ALKYLATION OF PARTIALLY PROTECTED XYLOFURANOSES AND TETRITOLS WITH (2,2,3,3,4,4,5,5,6,6,7,7,7-TRIDECAFLUOROHEPTYL)-OXIRANE AND THE STABILITY OF PROTECTING ACETAL GROUPS TOWARDS LEWIS ACID-TYPE CATALYST

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1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-xylofuranose (**2**), 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**), 2,4-*O*-ethylidene-D-erythritol (**4**) and 1,3-*O*-ethylidene-D-threitol (**5**) were alkylated with racemic (2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxirane (**1**) using boron trifluoride diethyl etherate as a catalyst. The desired mono- or disubstituted polyfluoroalkyl derivatives **6**–**11** were isolated only in low to medium yields. The fluoroalkylation was accompanied with disproportional distributions of the protecting acetal/ketal groups and polymerization of saccharides. Therefore the stability of **3**, **4**, **5**, 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**14**) and 1,2-*O*-isopropylidene-α-D-glucofuranose (**15**) in the presence of a catalytic amount of boron trifluoride diethyl etherate was investigated in various solvents. A mechanism explaining the effect of the catalyst has been proposed.

Keywords: Carbohydrates; Fluoroalkylated epoxides; Ring opening; Lewis acid catalysis; Fluoroalkylations; Fluorophilic sugars; Oxygen carriers; Fluorinated sugars.

Perfluoroalkylated carbohydrates and their derivatives exhibit interesting surface, colloidal and biological properties[1]. Some of them have been employed in microemulsions used as oxygen carriers for various biomedical purposes including blood substitutes[2,3], organ preservation under aerobic conditions[4], liquid ventilation or as contrast agents for ultrasound diagnosis[1], *etc.* Stable fluorocarbon–water emulsions are very important for these purposes[5]. In this respect, polyhydroxy compounds, *e.g.* sugars, bearing a straight polyfluoroalkyl chain have attracted a remarkable interest due to

their known amphiphilicity. Syntheses and use of several polyfluoroalkyl carbohydrates as emulsifying agents have been patented[6,7].

Various synthetic strategies have been used for perfluoroalkylated surfactants with a hydrophilic carbohydrate moiety in dependence on the reactivity of reaction sites in the starting carbohydrate derivatives[1]. Some of the amphiphilic compounds reported in the literature[1] are esters or amides. These compounds generally suffer from lower hydrolytic stability than surfactants containing fluoroalkyl group attached to carbohydrate derivatives with an ether linkage. Recently, we have developed a convenient method for fluoroalkylation of hydroxy compounds by their reaction with perfluoroalkylated epoxides[8–11].

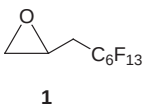
In continuation of our research[8–11], we present here a study of *O*-alkylation of partially protected pentofuranoses and tetritols with (2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxirane (**1**).

RESULTS AND DISCUSSION

The easily available 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose[12] (**2**), 1,2-*O*-isopropylidene-α-D-xylofuranose[13] (**3**), 2,4-*O*-ethylidene-D-erythritol[14] (**4**) and 1,3-*O*-ethylidene-D-threitol (**5**) were chosen as model compounds differing in variable accessibility of their unprotected hydroxy groups. Acetal **5** was prepared from 4,6-*O*-ethylidene-D-galactose[15] analogously to the method[14] described for **4**. In consequence of racemic epoxide **1**, mixtures of badly separable diastereoisomers differing in the configuration on the asymmetric carbon of the attached polyfluoroalkyl chain can be expected in products of the alkylation of the chiral substrates **2**–**5**. From the point of view of the potential application of the products as co-emulsifiers in oxygen carriers, both diastereoisomers should display bioinert properties. Therefore it is not necessary to separate them for introducing testing. Owing to instability of polyfluoroalkyls in alkaline medium[8], a strong basic catalyst of the metal alkoxide type[16] had to be excluded. Hence, the conditions previously employed[11] (boron trifluoride diethyl etherate as a catalyst, equimolar ratio of the reactants, diisopropyl ether as a solvent, temperature near to the boil and dry atmosphere) were first tested.

In contrast to the described reaction[11] of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, fluoroalkylations of the all studied compounds **2**, **3**, **4** and **5** with **1** proceeded slowly and, in addition, they were complicated with the formation of several side products as checked by TLC. The desired fluoroalkylated compounds **6**–**11** were obtained by a tedious repeated chromatography lowering the preparative yield substantially. Separation

of the diastereoisomers arising from reaction of the saccharides with the racemic oxirane **1** failed. Thus, 1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-α-D-xylofuranose (**6**) was obtained from **2** in a yield of 30%. In an attempt to improve the yield, molar ratio of the reactants, relative amount of the catalyst, temperature, or reaction time were varied, but with only small effect (yield 34%)



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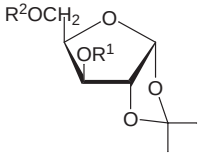
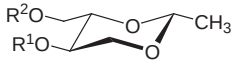
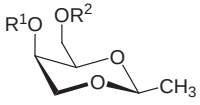


