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Acetylation of Secondary Hydroxy Groups of α- and β-Cyclodextrines Silyl Derivatives

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Abstract—The application of acetyl chloride in the combination with different solvents and bases permitted the preparation of silyl derivatives of α- and β-cyclodextrines containing a definite amount of acetyl substituents on the secondary hydroxy groups. It was found that by means of the ^{1}H and ^{13}C NMR spectroscopy it is possible to make an exact attribution of acetyl groups to C^2 or C^3 carbon atoms of carbohydrate fragments of α- and β-cyclodextrines. Desilylation with ammonium fluoride in methanol gives acetyl derivatives of cyclodextrines containing free primary hydroxy groups.

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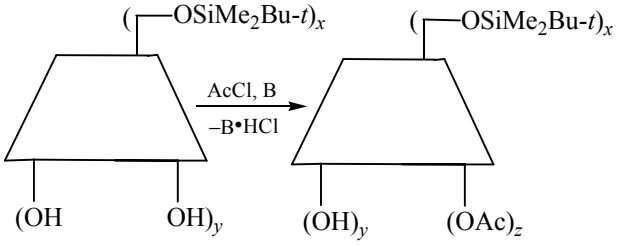
As is known, a selective modification of cyclodextrines is the experimentally complicated problem due to the presence of a large amount of hydroxy groups of different nature including primary groups in the positions C^6 and two sets of secondary hydroxy groups in the positions C^2 and C^3 of carbohydrate fragments (for example, see the review [1]). Therefore when it is necessary to prepare cyclodextrines selectively substituted at the secondary hydroxyls, the protection of primary hydroxy groups and subsequent removal of such protective groups is used. Another specific complication in the regioselective functionnalization of cyclodextrines is the necessity of consideration of the statistical and sterical factors [2]. The first groups easily enter cyclodextrine molecule while the subsequent ones meet complications connected with the increase in sterical hindrances at the consecutive introduction of functional groups. Due to that despite of the abundance of publications concerning the synthesis of modified cyclodextrines the general recommendations are absent and in each case individual approach to the choice of synthetic procedures is required. The aim of this work was the investigation of synthesis of α- and β-cyclodextrines containing acetyl groups in the positions C^2 and C^3 of he carbohydrate fragment. The choice of α- and β-cyclodextrines is caused by their availability and characteristic capability to form various host-guest type compounds with hydrophobic guests due to the presence of hydrophobic chiral cavity which has found a wide application in the fine organic synthesis for solving a series of modern applied problems (for example, see [3–5]). Meanwhile cyclodextrines are poorly soluble in water (solubility of β-cyclodextrine in water is 18.5 g l^{-1} at 25°C) and in the organic solvents what limits their practical use. But such procedures as acetylation, methylation [5], and hydroxypropylation [6] lead to significant increase in their solubility. For the increase in water solubility the introduction of a small amount of modifying groups in the basic molecule is sufficient. In contrast, to increase the solubility in the organic solvents a high degree of substitution with the modifier is required. It is important that in general case the modification of cyclodextrines must lead to the increase in the internal cavity, and hence to improving the ability of formation of the stable host-guest compounds, among them with the guests presenting pharmacological interest [7]. Among the above-mentioned cyclodextrine derivatives the acetyl ones are the most important that are synthesized by treating with acetic anhydride in the presence of pyridine, the procedure widely used in sugar chemistry. This method is not regioselective. It is used as a rule for peracetylation of free hydroxy groups of cyclodextrine and its derivatives [8–11]. Besides it must be considered that cyclodextrine can reveal the unusual supramolecular properties due to the presence of the internal cavity as we have observed while phosphorylating it with the phosphorous acid chloride [12] and acylation with the valeryl and

palmitoyl chlorides [13]. In connection with that it seemed interesting to compare the acetylation of structurally close α- and β-cyclodextrines differing significantly in the size of the internal cavity (174 and 262 A^3 respectively) [3].

In this work we have studied acetylation of cyclodextrines with acetyl chloride in the presence of different amines such as triethylamine, pyridine, and *N,N*-dimethylaniline playing the role of hydrogen chloride acceptor and the acetylation activator. Available per-6-*O*-(*tert*-butyl)(dimethyl)silyl-α- (**I**) and β- (**II**) cyclodextrines were chosen as objects for investigation. Note that the acylation of secondary hydroxy groups of the silyl derivatives **I**, **II** with acid chlorides was reported previously, but acid chlorides of the valeric [13] and higher fatty acids [13, 14] were used. Benzene, DMF, and pyridine were chosen as solvents. The latter compound was also the hydrogen chloride acceptor. For comparison of the results all the experiments were carried out under analogous conditions. A solution of acetyl chloride was added dropwise with stirring to cyclodextrine solution at 0°C, the mixture obtained was stirred for 24 h at 20°C, and the reaction products were isolated as described in the Experimental. Acetyl chloride was taken in about 15% molar excess as compared to the total amount of hydroxy groups at C^2 and C^3 atoms of cyclodextrines.



