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The Features of the Synthesis and Chemical Behavior of Some β-Cyclodextrin Silyl Derivatives

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Abstract—Conditions are found for the regioselective silylation of the β-cyclodextrin primary hydroxy groups by diphenylmethylsilyl chloride and trimethylsilyl chloride. It is shown that the position of silyl substituents at the primary or secondary hydroxyl can be determined using ^{29}Si NMR spectroscopy. In the case of acetic and phosphorous acid chlorides, the subsequent functionalization of the secondary hydroxyls occurs with a significant removal of the protective silyl groups.

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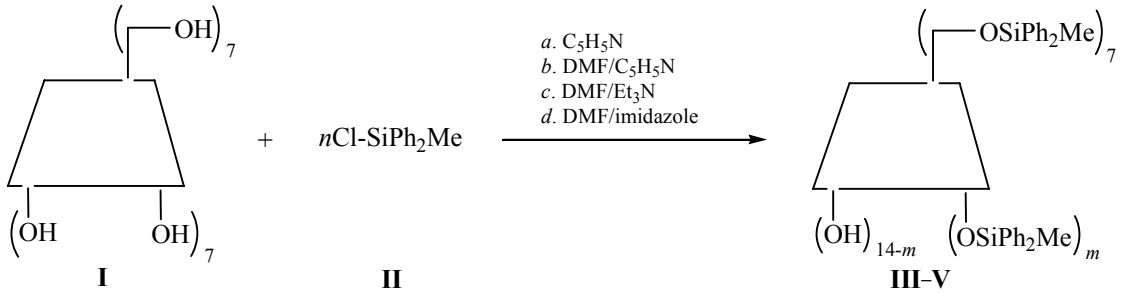
It is known that among the multitude of protecting groups in the chemistry of cyclodextrins, the *tert*-butyldimethylsilyl group has been widely used to protect the primary hydroxy groups [1]. To regioselective fixation at the the primary hydroxyls the processing of unprotected cyclodextrin using *tert*-butyldimethylsilyl chloride in pyridine is performed [2], or in DMF, in the presence of imidazole [3]. Further functionalization, for example, acylation [3–5] or phosphorylation [6] usually resulted in good yields of the corresponding esters at the secondary hydroxy groups. However, in the case of processing with phosphorous diamidoester [7] or phenylphosphonous dichloride [8] we observed an unexpected removal of the protective *tert*-butyldimethylsilyl groups, apparently due to the influence of supramolecular cyclodextrin cavity [9]. Given these data, it was interesting to check as protection for the primary hydroxy groups of the other protecting group known in the chemistry of sugars, namely, diphenylmethylsilyl group. For this purpose, β-cyclodextrin (**I**) was treated with 8.5 (*n*) molar equivalents of diphenylmethylsilyl chloride (**II**) in a solution of pyridine (method *a*) or in DMF solution in the presence of different acceptor of hydrogen chloride: pyridine (method *b*), triethylamine (method *c*), and imidazole (method *d*). To test the possibility of a deeper silylation, that is, further at the secondary hydroxyls, the β-cyclodextrin was treated similarly to method *a* in pyridine with 12 and 24 molar equivalents of diphenylmethylsilyl chloride **II**.