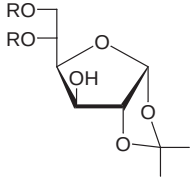
	R^1	R^2
2	CH_3	H
3	H	H
6	CH_3	$CH_2CH(OH)CH_2C_6F_{13}$
7	H	$CH_2CH(OH)CH_2C_6F_{13}$
12	R^1,R^2 =	$>C(CH_3)_2$
14	H	$COCH_3$



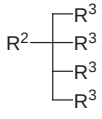
	R^1	R^2
4	H	H
8	H	$CH_2CH(OH)CH_2C_6F_{13}$
9	$R^1 = R^2$ =	$CH_2CH(OH)CH_2C_6F_{13}$
17	R^1, R^2 =	$>CHCH_3$



	R^1	R^2
5	H	H
10	H	$CH_2CH(OH)CH_2C_6F_{13}$
11	$R^1 = R^2$ =	$CH_2CH(OH)CH_2C_6F_{13}$
19	R^1, R^2 =	$>CHCH_3$



	R
15	H
16	$>C(CH_3)_2$



	R^1	R^2	R^3
18a	H	H	OH
18b	Bz	H	OBz
20a	H	OH	H
20b	Bz	OBz	H

(Table I, entries 1–5). The use of magnesium perchlorate[11] as a catalyst completely failed in the fluoroalkylation of **2**. In *O*-alkylation of the diols **3**–**5**, a possibility of the formation of mono- and disubstituted derivatives should be considered. Notwithstanding, only 1,2-*O*-isopropylidene-5-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-α-D-xylofuranose (**7**) was obtained from **3** in a very low yield of 6% (Table I, entries 6,7). In contrast, the reaction of acetal **4** with oxirane **1** afforded 2,4-*O*-ethylidene-1-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-erythritol (**8**) in the 27% yield only if a 1 : 1 molar ratio of reactants was kept. Higher ratio of oxirane **1** caused the formation of disubstituted 2,4-*O*-ethylidene-1,3-di-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-erythritol (**9**), which was isolated in a low yield in addition to

TABLE I
Alkylation of compounds **2**–**5** with oxirane **1** catalyzed by $BF_3 \cdot Et_2O$

Entry No.	Saccharide (mmol)	Mole ratio		Temperature °C	Time h	Product	Yield %
		Saccharide/**1**	Saccharide/$BF_3 \cdot Et_2O$				
1	**2** (0.85)	1/1	1/0.04	85	8	**6**	26
2	**2** (1.70)	1/2	1/0.02	80	9	**6**	25
3	**2** (2.43)	1/1	1/0.014	70	5	**6**	28
4	**2** (1.66)	1/2	1/0.021	60	7	**6**	31
5	**2** (2.43)	1/1.5	1/0.014	50	8	**6**	34
6	**3** (2.07)	1/1	1/0.09	95	11	**7**	6
						12[a]	8
7	**3** (2.07)	1/1	1/0.09	80	7	**7**	3
						12[a]	5
8	**4** (2.50)	1/1.1	1/0.1	95	11	**8**	27
						4[b]	21
						17[a,c]	12
9	**4** (1.89)	1/2.3	1/0.11	95	11	**8**	13
						9	3
						4[b]	5
						17[a,c]	9
10	**5** (2.63)	1/1	1/0.08	95	11	**10**	4
						11	2.2
						5[b]	27
						19[a]	15
11	**5** (2.53)	1/2.3	1/0.11	95	11	**10**	2.6
						11	12
						5[b]	13
						19[a]	13

[a] By-products from the side activity of catalyst; [b] the starting saccharide recovered; [c] unsuccessful to obtain in pure state.

the monosubstituted product **8** (Table I, entries 8, 9). The reaction of acetal **5** with oxirane **1** yielded (Table I, entries 9–11) a mixture of both 4-*O*-monosubstituted and 2,4-*O*-disubstituted derivatives, *i.e.* 1,3-*O*-ethylidene-4-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-threitol (**10**) and 1,3-*O*-ethylidene-2,4-di-*O*-((*RS*)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-threitol (**11**). As summarized in Table I, the conversions of acetals **4** or **5** were not complete in all experiments and from the reaction mixtures of experiments with compounds **3**–**5** some other by-products, hereinafter discussed, were isolated (Table I, note[a]).

Spectral data and elemental analyses of all fluorinated products **6**–**11** confirmed the structures suggested. The presence of the $-(CF_2)_5CF_3$ chain was proved by six separated signals in ^{19}F NMR spectra with the characteristic chemical shift from –78 to –130 ppm, of the corresponding integral intensity and multiplicity[11] (Table II). In ^1H NMR spectra of the monosubstituted derivatives **6**–**8** and **10** the H-1′ and H-3′ signals of hydrogens on fluoroalkyl substituent were observed in the range of 3.7 to 2.15 ppm and their duplicity demonstrated a diastereoisomeric composition of all these compounds. The relative integral intensities of the two pairs of distinctly separated dd signals assigned to H-1′ methylene protons corresponded a 1 : 1 molar ratio of diastereoisomers. The positions of the *O*-fluoroalkyl substituent on a saccharide chain were assigned on the basis of downfield shifts of the signals of the corresponding **H**–C–OR nuclei relatively to their chemical shifts in the unsubstituted parent structure. A complex character of the ^1H NMR spectra of both dialkylated derivative **9** or **11** did not allow