I, II **III–XIV**

I, $x = y = 6$; **II**, $x = y = 7$; **III,** $x = 6$, $y = 0$, $z = 12$; **IV**, $x = 7$, $y = 0$, $z = 14$; **Va–Vc**, $x = 6$, $y = 3$, $z = 9$; **VI**, $x = 6$, $y = 6$, $z = 6$; **VII**, $x = 7$, $y = 4$, $z = 10$; **VIII**, $x = 7$, $y = 2$, $z = 12$; **IXa, IXb**, $x = 7$, $y = 8$, $z = 6$; **X**, $x = 7$, $y = 6$, $z = 8$; **XI**, $x = 7$, $y = 11$, $z = 3$.

Mean acetylation degree (z) was evaluated on the basis of the ^{1}H NMR data comparing the intensities of signals of the acetyl group protons at C^2 and C^3 in the range 1.85–2.30 ppm and of the signals of *tert*-butyl groups on silicon in the range 0.50–1.00 ppm. It proved that for the derivative of α-cyclodextrine **I** a complete acetylation of all hydroxy groups (compound **III**, see Table 1) took place only in DMF in the presence of *N,N*-dimethylaniline. In the case of β-cyclodextrine derivative **II** the complete acetylation took place in DMF in the presence of dimethylaniline (compound **II**, method *b*) and pyridine (compound **I,** method *a*, see Table 2). In all other cases the acetylation degree $z = 6$ and 9 (that means, 50 and 75%) for the derivative **I** (compounds **VI** and **Va–Vc** respectively) and z – 6–12 (that is 43–86%) for the derivative **II** (compounds **VII–X**). Note that prolonged keeping of the reaction mixture does not lead to the increase in the acetylation degree, but only to accumulation of by-products.

While analyzing the ^{1}H NMR spectra of the acetylated products we have made an important observation. The acetyl group protons of peracetylated derivatives **III** and **IV** give the broadened signal at 2.09 ppm, but in the case of partially acetylated compounds **V–X** the acetyl group protons give two signals at 1.87–2.16 ppm and at 2.08–2.30 ppm. For compounds **Va, VI, VII, IXb,** and **X** these signals have equal intensity, but in the spectrum of compound **Vb** the downfield signal is more intense. It may be suggested that this effect is caused by the different magnetic surrounding of acetyl group in different positions at C^2 and C^3 atoms. Similar picture was observed by us in the ^{13}C NMR spectra for the signals of carbon atoms of the acetyl fragments of compounds **Va**, **Vb**, **X**. In these substances the carbonyl carbon atoms give two singlets at 170.5 ppm and in the range 169.2–169.6 ppm. The carbon atoms of methyl groups give two signals at 20.9 ppm and in the range 20.7–20.8 ppm. In the Experimental the chemical shifts of protons and carbon atoms of acetyl groups are given by italics for the convenience of comparison. These and another attributions of signals of the carbon atom nuclei belonging to cyclodextrine frame and the silyl groups were in agreement with the data on the ^{13}C NMR spectra of compounds **III** and **IV** prepared by means of another method [10, 11]. It is evident that though the derivatives of α-cyclodextrine **Va**–**Vc** and β-cyclodextrine **XIa**, **IXb** have the same degree of acetylation (z = 9 and 6 respectively), they differ in structure.

That is why three compounds **V** and two compounds **IX** prepared under different conditions are geometric isomers marked as **Va**–**Vc** and **IXa, IXb**. As it was impossible to make accurate attribution of acetyl groups to C^2 and C^3 atoms on the basis of the ^{1}H and ^{13}C NMR data, we have prepared compound **XI** containing only three acetyl groups. It is important that in the ^{1}H NMR spectra of compound **XI** the acetyl

Table 1. Acetylation of per-6-*O*-(*tert*-butyl)(dimethyl)silyl-α-cyclodextrine **I** with acetyl chloride

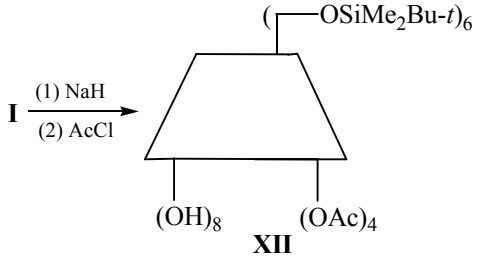
Comp. no. (method)	Solvent	Amine	Mean substitution degree (*z*)	Yield, %
Va (*a*)	C_6H_6	NEt_3	9	59
Vb	C_6H_6	C_5H_5N	9	82
Va (*b*)	C_6H_6	$Me_2NC_6H_5$	9	73
Va (*c*)	DMF	NEt_3	9	69
Vc	DMF	C_5H_5N	9	73
III	DMF	$Me_2NC_6H_5$	12	59
VI	C_5H_5N	C_5H_5N	6	61

Table 2. Acetylation of per-6-*O*-(*tert*-butyl)(dimethyl)silyl-)-β-cyclodextrine **II** with acetyl chloride

