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PREPARATION OF TRITYLATED 1,2-O-(1-METHOXYCARBONYL)ETHYLIDENE DERIVATIVES OF CARBOHYDRATES AND THEIR CONVERSION INTO TRITYLATED 1,2-O-(1-CYANO)ETHYLIDENE DERIVATIVES

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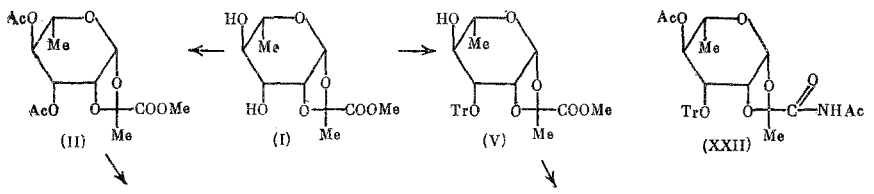
In the preceding article [1], we have shown the outstanding possibility of using 1,2-O-(1-methoxycarbonyl)ethylidene derivatives (MED) of sugars as compounds containing a cyanoethylidene group in a "latent" form. In the present article we describe the synthesis of tritylated cyanoethylidene derivatives (CED) from MED by their tritylation, followed by a reverse transformation of the methoxycarbonylethylidene function into the cyanoethylidene function.

As models for the tritylation we selected MED (I), (III), (IV), and derivatives of disaccharide (IX). This selection was dictated by the fact that after the transforming the methoxy carbonylethylidene function into the cyanoethylidene function in compounds (V), (VI), (VII), and (XII), obtained from (I), (III), (IV), and (IX), respectively, we should obtain the previously described tritylated CED (XV) [2], (XVI) [3, 4] and the disaccharide derivative (XIX) [5] (see scheme 1)

Scheme 1



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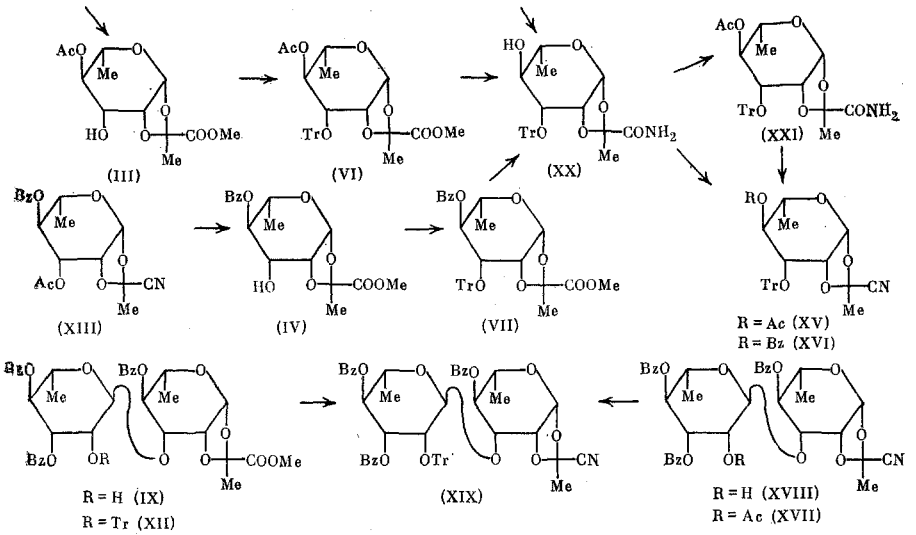
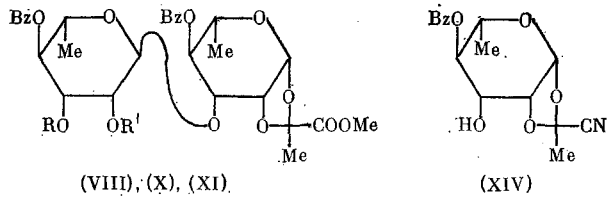