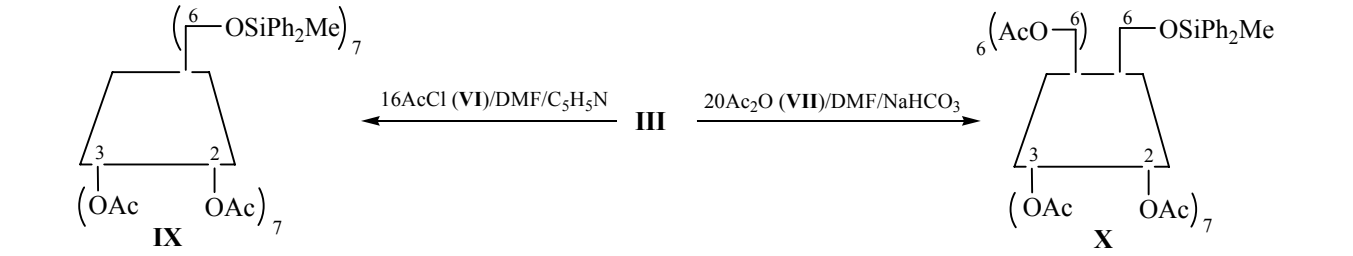


I **II** **III–V**

III, $m = 0$; **IV**, $m = 2$; **V**, $m = 9$.

At treating 8.5 molar equivalents of the reagent **II** by the *a–d* methods silyl derivatives **III** were isolated containing by the data of ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry seven silyl groups, and at the processing with 12 or 24 molar equivalents of the reagent **II** were isolated respectively derivatives **IV** or **V**, containing 9 (*m* = 2) and 16 (*m* = 9) silyl groups. Previously the position of substituents on the cyclodextrin skeleton, that is, their location at the primary hydroxyl groups in positions 6 or secondary in positions 2 and 3 was determined with the use of ^{13}C NMR spectroscopy; the approach based on the fact that at the replacement of primary hydroxy groups the signals of carbon nuclei C^6 shifted markedly downfield [10], like in the case of phosphorylation [11] and acetylation [12]. However, this method was not applicable to determine the position of silyl protection in the derivatives **III–V**, because the shift of the C^6 carbon with the introduction of silyl substituents was almost imperceptible. Therefore, to determine region-selectivity of silylation we used ^{29}Si NMR spectroscopy. It was found that the signal of the silicon nucleus located at C^6 appears at much stronger field (–2.3 to –2.5 ppm) than at C^2 and C^3 (1.4–2.2 ppm) (see Experimental) . Applicability of this approach was confirmed additionally by the example of trimethylsilyl and *tert*-butyldimethylsilyl derivatives of β-cyclodextrin (see below). Thus, we found that silylation (by methods *a–d*) with a small molar excess of silylating agent **II** with respect to the primary hydroxy groups (*n* = 8.5) occurs only at the C^6 position to form a *per*-6-O-silyl derivative **III**, whereas the use of increased amounts of silylating agent **II** (*n* = 12 and 24) leads to further silylation at the positions of secondary hydroxyls, C^2 and C^3. In the case of an excess of silylating agent (*n* = 24) relative to the entire amount of hydroxy groups (21), a part of the secondary hydroxy groups still remained free, probably due to steric hindrances, and further maintaining of the reaction mixture led only to the accumulation of by-products.

Derivative **III** was investigated in the reactions of acetylation with acetyl chloride **VI** and acetic anhydride **VII** and in the phosphorylation with cycloalkylenephosphorous acid chloride **VIII** in pyridine and in benzene with triethylamine.



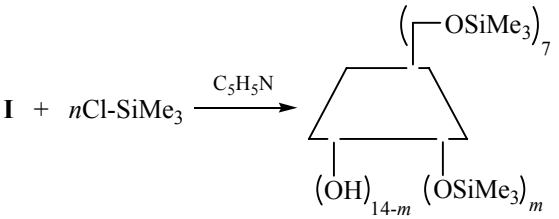
It turned out that only the use of acetyl chloride **VI** in the presence of pyridine leads to the expected product **IX**, with retention of 7 silyl substituents at C^6 and containing 14 acetyl groups at C^2 and C^3 atoms. The structure of product **IX** was proven using ^{1}H and ^{13}C NMR spectroscopy. The completeness of acetylation was assessed by analyzing the ^{1}H NMR spectrum by measuring the ratio of integral intensities of proton signals of acetyl groups at C^2 and C^3 atoms at 1.85–2.30 ppm to the signals of protons of cyclodextrin skeleton at 3.30–4.85 ppm. In the ^{13}C NMR spectrum the appearance was observed of signals at 169.6 and 170.5 ppm belonging to the carbonyl carbon atoms at the atoms C^2 and C^3, and the methyl carbons at 20.7 and 20.9 ppm [5]. In the ^{29}Si NMR spectrum a broad singlet at –2.4 ppm characteristic of the silicon nuclei at C^6 was found.

