20-Ethoxy-16α,17α-epoxypregn-5-en-3β-ol-[20,21-d]-1'3'-oxazoline-2-thione 3-Acetate(Vb). A solution of 0.03 g of (Va) in 0.3 ml of Py and 0.1 ml of Ac_2O was acetylated by the method described above for (IVa). Yield, 0.02 g of (Vb), mp 201-206°C (dec.) (from Me_2CO–C_6H_{14}). IR spectrum (ν, cm^{-1}): 1040, 1055, 1250, 1442 sh, 1455, 1490, 1728, 3250, 3420. PMR spectrum (δ, ppm): 1.00 s (18-Me), 1.03 s (19-Me), 1.28 t ($OCH_2\underline{Me}$), 2.02 s (3-OAc), 3.31 br. s (16-H), 3.5 (3H, $O\underline{CH_2}Me$, AB-system on multiplet, J = 6.4 Hz), 4.47 (21-CH_2, AB-system, J = 10.3 Hz), 5.35 m (6-H), 7.38 br. s (NH).

CONCLUSION

The reaction of 20,20-dimethoxy-16α,17α-epoxypregn-5-ene-3β,21-diol-20-one with pyridine thiocyanate in the presence of carbethoxyhydrazine proceeds by two competing paths: cis-opening of the oxide ring by a –SCN ion at the C^{17} atom, and substitution of one of the methoxyl groups by –NCS ion. As a result 2',20-dicarbethoxyhydrazones of pregn-5-ene-3β,21-diol-20-one-[17α,16α-d]-1',3'-oxathiolan-2'-one and 20-methoxy-16α,17α-epoxypregn-5-ene-3β-ol-[20,21-d]-1',3'-oxazolidine-2'-thione are formed.

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GLYCOSYLATION OF METHYL-2,3-DI-O-ACETYL-β-D-XYLOPYRANOSIDE TRIARYLMETHYL ETHERS WITH ELECTRON-DONOR SUBSTITUENTS IN THE AROMATIC RING BY 3,4-DI-O-ACETYL-1,2-O-[1-(ENDO-CYANO)-ETHYLIDENE]-α-D-XYLO-PYRANOSE

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UDC 542.91:547.455

The reaction of 1,2-O-(1-cyano)ethylidene derivatives of sugars with triphenylmethyl ethers of carbohydrates in the presence of triphenylmethylium perchlorate as catalyst leads smoothly to glycosides with 1,2-trans-configuration of the glycoside bond formed [1]. Polycondensation of the tritylated 1,2-O-(1-cyano)ethylidene derivatives of mono- and oligosaccharides usually proceeds stereospecifically, and serves as a method for synthesizing regio- and stereoregular polysaccharides [1].

However, a study of the glycosylation of methyl-2,3-di-O-acetyl-4-O-trityl-β-D-xylopyranoside (IIa) by 1,2-O-(1-cyano)ethylidene derivatives of certain monosaccharides in the presence of Ph_3CClO_4 showed that not only 1,2-trans-disaccharides are formed (up to 25%), but also 1,2-cis-isomers are obtained [2]. The disturbance of the stereospecificity of

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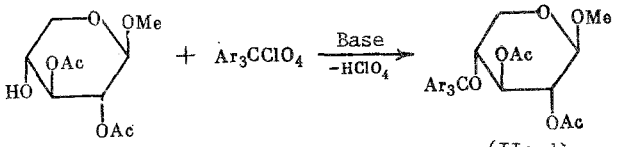
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 914-920, April, 1987. Original article submitted September 17, 1985.

0568-5230/87/3604-0840$12.50

glycosylation may be due to either decreased reactivity of the above trityl ether, (i.e., decreased nucleophilicity of the O^4 atom), compared with trityl ethers that are glycosylated stereospecifically, or to the participation of the catalyst anion in the glycosylation reaction evident under these conditions. When triphenylmethylium salts with anions with nucleophilicity lower than that of the perchlorate anion, in particular with complex anions ($TrBF_4$, $TrPF_6$), are used as catalysts, there is a noticeable decrease in the fraction of the 1,2-cis-bound disaccharides [3].