The MED (III) with a free OH group at C^3 [6, 7] is readily obtained by treating the diacetate (II) with 0.5 M HCl in MeOH. The MED (IV) was obtained in 27% yield by doubly treating 3-O-acetyl-4-O-benzoyl-1,2-O-[1-(exo-cyano)ethylidene]-β-L-rhamnopyranose [3] with 0.5 M HCl in MeOH. Disaccharide (IX) and its acetate (VIII) were isolated as by-products during selective deacylation of the disaccharide CED (XVII) while building up the monomer for polycondensation in the synthesis of the main chain of O-antigenic polysaccharides of *Shigella flexneri* [8]. We, have however, studied the behavior of the disaccharide MED (VIII) under the selective deacylation conditions. On treating acetate (VIII) with 0.5 M HCl in a MeOH–$CHCl_3$ mixture, after 11 h, MED (IX) is formed in 82% yield, but up to 12% of the initial (VIII) and traces of a low-boiling product remain*



R = Bz, R′ = Ac (VIII); R = H, R′ = Bz (X), R = R′ = H (XI).

Tritylation of hydroxyl-containing MED (I), (III), (IV), and (IX) by the action of $TrClO_4$ in CH_2Cl_2 in the presence of sym.-collidine [9] proceeded smoothly and gave practically with quantitative yields for the corresponding trityl ethers (V), (VI), (VII), and (XII).

The ammonolysis of the trityl ethers (V)-(VII) under the conditions of [1] led to amide (XX) with a free OH group at C^4 in a quantitative yield. Amide (XX) was then converted into CED (XV) and (XVI) according to a scheme proposed in the preceding article. Several factors in the data indicated that the 4-O-benzoylation is difficult to accomplish in 1,2-cis-linked bicyclic derivatives of rhamnopyranose, which carry a bulky substituent at O^3. Thus, about 3 to 4 days are required for the benzoylation of 3-O-trityl- and 3-O-(2-O-acetyl-3,4-di-O-benzoyl-α-L-rhamnopyranosyl)-1,2-O-[1-(exo-cyano)ethylidene]-β-L-rhamnopyranose by the action of PhCOCl in Py at 20°C [3]. Acetylation of amide (XX) by the action of Ac_2O in Py is incomplete after 16 h. Acetylation of amide (XX) in the presence of 4-dimethylaminopyridine (DAP) over a period of 18 h led to two products: the required acetate (XXI) and the product of its N-acetylation, imide (XXII). The structure of the crystalline (XXI) and (XXII) was confirmed by PMR spectral data. In the spectrum of amide (XXI) there were broadened signals of two amide group hydrogen atoms at 5.52 and 6.10 ppm. In the spectrum of imide (XXII), these two signals were absent, a signal of the sole hydrogen atom of the imide group was present at 8.56 ppm, and a signal of the N-acetate methyl group appeared at 2.50 ppm. Amide (XXI) could be obtained from (XX) in 86% yield when the acetylation was carried out without DAP (6 days, 20°C).

*On more prolonged treatment (24 h), diol (XI) and MED (X), a product of migration of the 3-O-benzoyl group into the O-2 position, were isolated and identified by NMR spectroscopy.

Dehydration of amides (XX) and (XXI) was effected by the action of PhCOCl in Py (in the case of amide (XX), the reaction was carried out in the presence of DAP): in both cases after 16 h the corresponding nitriles (XVI) and (XV) are readily formed. The thus obtained CED (XVI) and (XV) were identical to those describe previously. The conversion of the tritylated disaccharide MED (XII) into CED (XIX) was carried out in a similar way. The ammonolysis product(s) of MED (XII) were treated with PhCOCl in Py, resulting in CED (XIX) in 90% yield. The same comopund was obtained in 82% yield by an alternative path by direct tritylation of disaccharide CED (XVIII) [5].

It can thus be stated that the method proposed by us for protecting the cyanoethylidene function is entirely suitable for the synthesis of tritylated CED, for use as monomers for polycondensation.

EXPERIMENTAL

The TLC was carried out in the following systems of solvents: EA–toluene, 2:1 (A), 1:6 (B), 1:2 (C), 1:1 (D), 1:9 (E). The column chromatography (CC) was carried out in a benzene–EA system (up 15-20% of EA). The instruments used are listed in [1].