However, in the case of acetic anhydride **VII** and chlorophosphite **VIII** we observed a significant desilylation of the protective silyl groups in compound **III**. Thus, treating with anhydride **VII** in our synthesis conditions we were able to isolate derivative **X** containing, as shown by ^{1}H NMR spectroscopy, a single diphenylmethylsilyl group and six acetyl groups at the primary, and 14 acetyl groups at the secondary hydroxyls. Additionally, the structure of compound **X** was confirmed by ^{13}C NMR spectroscopy, using our suggested criteria for determining the location of acetyl groups. So, we have previously shown that by using ^{13}C NMR spectroscopy, the analysis of the signals of the methyl and carbonyl carbons of acetyl groups can indicate the acetyl substituent at the C^2 (the signals of carbon nuclei of CH_3 groups at 20.9 ppm and of C = O groups at 170.5 ppm), and at the C^3 (the

signals of the carbon nuclei of CH_3 groups at 20.7–20.8 ppm and C=O groups at 169.4–169.6 ppm) [5]. In the case of the acetyl derivatives **IX** and **X** we also observed a similar picture, and in the ^{13}C NMR spectrum of derivative **X** we observed a downfield (63.1 ppm) and upfield (69.8 ppm) shifts the signals of carbon nuclei of glucoside fragments carrying the acetyl substituents (indicated in the experimental part as the $C^{6'}$ and $C^{5'}$, respectively), compared with the signals of carbon nuclei in the same positions at C^6 and C^5 of glucoside fragment carrying the diphenylmethylsilyl substituent (61.6 ppm and 74.8 ppm, respectively) that confirms additionally the structure of compound **X**.

At processing the silyl derivative **III** with chlorophosphite **VIII** in our synthesis conditions by the methods *a* and *b*, we also observed a significant desilylation, so that the isolated product contained about 3–4 diphenylmethylsilyl groups, as revealed by means of ^1H NMR spectroscopy, but we failed to estimate its exact structure.

Given these data, it was of interest to test a similar acetylation and phosphorylation of other β-cyclodextrin silyl derivative (**XI**), containing significantly less sterically hindered trimethylsilyl groups. We first investigated a possibility of the regioselective silylation of β-cyclodextrin **I** with trimethylsilyl chlo-ride **XII** in pyridine. It was noted in the literature that the silylating reagent **XII** shows low selectivity and would lead to "chaotic" silylation of primary and secondary hydroxy groups of cyclodextrins [1, 13].

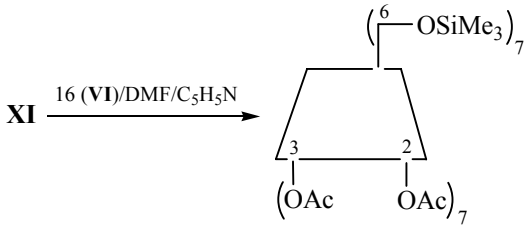


XII **XI, XIII**

XI, $m = 0$; **XIII**, $m = 14$.

We found that in the case of a small molar excess of silylating agent **XII** relative to the primary hydroxyls ($n = 8.5$) at 0°C only the derivative **XI** was produced ($m = 0$) silylated at the primary hydroxyls, whereas in more severe conditions (60°C) and with an excess of silylating agent **XII** relative to all hydroxyls ($n = 24$) persilylated derivative **XIII** was formed ($m = 14$). The number of trimethylsilyl groups in compounds **XI** and **XIII** is proved by means of ^1H NMR spectroscopy and molecular weights determined by MALDI-TOF mass spectrometry (see Experimental). The selective position of silyl groups in compound **XI** we proved based on the analysis of the ^{29}Si NMR spectra. Like in the case of derivatives **III–V,** the signals of the silicon nuclei at the primary hydroxy groups of compounds **XI, XIII** are located at stronger field (17.2–17.5 ppm) than the signals of the silicon nuclei at the secondary hydroxyls (compound **XIII**), 22.1– 22.4 ppm.

