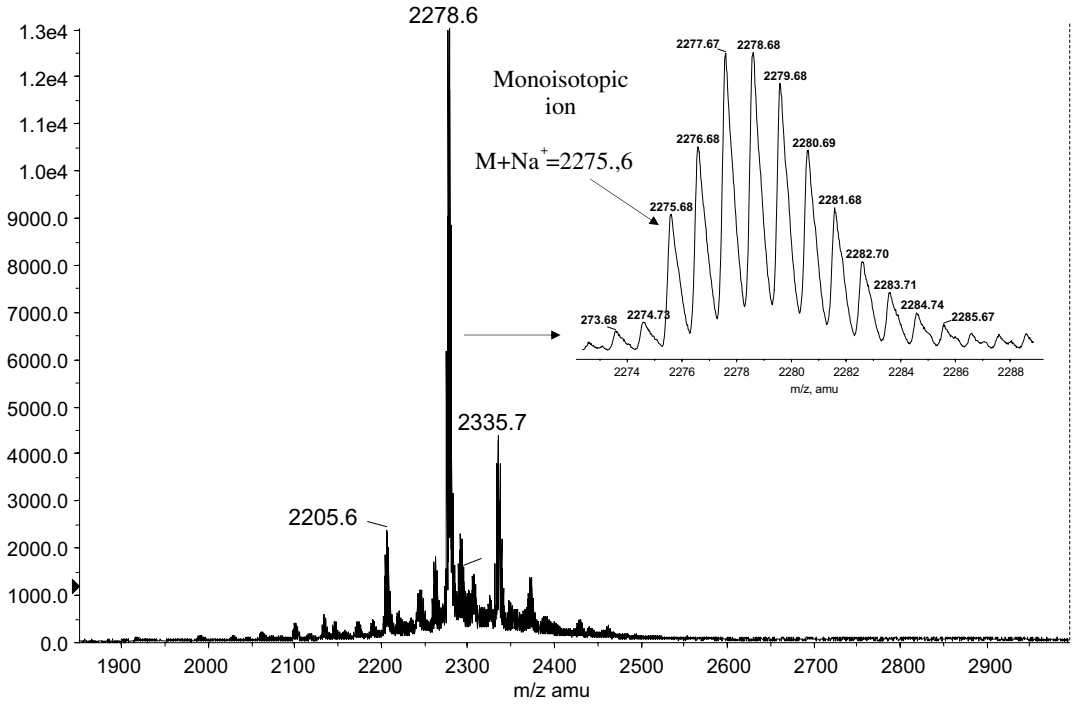


Fig. 3. ESI/MS spectrum of 5β in THF/MeOH (CH_3COONa added).