4-O-Acetyl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (III). A solution of 0.5 ml of AcCl in 5 ml of $CHCl_3$ was added at 0°C to a suspension of 330 mg (1 mmole) of (II) in 10 ml of absolute MeOH, and the mixture was allowed to stand for 2 h at 20°C. The mixture containing the main product (III) with R_f 0.36 (A), the initial (II) with R_f 0.63, and traces of a product with R_f 0.17 was neutralized by 0.5 ml of Py, and evaporated. The CC of the residue gave 20 mg of (II), yield 6% and 200 mg (69%) of (III), mp 170-172°C (EA–MeOH–hexane), $[\alpha]_D$ −11° (C 1.2) (cf. [6, 7]).

4-O-Benzoyl-1,2-O-[1-exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (IV). A solution of 5 ml of AcCl in 12 ml of $CHCl_3$ was added at 0°C to a solution of 5 g (13.9 mmoles) of CED (XIII) in 10 ml of $CHCl_3$ and 60 ml of MeOH, and the mixture was allowed to stand for 2 h at 20°C. The mixture was neutralized by a $KHCO_3$ solution, diluted with $CHCl_3$, evaporated, and the residue was distributed between water and $CHCl_3$ (70 ml of each), the aqueous solution was extracted with $CHCl_3$, the combined organic phases were washed with a saturated $NaHCO_3$ solution and water, dried, evaporated, and the residue was crystallized from 50 ml of EA to yield 2.4 g (54%) of CED (XIV). The mother liquor was evaporated, the residue was dissolved in 3 ml of $CHCl_3$, 20 ml of MeOH were added, and then, at 0°C, a solution of 1.2 ml of AcCl in 5 ml of $CHCl_3$ was added, and the mixture was left to stand for 16 h at 20°C. The mixture, still containing (XIV), was treated as described above. After the CC, 0.44 g (10%) of (XIV) and 1.33 g (27%) of (IV), mp 126-127°C (EA–hexane), $[\alpha]_D$ −3.5° (C 1.4) were isolated. Found: C 58.23; H 5.75%. $C_{17}H_{20}O_8$. Calculated: C 57.95, H 5.72%. PMR spectrum: 1.28 d (3H, $J_{6,5}$ = 8 Hz, H^6), 1.79 s (3H, $\underline{CH_3}C\text{-}COOCH_3$), 2.70 d (1H, J_{H^3OH} = 9 Hz, OH), 3.65 d.q (1H, H^5), 3.79 s (3H, $COO\underline{CH_3}$), 4.03 d.d (1H, $J_{3,4}$ = 9 Hz, $J_{3,2}$ = 4 Hz, H^3), 4.62 d.d (1H, $J_{2,1}$ = 2.5 Hz, H^2), 5.14 t (1H, $J_{4,5}$ = 9 Hz, H^4), 5.43 d (1H, H^1). ^{13}C NMR spectrum: 17.88 (C^6), 23.43 ($\underline{CH_3}CCOOCH_3$), 52.55 ($COO\underline{CH_3}$), 69.96, 70.71, 74.69 (C^3, C^4, C^5), 80.19 (C^2), 97.57 (C^1), 107.42 ($CH_2\underline{C}COOCH_3$), 166.6 and 169.2 (CO).

3-O-Trityl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (V). A 0.24-ml portion (1.80 mmole) of sym.-collidine was added to a suspension of 240 mg (0.97 mmole) of diol (I) in 10 ml of CH_2Cl_2, and then, with stirring, 600 mg (1.76 mmole) of $TrClO_4$ were added in portions. After 30 min, another 100 mg (0.30 mmole) of $TrClO_4$ and 0.07 ml (0.50 mmole) of sym.-collidine were added and the mixture was stirred for 30 min. It was then decomposed by 0.3 ml of Py, diluted with 50 ml of $CHCl_3$, the solution was washed with water, dried, and evaporated. From the residue, after CC, 480 mg (99%) of (V) were isolated in the form of white foam, R_f 0.53 (C), $[\alpha]_D$ +43.1° (C 1).