Another approach for increasing the degree of stereoselectivity of glycosylation could be the use of triarylmethyl derivatives with electron-donor substituents in the aromatic ring as the aglycone component. It is possible that the nucleophilicity of the glycosylated O atom in these derivatives will be higher than that in trityl ethers. To verify this supposition, we studied the glycosylation of methyl-2,3-di-O-acetyl-4-O-(p-tolyl)diphenylmethyl-di(p-tolyl)phenylmethyl- and (p-anisyl)diphenylmethyl-β-D-xylopyranosides (IIb-d) by 3,4-di-O-acetyl-1,2,-O-[1-(endocyano)ethylidene]-α-D-xylopyranose (III) [3, 4].

Compounds (IIa-d) were obtained by the reaction of the corresponding triarylmethyl perchlorates with methyl-2,3-di-O-acetyl-β-D-xylopyranoside (I).

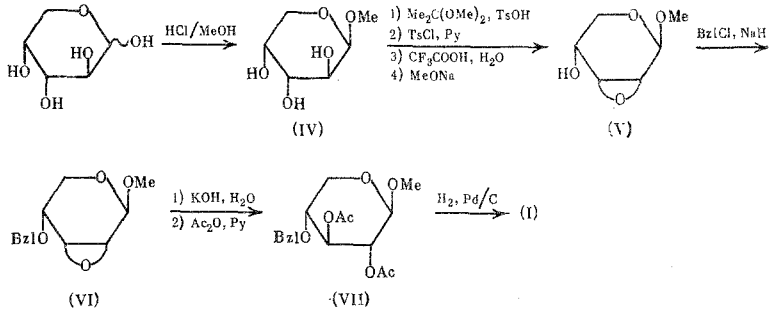


(I) (IIa-d)

$Ar_3C = Ph_3C$ (a), $(p\text{-}MeC_6H_4)Ph_2C$ (b), $(p\text{-}MeC_6H_4)_2PhC$ (c), $(p\text{-}MeOC_6H_4)Ph_2C$ (d).

Diacetate (I) was synthesized as in [5-7] with modifications at the stages of the preparation of methyl-β-D-arabinopyranoside (IV), its acetonation and deacetonation of methyl-3,4-O-isopropenylidene-2-O-tosyl-β-D-arabinopyranoside.

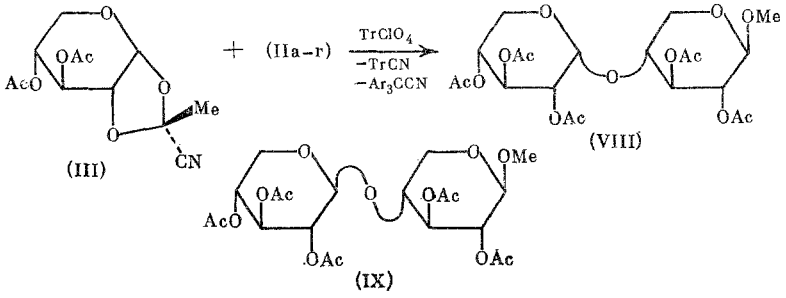
(p-Anisyl)diphenylmethyl (p-methoxy-trityl) group was introduced into xyloside (I), as in the case of the trityl group (see [2]), in the presence of 2,4,6-collidine. However, in the synthesis of derivatives (IIb) and (IIc), we had to use the more sterically hindered base 2,6-di-tert-butyl-4-methylpyridine, since 2,4,6-collidine reacts with (p-tolyl)diphenyl- and di(p-tolyl)phenylmethylium perchlorates, which completely hinders the triarylmethylation.



(IV) (V) (VI) (VII)

The structure of the compounds (IIa-d) obtained followed from the PMR spectra (Table 1).

The glycosylation of triarylmethyl ethers (IIa-d) by the action of 0.91 equivalent of acetal (III) was carried out in CH_2Cl_2 in the presence of 0.09 equivalent of Ph_3CClO_4 using a vacuum technique, i.e., under the conditions usual for the glycosylation by 1,2-O-(1-cyano)-ethylidene derivatives of sugars [1].