TABLE II
^{19}F NMR spectra of compounds **6**–**11**. Chemical shifts of the signals of perfluorohexyl chains

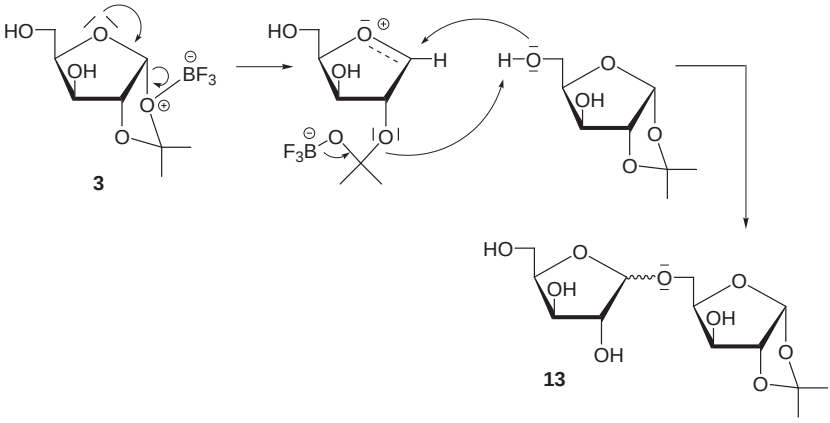
Compound	$-CH_2CF_2$	$3 \times CF_2$			$C\mathbf{F}_2-CF_3$	CF_3
6	–113.12	–122.22	–123.28	–124.01	–126.56	–81.29
7	–113.26	–122.22	–123.28	–124.01	–126.63	–81.30
8	–113.25	–122.31	–123.37	–124.08	–126.65	–81.33
9[a]	–113.15	–122.22	–123.28	–124.01	–126.56	–81.27
10	–113.15	–122.29	–123.35	–124.05	–126.64	–81.32
11[a]	–113.27	–122.33	–123.40	–124.11	–126.67	–81.36

[a] Signals of disubstituted derivatives were broad and pointless.

any reasonable structural elucidation. In the ^{13}C NMR APT spectra of **6**–**11**, the separated multiplets in the range from 120 to 108 ppm were assigned to carbons of the perfluorohexyl chain and a duplicity of some signals gave again an evidence of the near 1 : 1 diastereoisomeric composition. Attempts to deprotect the derivative **6** in various trifluoroacetic acid–water mixtures[11] was unsuccessful; a rich mixture of products was always indicated by TLC and separation on a column did not provide any pure compound.

Low yields of the expected fluoroalkylated products and presence of some other compounds in reaction mixtures as noted in Table I were imputed to a complex catalytic activity of $BF_3{\cdot}Et_2O$. As reported[17], this catalyst can be able to cleave various oxygen bonds in the protected saccharides. Although cyclic acetal is an excellent protective group it can possess its own reactivity[17,18] in some special cases. In general, the effect of the Lewis-type of catalyst can be currently exploited, *inter alia*, for the introduction, as well as for the cleavage of acetal/ketal protecting cycles[19]. Owing to these potential reactions, the behavior of 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**), 2,4-*O*-ethylidene-D-erythritol (**4**) and 1,3-*O*-ethylidene-D-threitol (**5**) in reaction media containing a catalytic amount of $BF_3{\cdot}Et_2O$ was examined under various conditions. The compounds structurally related to **3**, such as 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**14**) and 1,2-*O*-isopropylidene-α-D-glucofuranose (**15**) were included in the study for comparison. Usually, experiments were stopped after disappearing the TLC-spot of the starting compound and after that, the soluble and solid parts of reaction mixture were analyzed separately.

A solid was precipitated when the solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**) in diisopropyl ether was stirred with $BF_3{\cdot}Et_2O$. The amount of the precipitate increased with time (Table III, entries 1–3), with an increasing ratio of the catalyst to a substrate (Table III, entries 3–5) and with an increasing temperature of the reaction (Table III, entries 6–9), namely. The dry precipitate exhibited m.p. within a broad interval. It was soluble in water, but insoluble in ethanol, diethyl ether, acetone, chloroform and benzene. ^1H and ^{13}C NMR spectra of it were very complex as usual for a mixture of structurally related compounds. MS/ESI spectrum showed groups of ion-lines differing orderly by the *m/z* value of ≈132 ($C_5H_8O_4$). The first significant line at *m/z* 345.2 could correspond to a sodium cationised quasi-molecular ion of disaccharide **13** $[C_{13}H_{22}NaO_9]^+$ (Scheme 1). Acid hydrolysis of the precipitate incompletely yielded D-xylose which was identified by the comparison with the standard on TLC and HPLC. A mixture of oligomers or low polymers (2–12 pentose units of an undefined linking) could be deduced for the composition of precipitate