4-O-Acetyl-3-O-trityl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (VI). A 100-mg portion (0.30 mmole) of $TrClO_4$ was added in the course of 5 min, with stirring, to a solution of 40 mg (0.137 mmole) of MED (III) in 1.5 ml of CH_2Cl_2 and 0.04 ml (0.28 mmole) of sym.-collidine, and the mixture was stirred for 10 min. After treatment as described above and CC, 70 mg (96%) of (VI) were obtained, syrup. R_f 0.66 (C), $[\alpha]_D$ +33° (C 1.2). PMR spectrum: 1.12 d (1H, $J_{6,5}$ = 6 Hz, H^6), 1.72 s (3, CH_3CO), 1.83 s (3H, $\underline{CH_3}CCOOCH_3$), 3.12 d. q (1H, H^5), 3.55 d.d (1H, $J_{3,4}$ = 9.2, $J_{3,2}$ = 3.5 Hz, H^3), 3.69 s (3H, $COO\underline{CH_3}$), 3.96 d.d (1H, $J_{2,1}$ = 2.6 Hz, H^2), 5.01 d (1H, H^1), 5.26 t (1H, $J_{4,5}$ = 9.2 Hz, H^4). ^{13}C NMR spectrum: 17.80 (C^6), 20.94 ($\underline{CH_3}CO$), 23.77 ($\underline{CH_3}CCOOCH_3$), 70.29, 71.44, 71.57 (C^3-C^5), 79.99 (C^2), 52.31 ($COO\underline{CH_3}$), 88.6 ($\underline{C}Ph_3$), 97.22 (C^1), 107.31 ($CH_3\underline{C}COOCH_3$), 169.95, 169.3 (CO).

4-O-Benzoyl-3-O-trityl-1,2-O-[exo-methoxycarbonyl)ethylidene-β-L-rhamnopyranose (VII). A 260-mg portion (0.71 mmole) of MED (IV) was tritylated by 340 mg (1 mmole) of $TrClO_4$ in the presence of 0.16 ml (1.22 mmole) of sym.-collidine, for 1 h. After treatment as described above and CC, 420 mg (97%) of (VII) were isolated in the form of a white foam, R_f 0.50 (E), $[\alpha]_D$ +25° (C 0.9). The product crystallized by treatment with MeOH, mp 205-206°C (EA–MeOH–heptane). Found: C 72.39; H 5.95%. $C_{36}H_{34}O_8$. Calculated: C 72.71; H 5.76%. PMR spectrum: 1.17 d (1H, $J_{6,5}$ = 6 Hz, H^6), 1.87 s (3H, $\underline{CH_3}CCOOCH_3$), 3.33 d.q (1H, H^5), 3.68 s (3H, $COO\underline{CH_3}$), 3.75 d.d (1H, $J_{3,2}$ = 3.5 Hz, $J_{3,4}$ = 9.2 Hz, H^3), 3.95 d.d (1H, $J_{2,1}$ = 2 Hz, H^2), 5.11 d (1H, H^1), 5.55 t (1H, $J_{4,5}$ = 9.2 Hz, H^4), ^{13}C NMR spectrum: 17.86 ($\underline{C}^6$), 23.81 ($\underline{CH_3}CCOOCH_3$), 70.30, 71.45, 71.92 (C^3-C^5), 79.72 (C^2), 88.35 (CPh_3), 97.22 (C^1), 144.28 (quaternary C in the phenyl group), 107.29 ($CH_3\underline{C}COOCH_3$).

3-O-Trityl-1,2,O-[1-(exo-carbamoyl)ethylidene]-β-L-rhamnopyranose (XX). A solution of 320 mg (0.65 mmole) of (V) in 8 ml of absolute MeOH was saturated at −5°C with NH_3 and the mixture was left to stand in a stoppered flask for 24 h. The solvent was evaporated to yield 310 mg (100%) of a chromatographically homogeneous (XX), R_f 0.21 (D), mp 199-201.5°C (ether–hexane), $[\alpha]_D$ +82° (C 1). Found 70.93; H 6.29; N 2.90%. $C_{28}H_{29}NO_6$. Calculated: C 70.72; H 6.14; N 2.94%. PMR spectrum: 1.25 d (1H, $J_{6,5}$ = 6 Hz, H^6), 1.78 s, (3H, $\underline{CH_3}CCOOCH_3$), 1.83 d (1H, J_{OH,H^4} = 2 Hz, OH), 3.05 d.q (1H, H^5), 3.45 d.d (1H, $J_{3,2}$ = 3.5, $J_{3,4}$ = 9 Hz, H^3), 3.58 d.d (1H, $J_{2,1}$ = 2 Hz, H^2), 3.78 d.t (1H, $J_{4,5}$ = 9 Hz, H^4), 4.97 d (1H, H^1), 5.52 br. d, 6.14 br. d (2 × 1H, J = 3 Hz, NH_2).