Comp. no. (method)	Solvent	Amine	Mean substitution degree (*z*)	Yield, %
VII	C_6H_6	NEt_3	10	69
VIII	C_6H_6	C_5H_5N	12	77
IXa	C_6H_6	$Me_2NC_6H_5$	6	85
IXb	DMF	NEt_3	6	84
IV (*a*)	DMF	C_5H_5N	14	59
IV (*b*)	DMF	$Me_2NC_6H_5$	14	58
X	C_5H_5N	C_5H_5N	8	93

group protons give one signal at 2.16 ppm, and in ^{13}C NMR spectrum the carbon atoms of carbonyl and the methyl groups give only signals at 170.5 and 20.9 ppm respectively. Thus we were able to use the two-dimensional {^1H–^{13}C} HETCOR NMR spectroscopy (see the figure) and with its help to establish the correlation between the signals of C^2 (73.7 ppm), C^3 (73.8 ppm), and C^5 (72.6 ppm) and the signals of the protons H^2 (3.65 ppm), H^3 (4.03 ppm), and H^5 (3.57 ppm). Note that in the ^{13}C NMR spectrum of the starting substance **II** the signals of C^2 carbon atoms appear at 72.7 ppm, of C^3 at 74.4 ppm, and of C^5 at 73.0 ppm (see Experimental). On the basis of these data we have shown that acetylation of the position C^2 leads to the significant downfield shift of the signals of these carbon atom. Analogous shift of C^2 signals caused by acetylation was reported in [15]. Considering the above-established correlation it can be concluded that the downfield signals in the ^1H NMR spectra in the range 2.08–2.30 ppm and the downfield signals of carbon atoms at 20.9 ppm correspond to the acetyl groups bound to the C^2 carbon atoms. Hence, the upfield signals in ^1H NMR spectra in the range 1.87–2.15 ppm, and the upfield signals of carbon atoms at 20.7–20.8 ppm can be attributed to acetyl groups bound to C^3.

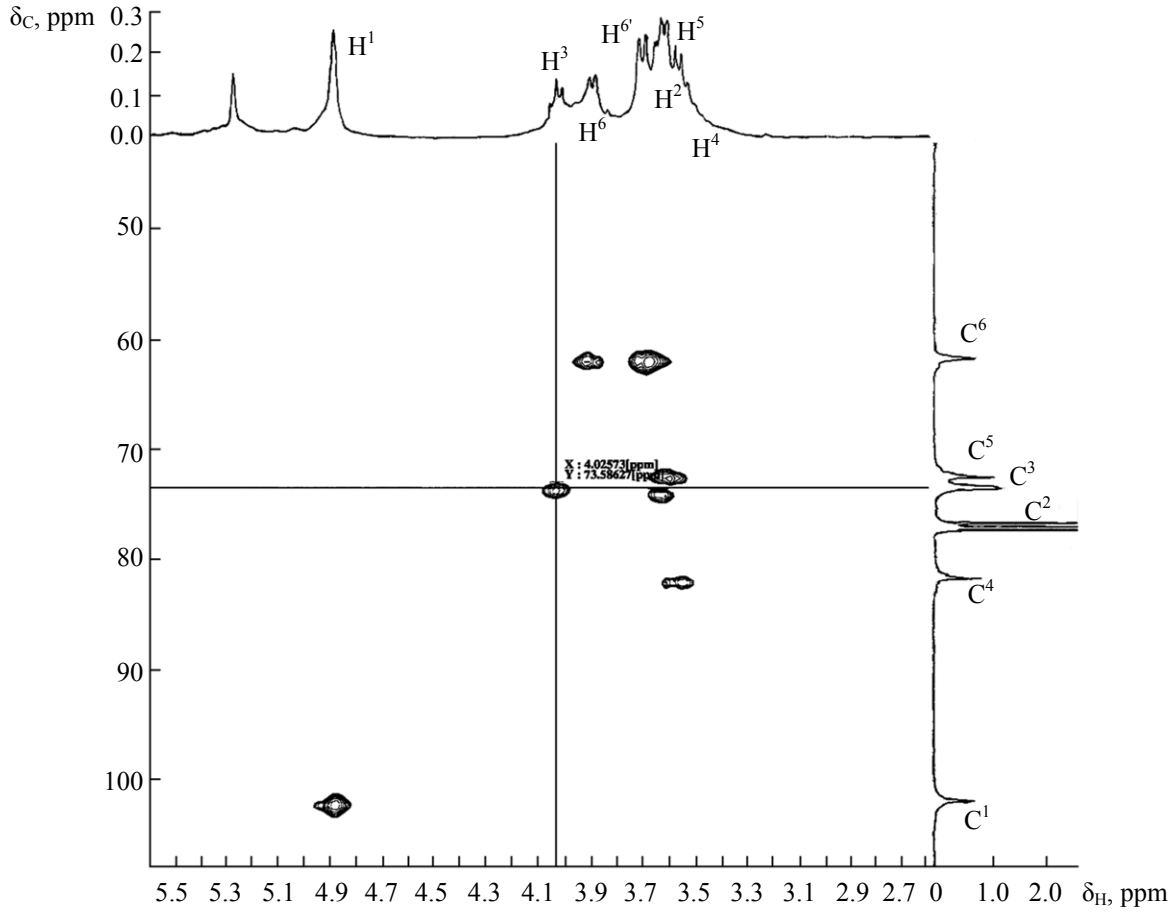
By treating compound **I** with sodium hydride followed by acetylation with acetyl chloride we have prepared tetraacetylated derivative **XII**.