(III) (VIII) (IX)

TABLE 1. Data of PMR Spectra of Compounds (IIa-d) ($CDCl_3$, δ, ppm, J, Hz)

Compound	H^1	H^2	H^3	H^4	H^5_a	H^5_e	OCH_3	$COCH_3$	C_6H_5	*
(IIa)	4,29 d	4,68 d. d	5,34 t	3,58 d. d. d	3.11 d. d	3.21 d. d	3.35	1,89 2.03	7.15 7,50 m	
(IIb)	4,27 d	4,66 d. d	5,32 t	3,55 d. d. d	3,11 d. d	3.21 d. d	3,38	1,90 2.06	7,06– 7,46 m	2,35
(IIc)	4,27 d	4,66 d. d	5,32 t	3,54 d. d. d	3,11 d. d	3.23 d. d	3.38	1,90 2,06	7,06– 7,47 m	2,34
(IId)	4,23 d	4,67 d. d	5,33 t	3,47 d. d. d	3,11 d. d	3,23 d. d	3,38	1,90 2,06	6,80–6,88 7,17–7,47 m	3,82

(Continued)

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$
(IIa)	7,4	9,0	9,0	9,1	5.2	12.0
(IIb)	7,0	8,6	8,6	8,9	4,7	11,3
(IIc)	7,0	8,7	8,7	9,0	4,7	11,2
(IId)	7,0	8,6	8,6	9,1	4,9	11,4

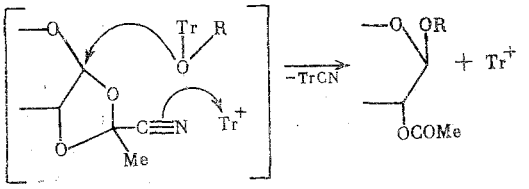
*Signal of substituent in the trityl group.

TABLE 2. Results of Glycosylation of Ethers (IIa-d) by Acetal (III)

Experiment	Aglycone	Yield of (VIII), % (mg)	Yield of (IX), % (mg)	Ratio of (VIII):(IX)	Recovery of (III), % (mg)	Recovery of trimethyl ether, % (mg)
1*	(IIa)	24.5(62)	68.0(171)	1:2.8	–	†
2*	(IIb)	23.0(58)	72.0(183)	1:3.1	–	†
3*	(IIc)	3.2(8)	9.9(25)	1:3.1	78.5(112)	76(217)
4*	(IId)	†	†	–	91.0(130)	92.5(250)
5‡	(IIa)	24.0(30)	64.0(80)	1:2.7	†	†
6‡	(IId)	13.0(17)	42.0(53)	1:3.2	39.0(28)	**

*The condensation was carried with initiation by 10% $Ph_3 \cdot CClO_4$.
†The compound was not isolated, since it was present in trace amounts only.
‡The condensation was carried with initiation by 100% $Ph_3 \cdot CClO_4$.
**Compound (IId) was absent, 17% (23 mg) of trityl ether were isolated.

The experimental results are listed in Table 2. It is seen that the introduction of electron-donor substituents into the aromatic ring practically does not influence the ratio of the anomeric disaccharides (VIII) and (IX) formed, but affects their yield. In experiments 3 and 4, the xylobiosides (VIII) and (IX) were formed in a yield of only 13% and in traces, respectively, and large amounts of unreacted acetal (III) and aglycones (IIc, d) were present in the reaction mixture. This result can possibly be explained as follows. According to the proposed scheme of glycosylation of trityl ethers by 1,2-O-(1-cyano)ethylidene derivatives [1], the triphenylmethylium cation reacts with the cyano group of the cyanoethylidene derivative to form a reactive intermediate, which (in a synchronous or a stepwise process) reacts with trityl ether



Thus, a 1,2-trans-glycoside is formed and the triphenylmethylium cation is regenerated. Therefore, the triphenylmethylium salt can be used in a catalytic amount.

It is clear that in the case of triarylmethyl ethers (IIc, d), as a result of glycosylation, a Tr^+-cation is removed from the reaction sphere in the form of a covalently bound and unreactive trityl cyanide, and di(p-tolyl)phenyl- and (p-anisyl)diphenyl-methylium cations are liberated with a lower electrophilicity than in the case of triphenylmethylium cations, i.e., with a lower ability to split the cyano group. This leads to a decrease in the yield of disaccharides [in the case of (IIc)] or even to no reaction [in the case of (IId)].

The prevention of cessation of the reaction [in the case of (IId)] and comparison of the reactivity of ethers (IIa) and (IId) were possible if the glycosylation was carried out in the presence of an equimolar amount of Ph_3CClO_4. However, in these experiments, the glycosylation in experiment 6 (see Table 2) again did not proceed to completion, and the reaction mixture contained not only 39% of the initial acetal (III) and xylobiosides (VIII) and (IX), but also the trityl ether (IIa) (see Table 2). These data show that Ph_3CClO_4 is consumed in both the formation of trityl cyanide, and the formation of trityl ether (IIa) from p-methoxytrityl ether (IId). The latter is accompanied by the disappearance of Ph_3CClO_4 from the reaction mixture and the liberation of (p-anisyl)diphenylmethylium perchlorate, which leads, as in experiment 4, to the cessation of the process. A comparison of the yield of disaccharides (VIII) and (IX) with that of the trityl ether (IIa) shows that the glycosylation and trans-triarylmethylation proceed at commensurable rates.