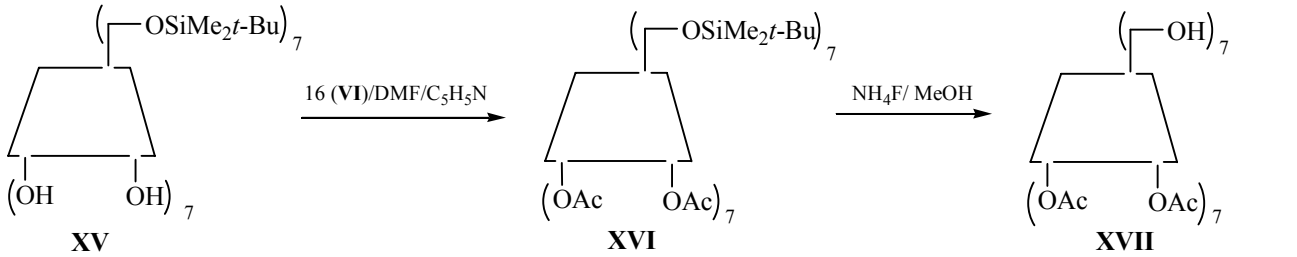
We tested the silyl derivative **XI** in the acetylation with acetyl chloride **VI** and acetic anhydride **VII** in the same way as the derivative **III**.



XIV

It turned out that only in the case of the acetyl chloride **VI** derivative **XIV** formed containing seven silyl groups at the primary and containing 14 acetyl groups at the secondary hydroxy groups. Number of silyl and acetyl groups determined by us is based on the analysis of the ^1H NMR spectra, and the location of silyl and acetyl groups, as above, we confirmed on the basis of the ^{29}Si and ^{13}C NMR spectra, respectively (see Experimental). In the case of acetylation with acetic anhydride **VII** and phosphorylation with the chlorophosphite **VIII** we found by analyzing the ^1H NMR spectra a significant desilylation of trimethylsilyl group of the derivative **XI**, like in the case of compound **III**, with the formation of a complex mixture of products, and we failed to establish their structures.

To confirm the reliability of the ^{29}Si NMR spectroscopy in determining the position of silyl groups, we prepared by a known procedure the *per*-6-O-(*tert*-butyl)dimethylsilyl derivatives of β-cyclodextrin (**XV**) (^{29}Si NMR, δ 19.7 ppm), then its 2,3-O-*per*-acetylated derivative **XVI** (^{29}Si NMR, δ 19.5 ppm) [5], and after desilylation of the latter we obtained the β-cyclodextrin derivative **XVII** containing a free primary hydroxy groups (see Experimental).



XV **XVI** **XVII**

Further, processing derivative **XVII** with silylating agents **II** or **XII**, we obtained in authentic synthesis the above compound **IX** or **XIV**, respectively (method *b*, see Experimental).

It is important that the signals of the silicon nuclei in the ^{29}Si NMR spectra of compounds **IX** (–2.4 ppm) and **XIV** (17.2–17.5 ppm) (method *b*) coincided with the signals of the silicon nuclei of the same compounds obtained by the acetylation of the regioselectively silylated derivatives (method *a*) **III** and **XI**, containing free secondary hydroxy groups. Based on these data, we can conclude that the signals of the silicon nuclei in the ^{29}Si NMR spectra can be reliably used to determine the position of silyl protecting groups at the primary or secondary hydroxyls of β-cyclodextrin.

Thus, we selected the conditions of selective silylation with diphenylmethylsilyl and trimethylsilyl chlorides of the primary hydroxy groups of β-cyclodextrin. At the same time we showed that by ^{29}Si NMR spectroscopy it is possible to determine region-selectivity of the silylation. However, the subsequent functionalization of the secondary hydroxy groups with acetic anhydride and phosphorous chloride is accompanied by a significant removal of the protective silyl groups.