XII

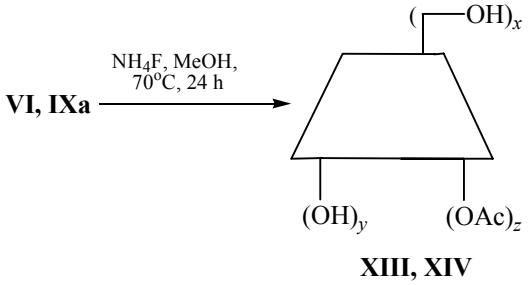
As known while treating cyclodextrine with sodium hydride the hydroxy groups on C^2 carbon atom are the first to be deprotonated due to their higher acidity and to the stability of the anions formed. The anions obtained attack the electrophilic reagent [15]. In our case it really occurred that in ^1H NMR spectrum of the derivative **XII** higher integral intensity of the downfield signals of the acetyl group protons at 2.13 ppm as compared to the upfield signals at 2.06 ppm (3:1, see Experimental) was observed. It may also serve the confirmation of the fact that the downfield signals in the range 2.08–2.30 ppm and the upfield ones at 1.87–2.15 ppm correspond to the acetyl groups in the positions C^2 and C^3 respectively.

On the final step of our work we have carried out the removal of the silyl protecting groups to give the corresponding derivatives containing free primary hydroxy groups. Such compounds present separate interest, for example, as the potential "hosts" carrying the hydrophilic hydroxy groups on the "narrow" part



{^{1}H–^{13}C} HETCOR NMR spectrum of compound **XI** ($CDCl_3$).

of cyclodextrine frame and exhibiting the increased water solubility, as well as in connection with their possible easy functionalization at the primary hydroxy groups. Note that for desilylation of the silyl derivatives of cyclodextrines a solution of tetrabutylammonium fluoride in THF [8–10] or the solution of the boron trifluoride etherate in methylene chloride [9, 10] were commonly used. But their use has some faults especially in the case of tetrabutylammonium fluoride. Due to that for desilylation of compounds **VI, IX** we have used a solution of ammonium fluoride in methanol [17] which occurred to be preferable from the point of view of the experimental procedure.



XIII, XIV

XIII, $x = 6$, $y = 6$, $z = 6$; **XIV**, $x = 7$, $y = 8$, $z = 6$.

In our case the desilylation proceeded in high yields and with the preservation of the introduced acetyl groups what was confirmed by the ^{1}H NMR spectra of the products **XIII** and **XIV** (see Experimental).

Hence, we have developed new ways to the preparation of α- and β-cyclodextrines containing definite number of acetyl groups on secondary hydroxy groups and free primary hydroxy groups. On the basis of analysis of the ^{1}H and ^{13}C NMR spectra of the acetyl derivatives obtained the conclusions can be made about belonging of acetyl groups to the positions C^2 and C^3 of carbohydrate fragments.

EXPERIMENTAL

All the experiments were carried out in anhydrous solvents purified according to the standard procedures.

^{1}H and ^{13}C NMR spectra were taken on a JEOL-ECX400 spectrometer (400 MHz and 100.53 MHz respectively) against internal TMS.

TLC was carried out on Silufol UV-254 plates, elution with 7:1 chloroform–methanol (A), 7:1 benzene–DMF (B), and 7:3 hexane–acetone (C).

Commercial α- and β-cyclodextrines (Merk, Germany) were additionally thoroughly dryed.

Per-6-*O*-(*tert*-butyl)(dimethyl)silyl-α-cyclodextrine (I). To a suspension of 2.00 g of α-cyclodextrine in 30 ml of pyridine a solution of 2.33 g of *tert*-butyldimethylsilyl chloride in 10 ml of pyridine was added with stirring in the course of 30 min at 0°C. The reaction mixture was kept for 24 h at room temperature. The solution obtained was filtered and poured in 200 ml of ice water. The precipitate formed was ground with 40 ml of water, filtered, washed with water (3×10 ml), dissolved in 50 ml of benzene, and the residual water was removed by the azeotrope distillation with the Dean-Stark trap. The solution was evaporated to dryness, and the residue was dried in a vacuum (1 mm Hg) for 8 h at 80°C. Yield 2.56 g (75%), mp 322–325°C with decomposition (reported data mp 323–326°C with decomposition [9]), R_f 0.60 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.03 s [36H, $Si(CH_3)_2$], 0.89 s [54H, $C(CH_3)_3$], 3.58 d.d [6H, C^4H, $^3J(H^3H^4)$ 8.7 Hz], 3.65 d.d [6H, C^2H, $^3J(H^2H^3)$ 9.7], 3.76 d.d [6H, C^4H, $^3J(H^3H^4)$ 8.7], 3.82 d.d [6H, C^5H, $^3J(H^4H^5)$ 10.0], 3.90 d.d [6H, C^6'H, $^3J(H^5H^6)$ 3.4], 4.01 d.d [6H, C^3H], 4.86 d [6H, C^1H, $^3J(H^1H^2)$ 3.2], 5.25 s and 6.52 s [12H, $C^{2,3}OH$]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –5.0 and –3.1 [$Si(CH_3)_2$], 18.5 [$C(CH_3)_3$], 26.1 [$C(CH_3)_3$], 62.1 (C^6), 73.2 (C^5). 74.5 (C^3), 72.3 (C^2), 81.4 (C^4), 101.6 (C^1). Found, %: C 52.30; H 8.80. $C_{72}H_{144}O_{30}Si_6$, Calculated, %: C 52.14; H 8.75.