The same product (TLC) was obtained during the ammonolysis of MED (VI) (the reaction was completed after 5 h) and MED (VII) (the reaction was carried out in a mixture of toluene and MeOH), according to TLC data, in a quantitative yield, and the compound was used at the following stage without further purification.

Acetylation of 3-O-trityl-1,2-O-[1-(exo-carbamoyl)ethylidene]-β-L-rhamnopyranose (XX). a) A solution of 180 mg (0.34 mmole) of (VI) in 8 ml of MeOH was treated with NH_3 as described above. After 16 h the solvent was evaporated, the residue was dissolved in 8 ml of Py, 4 ml of Ac_2O were added, and the mixture was left to stand for 6 days at 20°C. It was then decomposed by 0.5 ml of water, and poured into 150 ml of water with ice. The mixture was stirred for 30 min, the precipitate was separated, and dissolved in 50 ml of $CHCl_3$. The precipitate was separated, dissolved in 50 ml of $CHCl_3$, the solution was washed with 1 N HCl, water, a saturated solution of $NaHCO_3$, and water (50 ml of each), and dried. From the solution, 190 ml of a homogeneous product were obtained with R_f 0.28 (D). After crystallization from a mixture of ether with hexane, 150 mg (86%) of (XXI) were isolated, mp 119-120°C, $[\alpha]_D$ +79° (C 1). Found: C 69.79; H 5.99; N 2.82%. $C_{30}H_{31}NO_7$. Calculated: C 69.62; H 6.03; N 2.71%. PMR spectrum: 1.18 d (1H, $J_{6,5}$ = 6 Hz, H^6), 1.82 s (3H, $\underline{CH_3}CCOOCH_3$), 1.86 s (3H, Ac), 3.16 d.q (1H, H^5), 3.58 d.d (1H, $J_{3,4}$ = 9, $J_{3,2}$ = 3 Hz, H^3), 3.62 d.d (1H, $J_{2,1}$ = 2 Hz, H^2), 4.94 d (1H, H^1), 5.33 t (1H, $J_{4,5}$ = 9 Hz, H^4), 5.52 and 6.10 two br. s (2 × 1H, NH_2).

b) An 80-mg portion (0.275 mmole) of (III) was tritylated as described above. The product, without being purified by CC, was dissolved in 8 ml of MeOH, and treated with NH_3 as described above. After 48 h, the solvent was evaporated, and the residue was acetylated with 1 ml of Ac_2O in 5 ml of Py in the presence of 30 mg of DAP. The mixture was decomposed with 0.2 ml of water, poured into 50 ml of water with ice, and extracted with $CHCl_3$. The extract was washed with a $NaHCO_3$ solution and water, dried, and after the CC, 20 mg (14%) of (XXI) R_f 0.28 (D) and 120 mg (78%) of (XXII), R_f 0.65, in the form of a yellow syrup, were isolated. The latter product was dissolved in MeOH, the solution was clarified by carbon, and after crystallization from a mixture of EA with hexane, 100 mg (65%) of (XXII) were obtained, mp 94-98°C, $[\alpha]_D$ +63° (C 0.9). Found: N 2.57%. $C_{32}H_{33}NO_8$. Calculated: N 2.50%. PMR spectrum: 1.14 d (3H, $J_{6,5}$ = 6 Hz, H^6), 1.80 s (3H, Ac) 1.81 s (3H, $\underline{CH_3}CCOOCH_3$), 2.50 s (3H, NHAc), 3.16 d.q (1H, H^5), 3.42 d.d (1H, $J_{2,1}$ = 2, $J_{2,3}$ = 3.5 Hz, H^2), 3.66 d.d (1H, $J_{3,4}$ = 9.5 Hz, H^3), 5.10 d (1H, H^1), 5.26 t (1H, $J_{4,5}$ = 9.5 Hz, H^4), 8.56 br. s (1H, NH).