EXPERIMENTAL

All experiments were carried out in anhydrous solvents purified by standard methods.

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-ECX400 instrument at 400 MHz and 100.53 MHz, respectively. Chemical shifts are given relative to the ^{1}H NMR signal of the residual $CHCl_3$ (δ_H 7.27 ppm) for solutions in $CDCl_3$. Chemical shifts in the ^{13}C NMR spectra are given relative to the central signal of the solvent (δ_C 77.0 ppm) for solutions in $CDCl_3$. The ^{29}Si NMR spectra were recorded on a Bruker DRX-500 instrument at the frequency 99.37 MHz in CCl_4 relative to TMS.

The MALDI-TOF mass spectra were recorded on a Bruker Daltonics Ultraflex instrument in the positive ion mode using reflection option, the matrix was 2,5-dihydroxybenzoic acid.

Elemental analysis was performed on a FlashEA 1112HT instrument.

For TLC aluminum plates were used with a fixed layer of silica gel (Silufol UV-254), eluents benzene–ethanol–hexane 3:2:1 (A), hexane–acetone 3:2 (B), benzene–ethanol 3:1 (C), and chloroform–methanol 7:1 (D).

We used β-cyclodextrin from Merk (Germany) subjected to additional rigorous dehydration.

Compounds **XV** and **XVI** were synthesized as described in [5].

***per*-6-*O*-(Diphenylmethylsilyl)-β-cyclodextrin (III)**. *a*. To a solution of 3.00 g of β-cyclodextrin **I** in 40 ml of pyridine while stirring at 0°C was added within 30 min a solution of 5.23 g of silyl chloride **II** in 20 ml of pyridine. The mixture was stirred and then maintained for 24 h at 20°C, the solution was poured into 200 ml of ice water, the reaction mixture was kept for three days, a viscous bottom layer was separated and triturated with water (40 ml) to formation of a powder, which was filtered off, washed with water (3×10 ml), and dried in a vacuum (1 mm Hg) for 5 h at 80°C. Yield 5.64 g (85%), mp 107–109°C (decomp.), R_f 0.78 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.56 s (21H, $SiCH_3$), 3.34–3.93 m (42H, $C^{2-5}H$, C^6H_2), 4.80–5.05 m (7H, C^1H), 5.20–6.52 br.s [14H, $C^{2,3}OH$], 7.32–7.61 m (70H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: –3.7 and –3.6 ($SiCH_3$), 61.6 (C^6), 70.5–73.0 (C^2, C^3, C^5), 81.2 (C^4), 101.4 (C^1), 127.2–135.8 (C_6H_5). The ^{29}Si NMR spectrum, δ, ppm: –2.3 to –2.5 br.s. Mass spectrum, *m*/*z*: 2546.80 [*M* + K]. Calculated for $C_{133}H_{154}KO_{35}Si_7$ 2546.83. Found, %: C

63.71; H 6.15. $C_{133}H_{154}O_{35}Si_7$. Calculated, %: C 63.66; H 6.19.

b. Obtained similarly to the method *a* from 0.50 g of β-cyclodextrin and 0.33 g of pyridine in 7 ml of DMF and a solution of 0.87 g silyl chloride **II** in 3 ml of DMF. Yield 0.84 g (76%), mp 107–109°C (decomp.), R_f 0.78 (A). The ^{1}H, ^{13}C, ^{29}Si NMR spectra and MALDI-TOF mass spectrum are identical to those of the compound obtained by the method *a*.

c. Obtained similarly to the method *a* from 0.50 g of β-cyclodextrin and 0.42 g of triethylamine in 7 ml of DMF and a solution of 0.87 g of silyl chloride **II** in 3 ml of DMF. Yield 0.79 g (71%), mp 107–109°C (decomp.), R_f 0.78 (A). The ^{1}H, ^{13}C, ^{29}Si NMR spectra and MALDI-TOF mass spectrum are identical to those of the compound obtained by the method *a*.