Per-6-*O*-(*tert*-butyl)(dimethyl)silyl-β-cyclodextrine (II). This substance was obtained analogously to compound **I** from 3.00 g of β-cyclodextrine in 45 ml of pyridine and 3.39 g of *tert*-butyldimethylsilyl chloride in 15 ml of pyridine. Yield 4.30 g (84%), mp 297–300°C (with decomposition) {reported data 299–302°C (with decomposition) [10], 314–318°C (with decomposition) [18], 200–300°C (with decomposition) [19]}, R_f 0.56 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.03 s [42H, $Si(CH_3)_3$], 0.89 s [63H, $C(CH_3)_3$], 3.59 d.d [7H, C^4H, $^3J(H^3H^4)$ 8.7], 3.66 d.d [7H, C^5H, $^3J(H^4H^5)$ 9.7], 3.76 d.d [7H C^6H, $^2J(H^6H^{6'})$ 11.3], 3.84 d.d [7H, C^5H, $^3J(H^4H^5)$ 9.9], 3.91 d.d [7H, C^6'H, $^3J(H^5H^6)$ 3.4], 4.01 d.d (7H, C^3H), 4.86 d [7H, C^1H, $^3J(H^1H^2)$ 3.3], 5.27 s and 6.53 s (14H, $C^{2,3}OH$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –5.0 and –5.1 [$Si(CH_3)_2$], 18.2 [$C(CH_3)_3$], 25.8 [$C(CH_3)_3$], 61.6 (C^6), 73.0 (C^5), 74.4 (C^3), 72.2 (C^2), 81.2 (C^4), 102.05 (C^1). Found, %: C 52.18; H 8.79. $C_{84}H_{168}O_{35}Si_7$. Calculated, %: C 52.14, H 8.75.

Per[6-*O*-(*tert*-butyl)(dimethyl)silyl]-per[2,3-di-*O*-acetyl]-α-cyclodextrine (III). To a solution of 0.40 g of α-cyclodextrine derivative **I** and 0.45 g of *N,N*-dimethylaniline in 4 ml of DMF a solution of 0.27 g of acetyl chloride in 2 ml of DMF was added with stirring at 0°C in the course of 20 min. The mixture obtained was maintained for 24 h at 20°C, the solution formed was concentrated by half in a vacuum and poured in 30 ml of water. The precipitate formed was filtered off, dried, dissolved in 1 ml of acetone, poured in 10 ml of water, and stirred for a while. The precipitate was filtered off, washed with water (3x10 ml), and dried in a vacuum (1 mm Hg) for 4 h at 60°C. Yield 0.31 g (60%), mp 160–161°C, R_f 0.75 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm : 0.03 s [36H, $Si(CH_3)_2$], 0.89 s [54H, $C(CH_3)_3$], 1.90–2.30 br.s [36H, $CH_3C(O)OC^{2,3}$], 3.30–4.35 m (36H, C^2H–C^5H, C^6H_2), 4.80–5.05 m (6H, C^1H). Found, %: C 53.34; H 7.86, $C_{90}H_{168}O_{42}Si_6$. Calculated, %: C 53.31, H 7.83.

Per[6-*O*-(*tert*-butyl](dimethyl)silyl]-per[2,3-di-*O*-acetyl}-β-cyclodextrine (IV). *a*. This compound was obtained similarly to compound **III** from 0.40 g of β-cyclodextrine derivative **II**, 0.29 g of pyridine in 4 ml of DMF, and a solution of 0.26 g of acetyl chloride in 2 ml of pyridine. Yield 0.31 g (59%), mp 145–146°C, R_f 0.71 (B), 0.30 (C) {reported data 0.30 (C) [18]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.04 s [42H, $Si(CH_3)_2$], 0.87 s [63H, $C(CH_3)_3$], 1.85–2.30 br.s [42H, $CH_3C(O)OC^{2,3}$], 3.30–4.40 m (42H, C^2H–C^5H, C^6H^2), 4.85–5.25 m (7H, C^1H). Found, %: C 53.32, H 7.85. $C_{112}H_{196}O_{49}Si_7$. Calculated, %: C 53.31, H 7.83.

b. Compound **IV** was prepared analogously to compound **III** from 0.40 g of β-cyclodextrine derivative **II**, 0.44 g of *N,N*-dimethylaniline in 4 ml of DMF, and a solution of 0.26 g of acetyl chloride in 2 ml of DMF. Yield 0.30 g (58%), mp 145–146°C, R_f 0.79 (B) and 0.31 (C).^{1}H NMR spectrum of this sample is identical to that of compound **IV** prepared according to method *a*.