SCHEME 1
The starting steps of oligomerization of **3**

TABLE III
Composition of products of the reaction of 1,2-*O*-Isopropylidene-α-D-xylofuranose (**3**; 190 mg, 1 mmol) in diisopropyl ether (5 ml, entries 1–9) or dichloromethane (5 ml, entry 10) in presence of $BF_3 \cdot Et_2O$

Entry No.	$BF_3 \cdot Et_2O$ μmol	Bath temperature °C	Contact time h	Product composition, mg (%)[a]			
				3	**12**	D-xylose[b]	oligomer
1	40	55	1	45 (28)	21 (13)	60 (38)	34 (21)
2	40	55	3	34 (24)	19 (14)	26 (19)	61 (43)
3	40	55	5	35 (22)	22 (14)	38 (24)	62 (39)
4	60	55	5	21 (13)	11 (7)	22 (14)	108 (66)
5	80	55	5	[c]	[c]	[c]	153 (94)
6	40	60	5	18 (11)	5 (3)	23 (14)	120 (72)
7	40	70	5	12 (7)	5 (3)	13 (8)	134 (82)
8	40	80	2	0	0	0	164 (100)
9	40	90	1	0	0	0	165 (100)
10	40	55	5	9 (5)	21 (12)	20 (11)	126 (72)

[a] Per cent by the total weight of the product; [b] D-xylose with a little of oligomer; [c] compounds **1**, **3**, and D-xylose (Σ 10 mg) were not separated.

from the mentioned data. Formation of polymers in reactions of various saccharide derivatives catalyzed with $BF_3 \cdot Et_2O$ or other Lewis acids has already been reported[20]. Mostly, various 1,*n*-anhydroaldoses were used for polymerization aimed to formation of polysaccharide chains[20a]. Polymerization of 1,4-anhydro-2,3-*O*-benzylidene-α-D-ribopyranose or 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose was described[21] to yield [1→4]-2,3-*O*-benzylidene-α-D-ribopyranan and "[3→5]-1,2-*O*-isopropylidene-α-D-xylofuranan", respectively.

After removing solvents, a residue from the liquid part was chromatographed yielding 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (**12**), the starting **3**, D-xylose and a minor portion of oligomers. Analogous result was obtained using dichloromethane as solvent (Table III, entry 10). On the other hand, no change of the substrate was observed in diisopropyl ether solutions, when $Mg(ClO_4)_2$ was used as the catalyst for the reaction with **3**, or 5-*O*-acetyl derivative **14** was used as the substrate.

Regarding to the above mentioned experience with derivative **3**, a study of behavior of its homologue, 1,2-*O*-isopropylidene-α-D-glucofuranose (**15**), seemed to be of interest. Owing to a low solubility of **15** in diisopropyl ether, the experiments were carried out in dry 1,2-dimethoxyethane at 55, 70 and 80 °C (Table IV). At 55 °C, compound **15** remained unchanged within the experiment. However, at higher temperature, a complex mixture of soluble and insoluble products was obtained analogously to the reaction

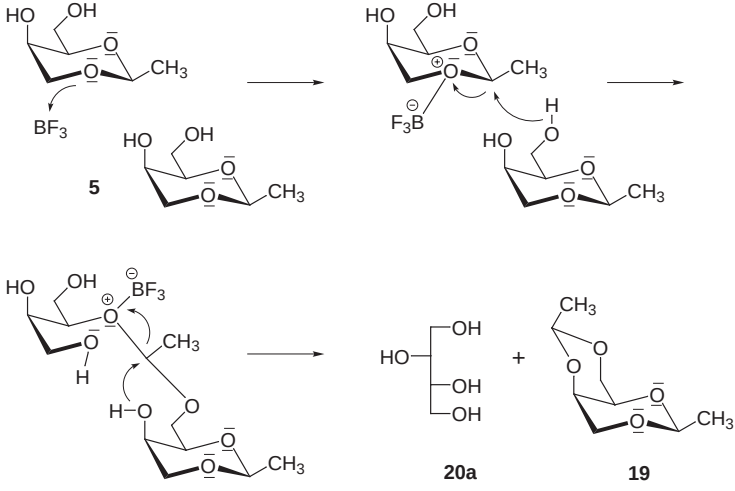
TABLE IV
Composition of products of the reaction of 1,2-*O*-isopropylidene-α-D-glucofuranose (**15**; 220 mg, 1.0 mmol) in 1,2-dimethoxyethane (5 ml) with $BF_3 \cdot Et_2O$ (40 μl) for 5 h

Entry No.	Bath temperature °C	Composition of product, mg (%)[a]			
		15	**16**	D-glucose	oligomer
1	55	220 (100)	0	0	0
2	70	90 (49)	12 (7)[b]	12 (7)[c]	44 (24)
3	80	76 (45)	10 (6)[b]	6 (4)[c]	54 (32)

[a] Per cent by the total weight of the product; [b] further part (*ca* 25 mg) was contamined by undefined compound with R_F close to **16**, possibly 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose; [c] a mixture of D-glucose and oligomer (HPLC).

of **3**. MS of the solid part similarly showed ion lines orderly differing by the *m/z* value 162 and the general formula $[C_{15}H_{26}NaO_{11} + (C_6H_{10}O_5)_n]^+$, for n = 0–6, could be considered for these ions. D-Glucose was identified in the acid hydrolyzate of the solid products by HPLC. Column chromatography of the soluble part of the reaction mixture afforded 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**16**), unchanged **15**, and D-glucose as prevailing compounds.