We confirmed the possible trans-triarylmethylation in a direct experiment. By reacting p-methoxytrityl derivative (IId) with 1 equivalent of Ph_3CClO_4, 82% of trityl ether (IIa) were obtained. We should note that there was no reverse reaction of formation of compound (IId) from ether (IIa).

Thus, the use of triarylmethyl ethers of carbohydrates with electron-donor substituents in the aromatic ring as aglycones, as the possible method to increase the stereoselectivity of glycosylation by 1,2-O-(1-cyano)ethylidene derivatives of sugars, discussed in the present article, was found to be not much effective.

EXPERIMENTAL

The melting points were determined on a Koeffler block. The optical rotations were measured in chloroform on a Perkin–Elmer-141 polarimeter at 20 ± 2°. The PMR spectra were run on a Bruker WM-250 spectrometer (250 MHz) in $CDCl_3$, using TMS as internal standard.

Dichloroethane CH_2Cl_2 was washed with concentrated H_2SO_4, water, and dried over $CaCl_2$, distilled over P_2O_5 and then over CaH_2. Benzene was dried over $CaCl_2$ and distilled over Na. Ether was dried over $CaCl_2$, distilled over P_2O_5, and then over $LiAlH_4$. Nitromethane $MeNO_2$ was distilled over urea (at 100 mm), twice over P_2O_5, and then over CaH_2. Dimethylformamide (DMFA) was dried over KOH and then was distilled over CaH_2. Dioxane was dried over KOH and distilled over Na. 2,4,6-Collidine was distilled over KOH, and then over CaH_2. The 2,6-di-tert-butyl-4-methylpyridine preparation from the firm "Fluka" was recrystallized from absolute MeOH, mp 33-34°C. Trityl perchlorate Ph_3CClO_4 was obtained according to [8] and for using it as a catalyst, it was additionally purified by the method in [9].

The TLC was carried out on a silica gel Kieselguhr-60 (Merck). The compounds were detected by spraying with 70% H_2SO_4, followed by heating at 150°C. Solvent systems for TLC: A) benzene:hexane (4:1), B) toluene:ethyl acetate (EA) (4:1), C) benzene:acetone (4:1). The column chromtography was carried out on silica gel L 40/100 μm (Czechoslovakia), using gradient elution from benzene to ether or to EA.

p-Tolyldiphenylcarbinol. A solution of 13.2 ml (0.1 mole) of p-tolyl chloride [bp 99-101°C (1 mm)] in 50 ml of absolute ether was added dropwise, with stirring, in a dry Ar atmosphere to a solution of PhMgBr obtained from 6.6 g (0.275 mole) of Mg and 26 ml (0.25 mole) of bromobenzene [bp 54°C (8 mm)] in 220 ml of absolute ether. The mixture was stirred for 20 min and then was poured into a mixture of 100 ml of water, 100 g of ice, 50 g of NH_4Cl, and 2 ml of AcOH. The ether layer was separated and the aqueous layer was extracted by 3 × 50 ml of ether. The ether layer and the extracts were combined, washed with 3 × 50 ml of water, passed through a layer of cotton wool, and evaporated, and the residue was crystallized from 50 ml of heptane. The crystals obtained were dissolved in 200 ml of MeOH, and the solution was clarified by activated charcoal and evaporated to a volume of ~50 ml (crystallization begins on evaporation). The crystals that separated were once again recrystallized from 75 ml of heptane. Yield 14.4 g (55%) of the carbinol, mp 69-71°C, R_f 0.27 (A); see [10].