Compound Va. *a*. To a solution of 0.40 g of α-cyclodextrine derivative **I** and 0.38 g of triethylamine in 4 ml of benzene a solution of 0.27 g of acetyl chloride in 2 ml of benzene was added with stirring in the course of 20 min at 0°C. The mixture obtained was

kept for 24 h at 20°C, the solvent was distilled off, and the residue was ground with 5 ml of water, the precipitate formed was dried, dissolved in 1 ml of acetone, and poured in 10 ml of water. The mixture obtained was stirred for some time, the precipitate formed was filtered off, washed with water (3×10 ml), and dried in a vacuum (1 mm Hg) for 4 h at 60°C. Yield 0.29 g (50%), mp 156–158°C, R_f 0.69 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [36H, $Si(CH_3)_3$], 0.89 s [54H, $C(CH_3)_3$], 2.05 s [13.5H, $CH_3C(O)OC^3$], 2.14 s [13.5 H, $CH_3C(O)OC^2$], 3.30–4.40 m (36H, C^2H–C^5H, C^6H_2), 4.80–5.15 m (5H, C^1H), 5.20–5.70 m (3H, $C^{2,3}OH$). ^{13}C NMR spectrum ($CDCl_3$), δ_c, ppm: –4.7 and –5.9 [$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 20.8 and 20.9 [$C(O)CH_3$], 25.9 [$C(CH_3)_3$], 61.9 (C^6), 70.5–72.1 (C^2, C^3, C^5), 80.5 (C^4), 101.5 (C^1), 169.4 and 170.5 (C=O). Found, %: C 53.05, H 8.01. $C_{90}H_{162}O_{39}Si_6$. Calculated, %: C 53.06, H 8.02.

b. The sample was obtained analogously to *a* from 0.40 g of α-cyclodextrine derivative **I**, 0.45 g of *N,N*-dimethylaniline in 4 ml of benzene, and a solution of 0.27 g of acetyl chloride in 2 ml of benzene. Yield 0.36 g (73%), mp 156–158°C, R_f 0.69 (A).

c. The sample was obtained analogously to **III** from 0.40 g of α-cyclodextrine derivative **I**, 0.38 g of triethylamine in 4 ml of DMF, and a solution of 0.27 g of acetyl chloride in 2 ml of DMF. Yield 0.34 g (69%), mp 156–158°C, R_f 0.6_9 (A).

^{1}H and ^{13}C NMR spectra in both cases were identical to that of compound **Va** obtained according to the procedure *a*.

Compound Vb. This compound was obtained analogously to **Va** (method *a*) from 0.40 g of α-cyclodextrine derivative **I**, 0.29 g of pyridine in 4 ml of benzene, and a solution of 0.27 g of acetyl chloride in 2 ml of benzene. Yield 0.40 g (82%), mp 158–160°C, R_f 0.64 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [36H, $Si(CH_3)_3$], 0.87 s [54H, $C(CH_3)_3$], 2.06 s [16H, $CH_3C(O)OC^3$], 2.15 s [9H, $CH_3C(O)OC^2$], 3.30–4.40 m (36H, C^2H–C^5H, C^6H_2), 4.60–5.20 m (6H, C^1H), 5.20–5.70 m (3H, $C^{2,3}OH$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –4.8 and –5.0 [$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 20.8 and 20.9 [$C(O)CH_3$], 25.9 [$C(CH_3)_3$], 61.9 (C^6), 70.5–72.1 (C^2, C^3, C^5), 80.5 (C^4), 101.9 (C^1), 169.6 and 170.5 (C=O). Found, %: C 53.07, H 8.01. $C_{90}H_{162}O_{39}Si_8$. Calculated, %: C 53.07, H 8.02.

Compound Vc. This compound was prepared analogously to **III** from 0.40 g of α-cyclodextrine derivative **I**, 0.29 g of pyridine in 4 ml of DMF, and a solution of 0.27 g of acetyl chloride in 2 ml of DMF. Yield 0.36 g (73%), mp 154–156°C, R_f 0.62 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.04 s [36H, $Si(CH_3)_2$], 0.89 s [54H, $C(CH_3)_3$], 2.06 s [9H, $CH_3C(O)OC^3$], 2.16 s [18H, $CH_3C(O)OC^2$], 3.32–4.45 m (36H, C^2H–C^5H, C^6H_2). 4.76–5.10 m (6H, C^1H), 5.15–5.65 m (3H, $C^{2,3}OH$). Found, %: C 53.09, H 8.05. $C_{90}H_{162}O_{39}Si_6$. Calculated, %: C 53.07, H 8.02.

Compound VI. This compound was prepared analogously to **III** from 0.40 g of cyclodextrine derivative **I** in 4 ml of pyridine and a solution of 0.27 g of acetyl chloride in 2 ml of pyridine. Yield 0.28 g (61%), mp 152–154°C, R_f 0.66 (A). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.05 s [36H, $Si(CH_3)_2$], 0.89 s [54H, $C(CH_3)_3$], 2.06 s [6H, $CH_3C(O)OC^3$], 2.16 s [9H, $CH_3C(O)OC^2$], 3.30–4.43 m (36H, C^2H–C^5H, C^6H_2), 4.75–5.20 m (6H, C^1H), 5.30–5.80 m (6H, $C^{2,3}OH$). Found, %: C 52.78, H 8.20. $C_{84}H_{156}O_{36}Si_6$. Calculated, %: C 52.80, H 8.23.