The action of $BF_3{\cdot}Et_2O$ on 2,4-*O*-ethylidene-D-erythritol (**4**) or 1,3-*O*-ethylidene-D-threitol (**5**) was studied in diisopropyl ether solution at 70–80 °C. After 5 h, the solvent was evaporated and products were separated by extraction and column chromatography. In the both cases, 1,3:2,4-di-*O*-ethylidene derivative **17** or **19**, starting acetal **4** or **5**, and tetritol **18a** or **20a** (in the form of its perbenzoate **18b** or **20b**) were isolated and identified, respectively. Also some minor compounds (<5%) showing TLC spots and GC-MS spectra close to **17** or **19** were obtained from these mixtures but their separation to individual compounds failed. According to ref.[22], diastereoisomeric tetraoxadecalin structures can be considered for these products. In contrast to the experiments with the derivative **3** and **15**, no polymerization was observed. For the purpose of identification, a standard sample of derivative **17** was prepared by means of reaction of **4** with paraldehyde in presence of $BF_3{\cdot}Et_2O$.



SCHEME 2
Disproportionation of the ethylidene group in 1,3-*O*-ethylidene-D-threitol (**5**)

In conclusion, the transformations of the substrates **3**, **4**, **5** and **15** induced by $BF_3 \cdot Et_2O$ catalyse proceeded in the tested solvents to various degree of conversions and were temperature dependent. Disproportionation of the acetal/ketal groups according to the Scheme 2 and formation of oligomers according to Scheme 1 were found in this work. A further investigation is necessary for any more precise determination of the last compounds.

All mentioned transformations, quickly proceeding simultaneously with fluoroalkylations could cause low yields of the expected products in the fluoroalkylations of **2**–**5** with oxirane **1**.

EXPERIMENTAL

Optical rotations were measured on a Jasco Model DIP-370 polarimeter and are given in 10^{-1} deg cm^2 g^{-1}. Melting points were determined on a Kofler block and are uncorrected. IR spectra were measured on a FT IR Nicolet 740 spectrometer, wavenumbers are given in cm^{-1}. NMR spectra were measured in $CDCl_3$ solutions (tetramethylsilane as an internal standard) at 25 °C on a Bruker AM 400 spectrometer (^1H, 400 MHz; ^{13}C, 100.62 MHz; ^{19}F, 376.2 MHz) or on a Bruker Avance DRX 500 spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{19}F, 470.6 MHz). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The assignment of the signals was confirmed with ^1H-^1H COSY and ^1H-^{13}C HMQC experiments. The nuclear Overhauser effect was measured by help of the double-pulsed-field-gradient-spin-echo (DPFGSE) method.

For the description of NMR spectra, the following formalism was used: (a) the polyfluoroalkyl carbon numbers are primed, *e.g.* C-1′, C-2′, H-2′, *etc.*; (b) the hydrogens of chain methylene groups are distinguished by a or b, *e.g.* H-1′a, H-5b, *etc.*; (c) the hydrogens of ring methylene groups (in **4, 5**, **8**, **10**) are denoted *a* or *e* indicating the axial or equatorial positions, respectively, *e.g.* H-4*a*, H-1*e*, *etc.*; (d) the separated signals of the same nuclei in the diastereoisomers are marked A or B, and the common, unseparated signals AB, *e.g.* H-1′aA, H-5aB, H-3AB, *etc.*; (e) the numbers 5, 6 or 5′, 6′ were assigned to the carbons of the ethane-1,1-diyl group(s), >CH-CH_3, *e.g.* C-5, H-5, C-6′, *etc.*, for description of NMR spectra of compounds **4**, **5**, **8**, **10** and **17**, **19**, respectively; (f) in ^{13}C NMR spectra (APT), signals of carbon atoms with 0 or 2 hydrogens are in italics.

Mass spectroscopy of the precipitates arose from **3** and **15** was realized on API 3000 Perkin–Elmer instrument, using electrospray ionization method. MS of the derivative **17** and its isomers were measured on the Hewlett–Packard GC/MS instrument 5890 with the quadrupol detector 5971A, using electron ionization at 70 eV. The APCI spectra of the derivative **19** were recorded on an LCQ mass spectrometer (ThermoFinnigan, San Jose). The sample was dissolved in MeOH–water 50 : 50 (10 μg/ml) and directly injected *via* a Valco sample loop (5 μl) into a stream of the mobile phase, MeOH–water 50 : 50, 0.5 ml/min.

HPLC: A glass jacket column (400 × 4 mm I.D.) with a strong cation exchanger OSTION LG-KS 0802 (Spolek pro chemickou a hutní výrobu a.s., Ústí nad Labem, Czech Republic) in Ca^{2+} form thermostated on 70 °C was used. The flow rate of deionized water was maintained at 6 ml/h with an INGOS LCP 5020 pump (pressure 850 kPa) and analyses were monitored with an differential refractometric detector Optilab Multiref 5902 (Tecator, Sweden) connected with a recorder TZ 4200 (Laboratorní přístroje, Czech Republic).