4-O-Acetyl-3-O-trityl-1,2-O-[1-(exo-cyano)ethylidene]-β-L-rhamnopyranose (XV). A solution of 110 mg (0.21 mmole) of (XXI) in 5 ml of Py and 0.5 ml of PhCOCl was allowed to stand for 16 h at 20°C. Then 0.1 ml of water was added, and the mixture was poured into 50 ml of water with ice containing solid $NaHCO_3$. The mixture was stirred for 15 min and extracted with 25 ml of $CHCl_3$. The extract was washed with 1 N HCl, water, a $NaHCO_3$ solution, water again, and dried. After CC, 90 mg (85%) of (XV) were isolated, mp 196-187°C (CH_2Cl_2–heptane), $[\alpha]_D$ +20.1° (C 1) (Cf. [2]).

4-O-benzoyl-3-O-trityl-1,2,O-[1-(exo-cyano)ethylidene]-β-L-rhamnopyranose (XVI). The product of the ammonolysis of 200 mg (0.33 mmole) of MED (VII), without special purification, was dissolved in 5 ml of Py, 0.5 ml of PhCOCl and 50 mg of DAP were added, the mixture was left to stand for 16 h at 20°C, and then treated in the usual way. After the CC, 180 mg (97%) of (XVI) were obtained in the form of a white foam, $[\alpha]_D$ +20.7° (C 1.1). The PMR spectrum was identical with that of an authentic sample (cf. [3]).

3-O-(2-O-Acetyl-3,4-di-O-benzoyl-α-L-rhamnopyranosyl)-4-O-benzoyl-1,2,O-[1-(exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (VIII). A 350-mg portion (0.5 mmole) of (IX), isolated during the selective decatylation of CED (XVII) [6, 7], was acetylated with 2.5 ml of Ac_2O in 5 ml of Py (48 h, 20°C). After the usual treatment, 370 mg (100%) of a chromatographically homogeneous (VIII) were obtained, mp 187-189°C (MeOH), $[\alpha]_D$ +11.1° (C 0.85). Found: C 62.29; H 5.26%. $C_{39}H_{40}O_{15}$. Calculated: C 62.56; H 5.38%. PMR spectrum: 1.28 and 1.35 two d (2 × 3H, $J_{6,5} = J_{6',5'} = 6$ Hz, H^6, $H^{6'}$), 1.89 s (3H, $\underline{CH_3}CCOOCH_3$), 2.03 s (3H, Ac), 3.70 d.q (1H, H^5), 3.74 s (3H, $CH_3CCOO\underline{CH_3}$), 4.10 d.d (1H, $J_{3,2} = 3.6$, $J_{3,4} = 9.2$ Hz, H^3), 4.40 d.q (1H, $H^{5'}$), 4.72 d.d (1H, $J_{2,1} = 1.8$ Hz, H^2), 5.03 d (1H, H^1), 5.15 d.d (1H, $H^{2'}$), 5.43 t (1H, $J_{4',3'} = J_{4',5'} = 9.8$ Hz, $H^{4'}$), 5.46 d (1H, $J_{1',2'} = 2$ Hz, $H^{1'}$), 5.48 t (1H, $J_{4,5} = 9.2$ Hz, H^4), 5.72 d.d (1H, $J_{3',2'} = 3.1$ Hz, $H^{3'}$). ^{13}C NMR spectrum: 17.53, 17.97 (C^6, $C^{6'}$), 20.62 ($CO\underline{CH_3}$), 23.59, 107.93, and 52.43 ($\underline{CH_3}CCOO\underline{CH_3}$), 67.55, ($C^5$), 69.54 ($C^{5'}$), 70.28, 70.40, 71.88, 72.08 (C^3, $C^{3'}$, C^4, $C^{4'}$), 78.84 (C^2), 79.93 ($C^{2'}$), 97.55 (C^1), 100.15 ($C^{1'}$) 164.99, 165.70, 165.90, 169.27, 169.40 (CO).