Compound VII. This compound was prepared analogously to compound **Va** (method *a*) from o.40 g of β-cyclodextrine derivative **II**, 0.37 g of triethylamine in 4 ml of benzene, and a solution of 0.26 g of acetyl chloride in 2 ml of benzene. Yield 0.34 g (70%), mp 142-144°C, R_f 0.67 g (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [42H, $Si(CH_3)_2$], 0.89 s [63H, $C(CH_3)_3$], 2.06 s [15H, $CH_3C(O)OC^3$], 2.16 s [15H, $CH_3C(O)OC^2$], 3.30–4.35 m (42H, C^2H–C^5H, C^6H_2), 4.60–5.05 m (7H, C^1H), 5.10–5.75 m (4H, $C^{2,3}OH$). Found, %: C 53.07, H 8.09. $C_{104}H_{188}O_{45}Si_7$. Calculated, %: C 53.04, H 8.05.

Compound VIII. It was prepared analogously to compound **Va** (method *a*) from 0.40 g of β-cyclodextrine derivative **II**, 0.29 g of pyridine in 4 ml of benzene, and a solution of 0.26 g of acetyl chloride in 2 ml of benzene. Yield 0.39 g (77%), mp 144–146°C, R_f 0.68 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [42H, $Si(CH_3)_2$], 0.89 s [63H, $C(CH_3)_3$], 2.06 s [24H, $CH_3C(O)OC^3$], 2.16 s [12H, $CH_3C(O)C^2$], 3.30–4.35 m (42H, C^2H–C^5H, C^6H_2), 4.55–4.95 m (7H, C^1H), 5.05–5.55 m (2H, $C^{2,3}OH$). Found, %: C 53.20, H 7.90. $C_{108}H_{192}O_{47}Si_7$. Calculated, %: C 53.18, H 7.93.

Compound IXa. It was prepared analogously to compound **Va** (method *a*) from 0.40 g of β-cyclodextrine derivative **II**, 0.44 g of *N,N*-dimethylaniline in 4 ml of benzene, and a solution of 0.26 g of acetyl chloride in 2 ml of benzene. Yield 0.59 g (85%), mp 138–140°C, R_f 0.63 (B). ^{1}H NMR spectrum, δ, ppm: 0.03 s [42H, $Si(CH_3)_3$], 0.87 s [63H, $C(CH_3)_3$], 2.05 s

[12H, $CH_3C(O)OC^3$], 2.14 s [6H, $CH_3C(O)OC^2$], 3.30–4.30 m (42H, C^2H–C^5H, C^6H_2), 4.50–4.90 m (7H, C^1H), 5.00–5.57 m (8H, $C^{2,3}OH$). Found, %: C 52.70, H 8.33. $C_{96}H_{180}O_{41}Si_7$. Calculated, %: C 52.72; H 8.30.

Compound IXb. This compound was prepared analogously to compound **III** from 0.40 g of β-cyclodextrine derivative **II**, 0.37 g of triethylamine in 4 ml pf DMF, and a solution of 0.26 g of acetyl chloride in 2 ml of DMF. Yield 0.38 g (84%), mp 139–141°C, R_f 0.62 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [42H, $Si(CH_3)_2$], 0.87 s [63H, $C(CH_3)_3$], 2.06 s [9H, $CH_3C(O)OC^3$], 2.15 s [9H, $CH_3C(O)C^2$], 3.30–4.30 m (42H, C^2H–C^5H, C^6H_2), 4.50–4.95 m (7H, C^1H), 5.00–5.60 m (8H, $C^{2,3}OH$). Found, %: C 52.69, H 8.32. $C_{96}H_{180}O_{41}Si_7$. Calculated, %: C 52.72, H 8.30.

Compound X. It was prepared analogously to compound **III** from 0.40 g of β-cyclodextrine derivative **II** in 4 ml of pyridine and a solution of 0.26 g of acetyl chloride in 2 ml of pyridine. Yield 0.44 g (93%), mp 140–141°C, R_f 0.65 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.03 s [42H, $Si(CH_3)_2$], 0.87 s [63H, $C(CH_3)_3$], 2.05 s [12H, $CH_3C(O)OC^3$], 2.14 s [12H, $CH_3C(O)OC^2$], 3.30–4.35 m (42H, C^2H–C^5H, C^6H_2), 4.50–4.95 m (7H, C^1H), 5.00–5.60 m (6H, $C^{2,3}OH$).

^{13}C NMR spectrum ($CDCl_3$), δ_c, ppm: –5 and –5.2 [$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 20.7 and 20.9 [$C(O)CH_3$], 26.0 [$C(CH_3)_3$], 61.7 (C^6), 71.7–73.5 (C^2,C^3, C^5), 81.8 (C^4), 102.1 (C^1), 169.2 and 170.5 (C=O). Found, %: C 52.85, H 8.19, $C_{100}H_{184}O_{43}Si_7$. Calculated, %: C 52.88, H 8.17.