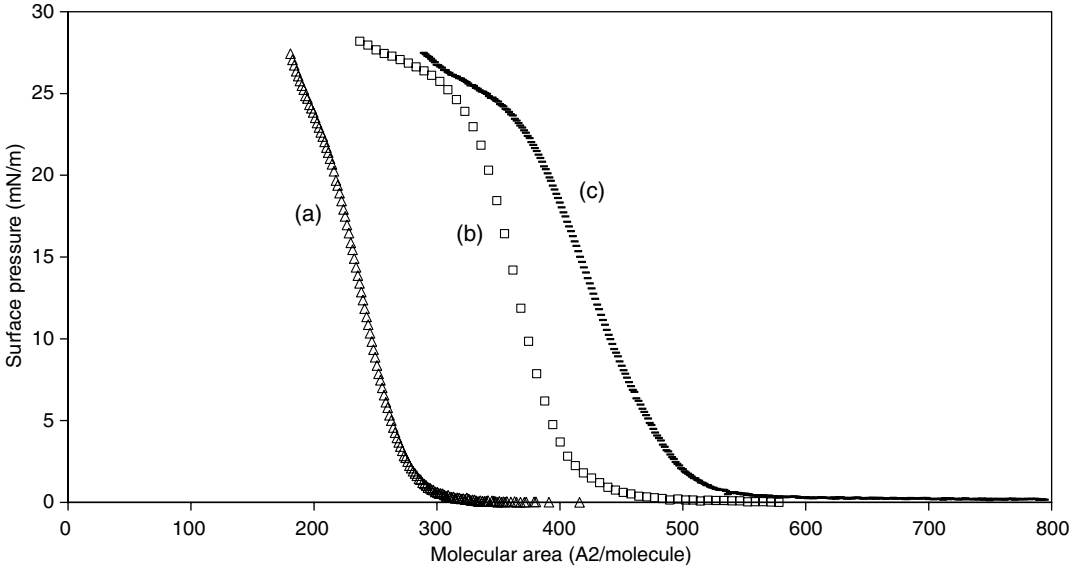


Fig. 4. Compression isotherms for 5α (a), 5β (b) and 5γ (c); ($T = 20$ °C, compression rate = 15 $cm^2\ min^{-1}$).

2275–2285 there was a mixture of the expected molecule (M) and (M−2) amu.

The modified cyclodextrin behavior at the air–water interface was studied. The compression isotherms show that these new molecules 5α, 5β and 5γ form a stable monolayer at the air–water interface until the collapse pressure of 25 mN m^{-1}. In addition, the isotherms are reversible during the monolayer decompression from 20 to 10 mN m^{-1} and no hysteresis is observed. Also, the hydroxyl secondary side modification by trimethylsilyl groups allows the CD molecules to acquire an amphiphilic character. This result is in agreement with the behavior at the air–water interface of βCD modified by substituting all primary hydroxyl groups with a SCF_3 group (Granger, Felix, Parrot-Lopez, & Langlois, 2000). Indeed, this βCD forms also a stable monolayer at the air–water interface until the collapse pressure of 25 mN m^{-1}.

In order to confirm the molecular organization of 5α, 5β and 5γ molecules at the air–water interface, the limiting areas, A_0, obtained by extrapolating the steeply rising section of the initial pressure rise to zero pressure (Gaines, 1966), were measured and they increase from 280 to 500 $Å^2$ $molecule^{-1}$ with the number of glucose units in the CD ring. These areas are larger than those calculated in literature (Saenger, 1980) for natural CDs but they are comparable with those of substituted CD reported by Greenhall et al. (1995) and Coleman et al. (1992). An arrangement, where the CD axis of rotation would be perpendicular to the water with one rim in contact with the water, is in agreement with the molecular structure (hydrophilic primary side). The molecular areas can thus be calculated assuming a hexagonal packed structure of the CD bases in a two dimensional layer, i.e. $A_\perp = \frac{\sqrt{3}}{2} d^2$ and can be compared to the experimental values. In this arrangement, the calculated areas vary from 310, 370 to 430 $Å^2$ for 5α, 5β and 5γ, respectively, and are very close to the experimental values ($A_0 = 280$, 420 and 500 $Å^2$ $molecule^{-1}$ for 5α, 5β and 5γ, respectively). Accordingly, it was assumed that the CD molecules are rather arranged in the closest packing mode of CD rings with their axis of rotation perpendicular to the water surface (Fig. 4).

The different cyclodextrin monolayers were transferred at 18 mN/m^{-1} without the addition of a fatty acid being necessary. The monolayers were transferred both on the upstroke and the downstroke of the substrate with a transfer ratio close to unity Ulman, 1992; Roberts, 1990). Thus, as expected, these modified cyclodextrins can be deposited on a solid substrate by the Langmuir–Blodgett technique.

4. Conclusion

New modified cyclodextrins in which the primary hydroxyl side is changed into thiol, and secondary hydroxyl side is modified with trimethylsilyl groups have been synthesized. This modification with a short organo-silicon group is sufficient to confer to the new molecules an amphiphilic character. Indeed, the modified cyclodextrins form stable monolayer at the air–water interface which can be transferred onto solid substrates. This result would enable us to show that the deposit imparts to the substrate the various properties of the cyclodextrins.

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