Di-p-tolylphenylcarbinol was synthesized under the above conditions from p-tolylmagnesium bromide, obtained from 46.9 g (0.27 mole) of p-tolyl bromide [bp 98-100°C (8 mm)] and 7.2 g (0.3 mole) of Mg in 220 ml of absolute ether and 12.8 ml (0.11 mole) of benzoyl chloride [bp 86°C (8 mm)]. The reaction mixture was subjected to column chromatography, using gradient elution from a 1:1 benzene–hexane mixture to benzene. The fractions appearing in TLC were yellow in color, and were combined, evaporated, and clarified by activated charcoal. After three successive crystallizations from 50, 50 and 75 ml, of heptane, respectively, 14 g (44%) of the carbinol were obtained, mp 73-75°C, R_f, 0.28 (A); see [11].

p-Tolyldiphenylmethyl perchlorate was obtained under the conditions of the synthesis of trityl perchlorate according to [8]. A 57% $HClO_4$ (1.2 ml) was added, with water cooling in 0.2 ml portions to a solution of 1.36 g (5 mmoles) of p-tolyldiphenylcarbinol in 14.3 ml of Ac_2O. The perchlorate was precipitated by 50 ml of ether, separated by decantation, washed with 5 × 30 ml of absolute ether, and dried in vacuo. Yield 1.5 g (85%) of p-tolyldiphenyl perchlorate in the form of a yellow amorphous powder.

Di-p-tolylphenylmethyl perchlorate was obtained in a similar way from 1.44 g (5 mmoles) of di-p-tolylphenylcarbinol and 1.2 ml of 57% $HClO_4$ in 14.3 ml of Ac_2O; yield 1.75 g (95%) of a yellow amorphous powder.

p-Anisyldiphenylmethyl perchlorate was obtained as described above from 750 mg (2.6 mmoles) of p-anisyldiphenylcarbinol and 0.61 ml of 57% $HClO_4$ in 7.5 ml of Ac_2O; yield 900 mg (94%) of red amorphous powder. To study the trans-triarylmethylation, the salt was additionally purified by reprecipitation from absolute $MeNO_2$ by absolute ether.

Methyl-β-D-arabinopyranoside (IV). A 23 ml portion of AcCl was added dropwise with stirring to a solution of 90 g (0.6 mole) of D-arabinose in 1.3 liters of absolute MeOH, and the mixture was boiled for 3 h. The solution was evaporated and the residue was crystallized from 500 ml of MeOH. Thus, 35.5 g of a product were obtained, from which 28.7 g of (IV) were isolated by recrystallization from 300 ml of MeOH. After concentration of mother liquors, another 25 g of (IV) was isolated by fractional crystallization from MeOH, overall yield 55%, mp 171.5-173°C, $[\alpha]_D$ −242.8° (C 1.0, water); see [5].

Methyl-2,3-anhydro-β-D-ribopyranoside (V). A 110 ml portion of 2,2-dimethoxypropane (Merck) and 200 mg of $TsOH \cdot H_2O$ were added to 28.7 g (175 mmoles) of arabinoside (IV). The mixture was stirred for 3-4 h up to the disappearance of the initial (IV) [TLC control, the 3,4-isopropylidene derivative formed was Rf 0.25 (B), while the initial (IV) has Rf ~ 0]. The mixture was diluted with 500 ml of $CHCl_3$, washed with 2 × 100 ml of a saturated aqueous $NaHCO_3$ solution and 2 × 100 ml of water, and evaporated in vacuo to yield 31 g of a syrup. The product was dissolved in 200 ml of pyridine, 57.3 g (300 mmoles) of tosyl chloride were added, and the mixture was allowed to stand for 17 h at 20°C. The reaction mixture was poured slowly, with stirring, into 1.5 liters of ice water, and the crystals were filtered, washed with 5 × 80 ml of water, and dried in a rotary evaporator at 60°C to yield 47 g of methyl-3,4-O-isopropylidene-2-O-tosyl-β-D-arabinopyranoside, Rf 0.76 (C). The product synthesized was dissolved in 80 ml of 90% CF_3COOH, the solution was held for ~1 h [TLC control, the diol formed has Rf 0.31 (C)], and the mixture was evaporated in vacuo, and then evaporated again with toluene up to the disappearance of CF_3COOH. The syrup obtained was dissolved in 70 ml of MeOH and a solution of MeONa, prepared from 1.7 g (74 mmoles) of Na and 80 ml of MeOH, was added. The mixture was allowed to stand for 17 h, and after addition of MeONa solution, prepared from 2 g (87 mmoles) of Na in 50 ml of MeOH, it was left again to stand for another 17 h. A 200-ml portion of absolute ether was added to the mixture, which was then held up to the end of crystallization. The TsONa precipitate was filtered and washed with 3 × 100 ml of absolute ether. The filtrates were combined and evaporated to a volume of ~100 ml. A 200-ml portion of water was added and the mixture obtained was extracted by 5 × 400 ml of $CHCl_3$ and the extracts were combined and evaporated in vacuo. From the residue, 16 g of anhydroriboside (V) were isolated by column chromatography, yield 62.5%, mp 52-53°C (hexane), $[\alpha]_D$ −57.2° (C 1.0), Rf 0.38 (C); see [6].