d. Obtained similarly to method *a* from 0.50 g of β-cyclodextrin, 0.28 g of imidazole in 7 ml of DMF and a solution of 0.87 g of silyl chloride **II** in 3 ml of DMF. Yield 0.77 g (69%), mp 107–109°C (decomp.), R_f 0.78 (A). The ^{1}H, ^{13}C, ^{29}Si NMR spectra and MALDI-TOF mass spectrum are identical to those of the compound obtained by the method *a*.

***per*-6-*O*-(Diphenylmethylsilyl)-di-(2(3)-*O*-diphenylmethylsilyl)-β-cyclodextrin (IV)** was obtained similarly to compound **III** by the method *a* from 0.50 g of β-cyclodextrin in 7 ml of pyridine and 1.23 g of silyl chloride **II** solution in 6 ml of pyridine. Yield 0.86 g (67%), mp. 95–97°C, R_f 0.81 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.56 s (27H, $SiCH_3$), 3.30–3.96 m (42H, $C^{2-5}H$, C^6H_2), 4.83–5.07 m (7H, C^1H), 5.15–6.55 br.s (12H, $C^{2,3}OH$), 7.32–7.61 (90H, C_6H_5). The ^{29}Si NMR spectrum, δ, ppm: –2.3 to –2.5 and 1.4 to 2.2 br.s. Mass spectrum, *m*/*z*: 2938.91 [*M* + K]. Calculated for $C_{159}H_{178}KO_{35}Si_9$: 2938.97. Found, %: C 65.73; H 6.25. $C_{159}H_{178}O_{35}Si_9$. Calculated, %: C 65.81; H 6.18.

***per*-6-*O*-(Diphenylmethylsilyl)-nona-[2(3)-*O*-diphenylmethylsilyl]-β-cyclodextrin (V)** was obtained similarly to compound **III** by the method *a* from 0.50 g of β-cyclodextrin in 7 ml of pyridine and 2.46 g of silyl chloride **II** solution in 9 ml of pyridine. Yield 1.20 g (64%), viscous oil, R_f 0.89 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.56 s (48H, $SiCH_3$), 3.32–3.97 m (42H, $C^{2-5}H$, C^6H_2), 4.78–5.03 m (7H, C^1H), 5.20–6.52 br.s (5H, $C^{2,3}OH$), 7.32–7.61 (160H, C_6H_5). The ^{29}Si NMR spectrum, δ, ppm: –2.3 to –2.5) and 1.4–2.2 br.s. Mass spectrum, *m*/*z*: 4312.39 [*M* + K]. Calculated for $C_{250}H_{262}KO_{35}Si_{16}$: 4312.47. Found, %: C 70.03; H 6.24. $C_{250}H_{262}O_{35}Si_{16}$. Calculated, %: C 70.22; H 6.18.

***per*-6-*O*-(Diphenylmethylsilyl)-*per*-(2,3-*O*-acetyl)-β-cyclodextrin (IX).** *a*. To a solution of 0.50 g of compound **III** and 0.28 g of pyridine in 5 ml of DMF while stirring at 20°C was added 0.25 g of acetyl chloride, the mixture was kept for 24 h at 20°C, the solution was evaporated by half, poured into 20 ml of water, the precipitate was filtered off, washed with water (3×5 ml), dried, dissolved in 3 ml of acetone, and poured into 20 ml of water. The precipitate was filtered off, washed with water (3×5 ml), and dried in a vacuum (1 mm Hg) for 3 h at 80°C. Yield 0.55 g (89%), mp. 139–140 ° C, R_f 0.87 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.56 s (21H, $SiCH_3$), 1.85–2.30 br.s [42H, $CH_3C(O)OC^{2,3}$], 3.32–4.85 m (42H, $C^{2-5}H$, C^6H_2), 4.93–5.05 m (7H, C^1H), 7.30–7.64 m (70H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: –3.6 and –3.5 ($SiCH_3$), 20.7 and 20.9 [C (O)$\underline{C}H_3$], 61.6 (C^6), 68.0–77.0 (C^2, C^3, C^5), 81.1 (C^4), 101.4 (C^1), 127.2–135.8 (C_6H_5), 169.6 and 170.5 [C=O]. The ^{29}Si NMR spectrum, δ, ppm: –2.4 br.s. Found, %: C 62.35; H 5.99. $C_{161}H_{182}O_{49}Si_7$. Calculated, %: C 62.42; H 5.92.