Column chromatography was performed on silica gel 60 (Fluka) and TLC on silica gel according to Stahl (10–40 μm, Merck, Germany). For chromatographic separations, the following eluting systems were used: petroleum ether–acetone 8 : 1 (S1), petroleum ether–acetone 4 : 1 (S2), benzene–ethanol 10 : 1 (S3), benzene–ethanol 7 : 1 (S4), benzene–ethanol 6 : 1 (S5) and ethyl acetate–petroleum ether 5 : 1 (S6). The TLC spots were detected by spraying with a solution of 1% $Ce(SO_4)_2$ in 10% H_2SO_4 and subsequent carbonization. Solutions were concentrated under reduced pressure at bath temperature below 40 °C.

Racemic (2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxirane (**1**) was prepared by the described method[8].

1,2-O-Isopropylidene-3-O-methyl-α-D-xylofuranose[12] (**2**) was prepared as a syrup distilling at 140 °C/1.3 Pa, $[\alpha]_D^{25}$ –64 (*c* 1.0, $CHCl_3$); ref.[23] gives $[\alpha]_D^{25}$ –64 (*c* 1.7, $CHCl_3$). ^{1}H NMR: 5.94 d, 1 H, *J* = 3.9 (H-1); 4.60 d, 1 H, *J* = 3.9 (H-2); 4.28 m, 1 H (H-4); 3.90 dd, 1 H, *J* = 5.3, 11.8 (H-5a); 3.85 dd, 1 H, *J* = 5.4, 11.8 (H-5b); 3.82 d, 1 H, *J* = 3.5 (H-3); 3.44 s, 3 H (OCH_3); 2.62 bs, 1 H (OH); 1.33, 1.50 2 × s, 2 × 3 H (2 × CH_3). ^{13}C NMR: *111.6* (>$C(CH_3)_2$); 104.7 (C-1); 85.2 (C-3); 81.6 (C-2); 80.0 (C-4); *60.6* (C-5); 57.7 (OCH_3); 26.7, 26.2 (>$C(CH_3)_2$).

1,2-O-Isopropylidene-α-D-xylofuranose (**3**) was prepared according to ref.[13]. In addition, 5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**14**) was obtained in 4.2% yield as an artefact arising in the course of preparative chromatography of **3** by means of transesterification with the eluting ethyl acetate, possibly. TLC: R_F 0.72 (S6). M.p. 99 °C, $[\alpha]_D^{20}$ +22 (*c* 1, $CHCl_3$). ^{1}H NMR: 5.9 d, 1 H, *J*(1,2) = 3.5 (H-1); 4.54 d, 1 H (H-2); 4.51 dd, 1 H, *J*(5,4) = 7.2, *J*(5,5′) = 11.5 (H-5); 4.25 dd, 1 H, *J*(4,5′) = 5.3 (H-4); 4.16 dd, 1 H (H-5′); 2.9 bs, 1 H (OH); 2.9 s, 1 H (H-3); 2.1 s, 3 H (CH_3CO); 1.31, 1.49 2 × s, 2 × 3 H (>$C(CH_3)_2$). ^{13}C NMR: 171.8 (C=O); *111.8* (>$C(CH_3)_2$); 104.7 (C-1); 85.0, 78.2, 74.4 (C-2, C-3, C-4); *61.1* (C-5); 26.8, 26.7, 26.1 (CH_3CO, >$C(CH_3)_2$). Literature[24] gives m.p. 100–102 °C and $[\alpha]_D^{20}$ +25.8 (*c* 1, $CHCl_3$) for **14**. For $C_{10}H_{16}O_6$ (232.2) calculated: 51.72% C, 6.94% H; found: 51.42% C, 6.77% H.

2,4-O-Ethylidene-D-erythritol[14] (**4**), m.p. 99.5 °C (diethyl ether–petroleum ether), $[\alpha]_D^{25}$ –52 (*c* 1.9, water); ref.[14] gives m.p. 99.5 °C and $[\alpha]_D^{25}$ –54.7 (*c* 2, water). ^{1}H NMR: 4.72 q, 1 H, *J* = 5.1 (H-5); 4.13 dd, 1 H, *J* = 5.4, 10.8 (H-4*e*); 3.81–3.89 m, 2 H (H-1a, H-1b); 3.77 dt, 1 H, *J* = 9.3, 5.4, 5.2 (H-3); 3.41 t, 1 H, *J* = 10.5, 10.8 (H-4*a*); 3.12 d, 1 H, *J* = 5.2 (OH-3); 2.67 t, 1 H, *J* = 5.4, 5.4 (OH-1); 1.40 d, 3 H, *J* = 5.1 (3 × H-6). ^{13}C NMR: 98.9 (C-5); 80.7 (C-2); *70.5* (C-4); *62.4* (C-1); 62.1 (C-3); 20.4 (C-6). DPFGSE-NOE: H-5 ↔ H-2; H-5 ↔ H-4*a*; H-2 ↔ H-4*a*.