Methyl-2,3-anhydro-4-O-benzyl-β-D-ribopyranoside (VI). A 4.1-g portion (136 mmoles) of an 80% suspension of NaH in mineral oil (Merck) was added to a solution of 10 g (68 mmoles) of anhydroriboside (V) in 100 ml of absolute dioxane and 25 ml of absolute DMFA. The mixture was stirred for 20 min, and 15.8 ml (130 mmoles) of benzyl chloride were added. After 20 min, excess benzyl chloride and NaH were decomposed by 10 ml of MeOH, and the mixture was diluted with 150 ml of water, stirred to complete dissolution of NaCl, and extracted by 4 × 150 ml of $CHCl_3$. The extracts were combined, washed with 3 × 100 ml of water, and evaporated in vacuo. From the residue, 15.8 g of benzyl ether (VI) were isolated by column chromatography in a quantitative yield, mp 47-48°C (i-PrOH–hexane), $[\alpha]_D$ +16.2° (C 2.0), Rf 0.58 (benzene–EA, 3:1), see [7].

Methyl-2,3-di-O-acetyl-4-O-benzyl-β-D-xylopyranoside (VII). The epoxide (VI) synthesized above was boiled for 4 h in 500 ml of a 10% solution of KOH in water. The mixture was cooled by water, neutralized by 30% H_2SO_4 to phenolphthalein, evaporated in vacuo, and then evaporated with toluene (2 × 25 ml) to dryness. The residue was dissolved in 50 ml of Py and 50 ml of Ac_2O, and allowed to stand for 17 h. At the end of the acetylation, excess of Ac_2O was decomposed by methanol. The mixture was diluted with 200 ml of $CHCl_3$, washed with 3 × 50 ml of water, and evaporated in vacuo and then with toluene (2 × 25 ml). From the residue 20.3 g (91%) of (VII) were isolated by column chromatography, mp 77-78°C (ether–hexane), $[\alpha]_D$ −63.5° (C 1.0), Rf 0.34 (benzene–ether, 4:1); see [7].

Methyl-2,3-di-O-acetyl-β-D-xylopyranoside (I). An 18-g portfon of benzyl ether (VII) was hydrogenated at 38°C at atmospheric pressure in 200 ml of MeOH over 0.5 g of 10% Pd/C. The filtrate was evaporated, and the residue crystallized from ether with hexane. Yield 12.1 g (92%) of (I), mp 83-85°C, $[\alpha]_D$ −82.8° (C 2.0), Rf 0.35 (benzene–ether, 1:1); see [7].

Methyl-2,3-di-O-acetyl-4-O-trityl-β-D-xylopyranoside (IIa) was synthesized as described in [2], Rf 0.53 (B).

Methyl-2,3-di-O-acetyl-4-O-(p-tosyl)diphenylmethyl-β-D-xylopyranoside (IIb). p-Tolyldiphenylmethyl perchlorate (1.2 g, 3.4 mmoles) was added in portions, with stirring at 20°C, to a solution of 0.85 g (3.4 mmoles) of diacetate (I) and 1.2 g (5.9 mmoles) of 2,6-di-tert-butyl-4-methylpyridine in 40 ml of CH_2Cl_2. The mixture was stirred for another 20 min, treated with 1 ml of a 1:3 MeOH–Py mixture, diluted with 50 ml of $CHCl_3$, and washed with water (3 × 20 ml). The organic layer was separated and evaporated, and from the residue 1.53 g of (IIb) was isolated by column chromatography, yield 89%, mp 72-74°C (ether–hexane), $[\alpha]_D$ −49.8° (C 1.35), Rf 0.53 (B). Found, %: C 71.02; H 6.64. $C_{30}H_{32}O_7$. Calculated, %: C 71.40; H 6.40.