b. To a solution of 0.40 g of compound **XVII** [5] in 4 ml of pyridine was added at stirring 0.46 g of silyl chloride (**II**), the mixture was kept for 24 h at 20°C, poured into 10 ml of water, the separated oil was triturated with water, the precipitate formed was filtered off, washed with water (3×5 ml), and dried in a vacuum (1 mm Hg) for 3 h at 80°C. The ^{1}H, ^{13}C, ^{29}Si NMR spectra were identical to the spectra of the compound obtained by the method *a*. Yield 0.62 g (86%), mp 139–140°C, R_f 0.87 (A).

***per*-6-*O*-(Diphenylmethylsilyl)-eicosa-(2,3,6-*O*-acetyl)-β-cyclodextrin (X)**. To a solution of 0.40 g of compound **III** in 10 ml of DMF was added 0.54 g of sodium hydrogen carbonate and 0.33 g of acetic anhydride, the mixture was kept for 5 h at 80°C, then 24 h at 20°C. The solution was filtered, concentrated to 1 ml, 10 ml of diethyl ether was added, the precipitate formed was filtered off, washed with ether (2×5 ml), dried, triturated with water (5 ml), filtered off, washed with water (3×5 ml), and dried in a vacuum (1 mm Hg) for 3 h at 80°C. Yield 0.25 g (70%), mp 187–188°C (decomp.), R_f 0.25 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.56 s (3H, $SiCH_3$), 2.09 s [18H, $CH_3C(O)OC^6$], 2.17 s to 2.33 s [42H, $CH_3C(O)OC^{2,3}$], 3.10–5.85 m (49H, $C^{1-5}H$, C^6H_2), 7.32–7.61 (10H, C_6H_5). ^{13}C NMR

spectrum ($CDCl_3$), δ, ppm: –3.7 and –3.6 ($SiCH_3$), 20.5, 20.9, 21.1 [C(O)$\underline{C}H_3$], 61.6 (C^6), 63.1 ($C^{6'}$), 69.8 ($C^{5'}$), 73.7, 73.9, 74.8 (C^2, C^3, C^5), 83.4 (C^4), 101.2 (C^1), 127.2–135.8 (C_6H_5), 168.2, 169.8, 170.5 [C=O]. Found, %: C52.62; H 5.51. $C_{95}H_{122}O_{55}Si$. Calculated, %: C 52.53; H 5.66.

***per*-6-O-(Trimethylsilyl)-β-cyclodextrin (XI)** was obtained similarly to compound **III** by the method *a* from 3.00 g of β-cyclodextrin **I** in 40 ml of pyridine and 2.44 g of trimethylsilyl chloride **XII** solution in 20 ml of pyridine. Yield 2.13 g (49%), mp 253–255°C (decomp.), R_f 0.27 (B). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.21 and 0.24 s (63H, $SiCH_3$), 3.34–3.93 m (42H, $C^{2–5}H$, C^6H_2), 4.80–5.05 m (7H, C^1H), 5.20– 6.52 br.s (14H, $C^{2,3}OH$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.2 and 0.4 ($SiCH_3$), 61.7 (C^6), 70.5–73.5 (C^2, C^3, C^5), 81.5 (C^4), 102.1 (C^1). The NMR spectrum of ^{29}Si, δ, ppm: 17.2–17.5 br.s. Mass spectrum, *m*/*z*: 1678.54 [*M* + K]. Calculated for $C_{63}H_{126}KO_{35}Si_7$: 1678.61. Found, %: C46.01; H 7.85. $C_{63}H_{126}O_{35}Si_7$. Calculated, %: C 46.13; H 7.74.