1,3-*O*-Ethylidene-D-threitol (**5**)

A mixture of 4,6-*O*-ethylidene-D-galactose[25] (11 g, 53 mmol), $NaIO_4$ (23.1 g, 108 mmol), $NaHCO_3$ (8.8 g, 105 mmol) was stirred in water (250 ml) at 20 °C for 2.5 h (TLC, S6: starting compound, R_F 0.46; oxidation product, R_F 0.86). After disappearance of the starting compound, the solution was concentrated in vacuum and extracted with EtOAc (3 × 50 ml). Organic layers were collected, solvent was evaporated and the residue was dissolved in a mixture of water (60 ml) and concentrated ammonia (0.5 ml). Saturated solution of $BaCl_2$ in water was then added to the solution and the liquid was filtered off. To the cooled filtrate containing 2,4-*O*-ethylidene-D-threose, $NaBH_4$ (1.5 g, 40 mmol) was added with stirring during 15 min and another portion of $NaBH_4$ (0.5 g, 13 mmol) was added after 2 h (TLC, S6: threose acetal, R_F 0.86; **5**, R_F 0.72), and the reduction was finished in 3 h. The excess of hydride was decomposed by 1 M HCl (3 ml), pH 9 was then adjusted with aqueous ammonia, the solution was evaporated and the residue extracted with boiling chloroform (8 × 200 ml). The crude syrupy acetal **5** (4.05 g, 52%) obtained after evaporation of chloroform was puri-

fied on a silica gel column (S5). Recrystallization of the chromatographically homogeneous product from acetone–petroleum ether gave 2.93 g (37%) of the acetal **5**, m.p. 77 °C, $[\alpha]_D^{20}$ –18 (*c* 1.8, $CHCl_3$); ref.[25] gives m.p. 78–80 °C, $[\alpha]_D^{20}$ –17.6 (*c* 2.5, $CHCl_3$). IR ($CHCl_3$): 3 574, 3 458, 3 020, 2 943, 2 917, 2 889, 1 454, 1 412, 1 390, 1 370, 1 355. ^{1}H NMR: 4.79 q, 1 H, *J* = 5.0 (H-5); 4.05 dd, 1 H, *J* = 1.6, 11.9 (H-1*e*); 3.86 dd, 1 H, *J* = 1.0, 11.9 (H-1*a*); 3.83–3.75 m, 3 H (H-3, H-4a, H-4b); 3.59 d, 1 H, *J* = 9.8 (H-2); 3.16 d, 1 H, *J* = 10.0 (OH-2); 2.68 t, 1 H, *J* = 5.2 (OH-4); 1.38 d, 3 H, *J* = 5.0 (3 × H-6). ^{13}C NMR: 99.5 (C-5); 78.9 (C-3); *72.0* (C-1); 64.4 (C-2); *62.8* (C-4); 20.8 (C-6). For $C_6H_{12}O_4$ (148.2) calculated: 48.64% C, 8.16% H; found: 48.55% C, 8.08% H.

1,3:2,4-Di-*O*-ethylideneerythritol (**17**)

A mixture of 2,4-*O*-ethylidene-D-erythritol (**4**; 126 mg, 0.85 mmol), paraldehyde (2 g, 15 mmol) and $BF_3{\cdot}Et_2O$ (20 µl, 0.4 mmol) was briefly stirred at room temperature. After 90 s, the reaction was stopped with methanol (2 ml) and aqueous $NaHCO_3$ (0.5 ml, 10%). Volatile parts were evaporated and a residue was extracted with diethyl ether. After evaporation of the solvent, derivative **17** (m.p. 88–89 °C) was obtained in the yield 104 mg (70%) by sublimation at 35 °C/1.6 kPa; ref.[26] gives m.p. 86–89 °C. ^{1}H NMR: 4.79 q, 2 × 1 H, *J* = 5.0 (H-5, H-5′); 4.10 dd, 2 × 1 H, *J*(1*e*,2) or *J*(4*e*,3) = 3.3, *J*(1*e*,1*a*) or *J*(4*e*,4*a*) = 9.9; 3.51–3.63 m, 4 H (H-1*a*, H-2, H-3, H-4*a*); 1.32 d, 2 × 3 H, *J*(6,5) or *J*(6′,5′) = 5.0 (H-6, H-6′). ^{13}C NMR: 99.9 (C-5, C-5′); 73.3 (C-2, C-3); *68.3* (C-1, C-4); 20.4 (C-6, C-6′). MS (*m/z*, rel.%): 173, 159, 130, 115, 100, 87 (100), 79, 69, 61, 59, 45, 43. For $C_8H_{14}O_4$ (174.2) calculated: 55.16% C, 8.10% H; found: 55.27% C, 8.29% H.