3-O-(3,4-Di-O-benzoyl-α-L-rhamnopyranosyl)-4-O-benzyl-1,2-O-[1-(exo-methoxycarbonyl) ethylidene-β-L-rhamnopyranose (IX). A 5-ml portion of MeOH, and then, at 0°C, 0.28 ml of AcCl were added to a solution of 380 mg (0.5 mmole) of (VIII) in 2 ml of $CHCl_3$. The solution was allowed to stand for 11 h at 20°C. The reaction mixture containing the main product (IX), R_f 0.32 (C), the initial compound (VIII), R_f 0.50, and traces of the product with R_f 0.10 was neutralized with 0.5 ml of Py, evaporated, and from the residue, after the CC, 40 mg (12.5%) of (VIII) and 300 mg (82%) of (IX), mp 228-234°, $[\alpha]_D$ +107.7° (C 0.65) were isolated. Found: C 62.57; H 5.37%. $C_{37}H_{38}O_{14}$. Calculated: C 62.88; H 5.42%. PMR spectrum: 1.30 and 1.24 two s (2 × 3H, $J_{6,5} = J_{6',5'} = 6$ Hz, H^6, $H^{6'}$), 1.88 s (3H, $\underline{CH_3}CCOOCH$), 2.20 br. s (1H, OH), 3.67 d.q (1H, H^5), 3.72 s (3H, $COO\underline{CH_3}$), 4.02 d.d (1H, $H^{2'}$), 4.10 d.d (1H, $J_{3,4} = 9.5$, $J_{3,2} = 4$ Hz, H^3), 4.37 d.q (1H, $H^{5'}$), 4.69 d.d (1H, $J_{2,1} = 2$ Hz, H^2), 5.00 d (1H, H^1), 5.40 t (1H, H^4), 5.45 d (1H, $J_{1',2'} = 2$ Hz, $H^{1'}$), 5.52 t (1H, $J_{4',3'} = 10$ Hz, $H^{4'}$), 5.62 d.d (1H, $J_{3',2'} = 3$ Hz, $H^{3'}$). ^{13}C NMR spectrum: 17.48 and 17.78 (C^6, $C^{6'}$), 23.63, 107.85, 52.49 ($\underline{CH_3}CCOO\underline{CH_3}$), 67.36 ($C^{5'}$), 69.66, 69.95 ($C^5$, $C^{2'}$), 71.51, 72.20 × 2 ($C^{3'}$, C^4, $C^{4'}$), 79.98 (C^2), 78.50 (C^3), 97.35 (C^1), 102.48 ($C^{1'}$), 165.13, 165.46 ($\underline{C}OPh$), 169.95 ($\underline{C}OOCH_3$).

4-O-Benzoyl-3-O-(3,4-di-O-benzoyl-2-O-trityl-α-L-rhamnopyranosyl)1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-β-L-rhamnopyranose (XII). A 690-mg portion (0.98 mmole) of (IX) was tritylated with 400 mg of $TrClO_4$ (1.17 mmole) in the presence of 0.16 ml (1.22 mmole) of sym.-collidine, as described above. The product was purified by CC. Yield 890 mg (96%) of MED (XII), white foam, $[\alpha]_D$ = +86° (C 1.3). PMR spectrum: 1.26 s (3H, $J_{6',5'} = 6$ Hz, $H^{6'}$) 1.34 s (3H, $J_{6,5} = 6$ Hz, H^6), 1.80 s (3H, $\underline{CH_3}CCOOCH_3$), 3.55 m (2H, $H^{5'}$, $H^{3'}$), 3.68 s (3H, $COO\underline{CH_3}$), 3.84 d.d. (1H, $J_{2,1} = 1.6$, $J_{2,3} = 3$ Hz, H^2), 4.01 d (1H, H^1), 4.34 d.q (1H, H^5), 4.53 d.d (1H, $J_{2',1'} = 2$, $J_{2',3'} = 4$ Hz, $H^{2'}$), 5.27 t (1H, $J_{4',5'} = J_{4',3'} = 9.5$ Hz, $H^{4'}$), 5.31 d (1H, $H^{1'}$), 5.54 d.d (1H, $J_{3,4} = 10$ Hz, H^3), 5.95 t (1H, $J_{4,5} = 10$ Hz, H^4). ^{13}C NMR spectrum: 17.92 × 2 (C^6, $C^{6'}$), 23.61, 107.73, 52.40 ($\underline{CH_3}CCOO\underline{CH_3}$), 67.66 ($C^{5'}$), 70.07 ($C^5$), 71.44, 71.83, 72.07, 72.27 (C^3, $C^{3'}$, C^4, $C^{4'}$), 78.21 ($C^{2'}$), 79.80 (C^2), 88.2 ($\underline{C}Ph_3$), 97.42, (C^1), 100.97 ($C^{1'}$), 144.20 (quaternary carbon atom in the phenyl group), 164.9, 165.3, 166.0 ($\underline{C}OPh$), 169.3 ($\underline{C}OOCH_3$).