***per*-2,3,6-*O*-(trimethylsilyl)-β-cyclodextrin (XIII)**. To a solution of 0.5 g of β-cyclodextrin **I** in 6 ml of pyridine while stirring at 20°C was added a solution of 0.15 g of silyl chloride **XII** in 3 ml of pyridine. The mixture was stirred for 5 h at 60°C, the solution was poured into 50 ml of ice-cold water, the precipitate formed was washed with water (5 ml), filtered off, washed with water again (3×10 ml) and dried in a vacuum (1 mm Hg) for 3 h at 80°C. Yield 0.95 g (81%), mp 148–150°C (decomp.) (published data: 145–155°C [13]), R_f 0.84 (B). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.19–0.27 br.s (189H, $SiCH_3$), 3.33–3.96 m (42H, $C^{2–5}H$, C^6H_2), 4.80–5.07 m (7H, C^1H). The ^{29}Si NMR spectrum, δ, ppm: 17.2–17.5 and 22.1–22.4 br.s. Mass spectrum, *m*/*z*: 2688.10 [*M* + K]. Calculated for $C_{105}H_{238}KO_{35}Si_{21}$: 2688.17. Found, %: C 47.47; H 9.19. $C_{105}H_{238}O_{35}Si_{21}$. Calculated, %: C 47.58; H 9.05.

***per*-6-*O*-(trimethylsilyl)-*per*-(2,3-*O*-acetyl)-β-cyclodextrin (XIV)**. *a*. It was obtained like compound **IX** (method *a*) from 0.50 g of compound **XI** and 0.42 g of pyridine in 5 ml of DMF and 0.38 g of acetyl chloride. Yield 0.60 g (88%), mp 149–150°C (decomp.), R_f 0.63 (B). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.21 and 0.24 s (63H, $SiCH_3$), 1.85–2.30 br.s [42H, $CH_3C(O)OC^{2,3}$], 3.34–3.93 m (42H, $C^{2–5}H$, C^6H_2), 4.79–5.05 m (7H, C^1H). The ^{29}Si NMR spectrum, δ, ppm: 17.2–17.5 br.s. Found, %: C49.15; H 6.89. $C_{91}H_{154}O_{49}Si_7$. Calculated, %: C 49.04; H 6.96.

b. Obtained like compound **IX** (method *b*) from 0.40 g of compound **XVII** in 4 ml of pyridine and 0.21 g of silyl chloride **XII**. Yield 0.44 g (85%), mp 149–150°C (decomp.), R_f 0.63 (B). ^1H and ^{29}Si NMR spectra are identical to those of compound obtained by the method *a*.

***per*-2,3-*O*-acetyl-β-cyclodextrin (XVII)**. To a solution of 2.00 g of compound **XVI** in 50 ml of methanol was added 0.60 g of ammonium fluoride. The mixture was refluxed at 70°C for 24 h, concentrated to 4 ml, and poured into 40 ml of ice water. The precipitate formed was filtered off, washed with water (2×10 ml), and dried in a vacuum (1 mm Hg) for 3 h at 80°C. Yield 1.21 g (86%), mp 185–186°C (published data: 184–188°C [14]), R_f 0.67 (D). ^1H NMR spectrum (C_5D_5N), δ, ppm: 1.80–2.25 br.s [42H, $CH_3C(O)OC^{2,3}$], 3.95–4.72 m (42H, $C^{2–5}H$, C^6H_2), 5.45–5.55 m (7H, C^1H), 5.60–6.40 br.s (6H, C^6OH). Found, %: C 48.61; H 5.77. $C_{70}H_{98}O_{49}$. Calculated, %: C 48.78; H 5.73.

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