Methyl-2,3-di-O-acetyl-4-O-(di-p-tolyl)phenylmethyl-β-D-xylopyranoside (IIc). Under the conditions of the synthesis of (IIb), from 0.75 g (3 mmoles) of diacetate (I) and 1.4 g (2.7 mmoles) of di-p-tolylphenylmethyl perchlorate in the presence of 1.1 g (3.0 mmoles) of 2,6-di-tert-butyl-4-methylpyridine in 30 ml of CH_2Cl_2, 0.93 g of (IIc) was obtained, yield 60%, syrup, $[\alpha]_D$ −43.0° (C 4.2), Rf 0.53 (B). Found, %: C 71.40; H 6.24. $C_{31}H_{34}O_7$. Calculated, %: C 71.80; H 6.61.

Methyl-2,3-di-O-acetyl-4-O-(p-anisyl)diphenylmethyl-β-D-xylopyranoside (IId). Under the conditions of the synthesis of (IIb), from 0.875 g (3.5 mmoles) of diacetate (I) and 1.3 g (3.5 mmoles) of p-anisyldiphenylmethyl perchlorate in the presence of 0.81 ml (5.5 mmoles) of 2,4,6-collidine in 15 ml of CH_2Cl_2, 1.61 g of (IId) was obtained, yield 89%, mp 87-89°C (ether–hexane), $[\alpha]_D$ −37.7° (C 0.9), Rf 0.49 (B). Found, %: C 69.13; H 6.44. $C_{30}H_{32}O_6$. Calculated, %: C 69.22; H 6.20.

Glycosylation of Ethers (IIa-d) by Acetal (III). The condenstations of ethers (IIa-d) with acetal (III) and the separation of the reaction mixtures were carried out according to [2]. The experimental results are shown in Table 2. In experiments 1-4, 0.5 mmole of the acetal and 0.55 mmole of aglycone in the presence of 0.05 mmole of Ph_3CClO_4 in 2 ml of CH_2Cl_2 were introduced. Experiments 5 and 6 were carried out in 6 ml of CH_2Cl_2 using 0.25 mmole of the acetal and 0.275 mmole of aglycone in the presence of 0.25 mmole of Ph_3CClO_4. The TLC of compounds isolated from the reaction mixtures gave results identical with those of authentic samples.

Reaction of Derivative (IId) with Ph_3CClO_4. The reaction of 130 mg (0.25 mmole) of ether (IId) [Rf 0.49 (B)] with 86.5 mg (0.25 mmole) of Ph_3CClO_4 in 5 ml of CH_2Cl_2 was carried out under the conditions of the above disaccharide syntheses. After the reagents were mixed, the yellow color of the mixture immediately turned to red, characteristic of solutions of p-anisyldiphenylmethyl perchlorate. After 17 h, the mixture in which, according to the TLC data, ether (IId) was absent, was treated as in the disaccharide syntheses. By column chromatography, 100 mg of trityl ether (IIa) were isolated, yield 82%, Rf 0.53 (B).

Reaction of Derivative (IIa) with p-Anisyldiphenylmethyl Perchlorate. The reaction of 122.5 mg (0.25 mmole) of trityl ether (IIa) with 93.1 mg (0.25 mmole) of p-anisyldiphenylmethyl perchlorate in 5 ml of CH_2Cl_2 was carried out in parallel and in analogy with the preceding experiment. After treatment of the mixture, which according to the TLC data did not contain the p-methoxytrityl derivative (IId), 105 mg (85%) of the initial (IIa) were isolated by column chromatography.

CONCLUSIONS

1. 4-O-(p-Tolyldiphenylmethyl)-, 4-O-(di-p-tolylphenylmethyl)- and 4-O-(p-anisyldiphenylmethyl) derivatives of methyl-2,3,-di-O-acetyl-β-D-xylopyranoside were synthesized.

2. A study of the reaction of the above compounds with 3,4-di-O-acetyl-1,2-O-[1-(endocyano)ethylidene]-α-D-xylopyranose showed that exchange of the trityl group in methyl-2,3-di-O-acetyl-4-O-trityl-β-D-xylopyranoside for triarylmethyl groups containing electron-donor substituents in the aromatic ring does not appreciably affect the stereochemistry of the glycosylation, but can lead to decrease in the yield of the disaccharides.

3. A trans-triarylmethylation reaction was discovered with the reaction of methyl-2,3-di-O-acetyl-4-O-(p-anisyldiphenylmethyl)-β-D-xylopyranoside with triphenylmethylium perchlorate as an example.

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