4-O-Benzoyl-3-O-(3,4-di-O-benzoyl-2-O-trityl-α-L-rhamnopyranosyl)-1,2,O-[1-(exo-cyano) ethylidene]-β-L-rhamnopyranose (XIX). a) A 140-mg portion (0.2 mmole) of (XVIII) [6, 8] was treated with 1.5 equ. of $TrClO_4$ in the presence of 4 equiv. of sym.-collidine in 2 ml of CH_2Cl_2. After CC, 150 mg (82%) of (XIX) were isolated in the form of a syrup, which was crystallized by treatment with a mixture of EA with hexane, mp 202-206°C, $[\alpha]_D$ +98.48° (C 0.8).

b) A 10-ml portion of absolute MeOH was added to a solution of 660 mg (0.70 mmole) of (XII) in 4 ml of toluene, the mixture was saturated at −5°C with NH_3 and left to stand for 16 h at 20°C. The solution was evaporated to dryness. The residue was dissolved in 15 ml of Py, and 5 ml of PhCOCl and 30 mg of DAP were added. After 2 h, the mixture was decomposed by water (0.2 ml), poured into 150 ml of water, and stirred with 1.5 g of solid $NaHCO_3$. The oil was separated, the aqueous layer was extracted with 50 ml of $CHCl_3$, and the oil was

dissolved in the extract. The solution was washed with 1 N HCl, (2 × 50 ml), water (50 ml), a $NaHCO_3$ solution (2 × 50 ml), water, and dried. According to TLC data (C), the residue, in the form of a syrup (1.15 g) contained one single product with R_f 0.57, identical with authentic (XIX), obtained above. After CC, 570 mg (90%) of (XIX) were obtained, light-yellow syrup. Crystallization from a mixture of EA with hexane gave 460 mg (72%) of (XIX), mp 212.5-214°C, $[\alpha]_D$ +99.7° (C 1). Found: C 71.73; H 5.35; N 1.72%. $C_{55}H_{49}NO_{12}$. Calculated: C 72.12; H 5.39; N 1.53%. PMR spectrum: 1.25, 1.31 two s (2 × 3H, $J_{6',5'} = J_{6,5}$ = 7 Hz, $H^{6'}$, H^6), 1.95 s (3H, $\underline{CH_3}CCOOCH_3$), 3.50 d.d (1H, $J_{3,2}$ = 4, $J_{3,4}$ = 10 Hz, H^3), 3.58 d.q (1H, $H^{5'}$), 3.88 m (2H, H^2, H^1), 4.30 d.q (1H, H^5), 4.52 d.d (1H, $J_{2',1'}$ = 2, $J_{2',3'}$ = 3.5, $H^{2'}$), 5.22 t (1H, $J_{4',5'} = J_{4',3'}$ = 9.5 Hz, $H^{4'}$), 5.34 d (1 H, $H^{1'}$), 5.51 d.d (1H, $J_{3',2'}$ = 2.5 Hz, $H^{3'}$), 5.95 t (1H, $J_{4,5} = J_{4,5}$ = 10 Hz, H^4). ^{13}C NMR spectrum: 17.95, 17.46 (C^6, $C^{6'}$), 26.64, 101.65, 117.01, ($CH_3\underline{C}N$), 68.05 ($C^{5'}$), 70.20 (C^5), 71.92, 71.82, 71.49, 71.36 (C^3, $C^{3'}$, C^4, $C^{4'}$), 78.1 ($C^{2'}$), 80.23 (C^2), 88.09 ($Ph_3\underline{C}$), 96.87 (C^1), 101.15 ($C^{1'}$) 144.09 (quaternary carbon atom in the phenol group), 164.99, 165.28, 166.08 ($\underline{C}OPh$).

CONCLUSION

Tritylation of 1,2-O-1-(methoxycarbonyl)ethylidene derivative of carbohydrates followed by ammonolysis of the methoxycarbonyl group and dehydration was proposed as an alternative method for the preparation of tritylated 1,2-O-1-(cyano)ethylidene derivatives for use as monomers for polycondensation.

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