Compound XI. This compound was prepared analogously to compound **III** from 0.40 g of β-cyclodextrine derivative **II**, 0.14 g of *N,N*-dimethylaniline in 4 ml of DMF, and a solution of 0.08 g of acetyl chloride in 2 ml of DMF. Yield 0.38 g (89%), mp 135–136°C, R_f 0.58 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 0.03 s [42H, $Si(CH_3)_2$], 0.89 s [63H, $C(CH_3)_3$], 2.16 s [9H, $CH_2C(O)OC^2$], 3.53 d.d [7H, C^4H, $^3J(H^3H^4)$ 8.9], 3.57 d.d [7H, C^5H, $^3J(H^4H^5)$ 8.4], 3.65 d.d [7H, C^2H, $^3J(H^2H^3)$ 9.16], 3.70 d.d [7H, C^6H, $^2J(H^6H^{6'})$11.3]. 3.89 d.d [7H, $C^{5'}H$, $^3J(H^5H^6)$ 3.3]. 4.03 d.d [7H, C^3H], 4.88 d [7H, C^1H $^2J(H^1H^2)$ 3.5], 5.27 s and 7.25 s [11H, $C^{2,3}OH$]. ^{13}C NMR spectrum, ($CDCl_3$), δ_C, ppm: –5.0 and –5.1 {$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 20.9 [$C(O)CH_3$], 26.0 [$C(CH_3)_3$], 61.7 (C^6), 72.6 (C^5), 73.6 (C^3), 73.7 (C^2), 81.8 (C^4), 102.1 (C^1), 170.5 (C=O). Found, %: C 52.47; H 8.50. $C_{90}H_{174}O_{38}Si_7$. Calculated, %: C 52.45, H 8.51.

Compound XII. To a solution of 0.40 g of cyclodextrine derivative **I** in 4 ml of freshly distilled DMF 0.05 g of sodium hydride was added at 0°C, the reaction mixture was stirred for 30 min, and a solution of 0.15 g of acetyl chloride in 2 ml of DMF was added dropwise with stirring at 0°C in the course of 10 min, and the reaction mixture was kept for 24 h at 20°C. After that 5 ml of methanol was added dropwise, the mixture obtained was filtered, and the filtrate was concentrated by half in a vacuum. The solution obtained was poured in 15 ml of water. The precipitate formed was filtered off, dried, dissolved in 1 ml of acetone, and poured in 10 ml of water. The precipitate obtained was filtered off, washed with water (3× 10 ml), and dried in a vacuum (1 mm Hg) for 4 h at 60°C. Yield 0.38 g (86%), mp 149–150°C, R_f 0.65 (B). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.02 s [36H, $Si(CH_3)_2$], 0.89 s [54H, $C(CH_3)_2$], 2.06 s [3H, $CH_3C(O)OC^3$], 2.13 s [9H, $CH_3C(O)OC^2$], 3.30–4.35 m (36H, C^2–C^5, C^6H_2), 4.70–5.10 m (6H, C^1H), 5.20–5.65 m (8H, $C^{2,3}OH$). Found, %: C 52.64, H 8.42. $C_{80}H_{152}O_{34}Si_6$. Calculated, %: C 52.69, H 8.39.

Compound XIII. To a solution of 0.20 g of compound **VI** in 5 ml of methanol 0.06 g of ammonium fluoride was added, and the mixture obtained was refluxed for 24 h at 70°C. After that the reaction mixture was evaporated to dryness, the residue was dissolved in 5 ml of water, and the solution obtained was passed through a layer of silica gel. The filtrate was evaporated to dryness, dissolved in 0.5 ml of water, and poured in 5 ml of acetone. The precipitate formed was filtered off and washed with acetone (2× 5 ml). Yield 0.11 g (85%), mp 161–163°C, R_f 0.54 (A). ^{1}H NMR spectrum (C_5D_5N), δ, ppm: 1.89–2.20 br.s [18H, $CH_3C(O)OC^{2,3}$], 3.95–4.72 m (36H, C^2H–C^5H, C^6H_2), 5.45–5.55 m (6H, C^1H), 5.60–6.40 m (12H, $C^{2,3,6}OH$). Found, %: C 47.09, H 5.96, $C_{48}H_{72}O_{36}$. Calculated, %: C 47.06, H 5.92.

Compound XIV. This compound was obtained analogously to sample **XIII** from 0.20 g of compound **IXa** and 0.06 g of ammonium fluoride. Yield 0.11 g (87%), mp 150-153°C, R_f 0.56 (B). ^{1}H NMR spectrum (C_5D_5N), δ, ppm: 1.87–2.19 br.s [18H, $CH_3C(O)OC^{2,3}$], 3.94–4.73 m (42H, C^2H–C^5H, C^5H_2), 5.44–5.55 m (7H, C^1H), 5.58–6.41 m (15H, $C^{2,3,6}OH$). Found, %: C 46.80, H 5.98. $C_{54}H_{82}O_{41}$. Calculated, %: C 46.75, H 5.96.

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