Reaction of Compounds **2**–**5** with Oxirane **1**. General Procedure

A *ca* 10% solution of a saccharide (**2**, **3**, **4** or **5**) in diisopropyl ether was stirred with oxirane **1** (1–2 mole equivalents), $BF_3{\cdot}Et_2O$ (0.02–0.1 equivalent) under gentle reflux and the reaction was monitored by TLC. When the starting substrate disappeared, the reaction mixture was evaporated and the residue was separated by flash chromatography on silica gel. Chromatographically non-uniform fractions were combined and repeatedly separated by column chromatography. Conditions and yields of all experiments on alkylation of **2**–**5** are summarized in Table I.

*1,2-O-Isopropylidene-3-O-methyl-5-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-*α*-D-xylofuranose* (**6**, a mixture of diastereoisomers ≈1 : 1) (550 mg, 34%) was obtained from 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose (**2**) (Table I, entry 5) by column chromatography (40 g of silica gel, S1) as a colorless syrup (TLC, S2: R_F 0.45). IR ($CHCl_3$): 3 500, 3 022, 2 937, 1 376, 1 365. ^{1}H NMR: 5.93 d, 1 H, *J* = 3.7 (H-1A); 5.92 d, 1 H, *J* = 3.7 (H-1B); 4.60 d, 2 H, *J* = 3.7 (H-2AB); 4.38 m, 2 H (H-4AB); 4.29 m, 2 H (H-2′AB); 3.81 dd, 1 H, *J* = 5.0, 10.5 (H-5aA); 3.79 dd, 1 H, *J* = 4.6, 10.4 (H-5aB); 3.75 d, 2 H, *J* = 3.5 (H-3AB); 3.74 dd, 1 H, *J* = 4.7, 10.5 (H-5bA); 3.72 dd, 1 H, *J* = 5.0, 10.4 (H-5bB); 3.65 dd, 1 H, *J* = 3.5, 9.9 (H-1′aA); 3.61 dd, 1 H, *J* = 3.7, 9.9 (H-1′aB); 3.52 dd, 1 H, *J* = 6.6, 9.9 (H-1′bA); 3.48 dd, 1 H, *J* = 6.6, 9.9 (H-1′bB); 3.405 s, 3 H (OCH_3 A); 3.401 s, 3 H (OCH_3 B); 2.87 d, 1 H, *J* = 4.4 (OH-2′A); 2.84 d, 1 H, *J* = 4.1 (OH-2′B); 2.42–2.20 m, 4 H (H-3′a, H-3′bAB); 1.52, 1.34 2 × s, 2 × 6 H (>$C(CH_3)_2$ AB). ^{13}C NMR: *120.6*, *118.1*, *116.0*, *112.7*, *110.7*, *108.6* 6 × m (C-9′–C-4′AB); *112.4* (>$C(CH_3)_2$ AB); 105.7 (C-1AB); 85.0 (C-3AB); 82.1 (C-2AB); 79.7 (C-4AB); *75.5* (C-1′AB); *69.8* (C-5AB); 64.9 (C-2′A); 64.75 (C-2′B); 58.4 (OCH_3 AB); *35.4–34.97* m (C-3′AB);

27.4, 26.9 (>C(CH_3)$_2$ AB). ^{19}F NMR: Table II. For $C_{18}H_{21}F_{13}O_6$ (580.4) calculated: 37.25% C, 3.64% H, 42.56% F; found: 37.15% C, 3.51% H, 42.56% F.

1,2-O-Isopropylidene-5-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-α-D-xylofuranose (**7**, a mixture of diastereoisomers ≈1 : 1) (65 mg, 6%) was obtained from 1,2-*O*-isopropylidene-α-D-xylofuranose (**3**) (Table I, entry 6) by column chromatography (35 g of silica gel, S2), m.p. 102–105 °C (diethyl ether–petroleum ether), (TLC, S2: R_F 0.32). ^{1}H NMR: 5.96 d, 2 H, *J* = 3.3 (H-1AB); 4.52 m, 2 H (H-2AB); 4.33–4.22 m, 6 H (H-3AB, H-4AB, H-2′AB); 3.98–3.90 m, 4 H (H-5aAB, H-5bAB); 3.68 dd, 1 H, *J* = 3.2, 10.2 (H-1′aA); 3.65 dd, 1 H, *J* = 3.2, 10.4 (H-1′a,B); 3.56 dd, 1 H, *J* = 6.4, 10.3 (H-1′bA); 3.51 dd, 1 H, *J* = 7.2, 10.1 (H-1′bB); 3.24–3.13 bd, 2 H (OH-2′AB); 2.44–2.15 m, 6 H (H-3′a, H-3′bAB, OH-3AB); 1.50, 1.32 2 × s, 2 × 6 H (>C(CH_3)$_2$ AB). ^{13}C NMR: *121–108* 6 × m (C-9′–C-4′AB); *111.9* (>C(CH_3)$_2$ AB); 104.8 (C-1AB); 85.3 (C-2AB); 78.4 (C-3A); 78.3 (C-3B); 76.0 (C-4AB); *75.7*, *75.4* (C-1′AB); *69.7*, *69.5* (C-5AB); 64.4, 64.1 (C-2′AB); *34.6–34.3* m (C-3′AB); 27.4, 26.9 (>C(CH_3)$_2$ AB). ^{19}F NMR: Table II. For $C_{17}H_{19}F_{13}O_6$ (566.3) calculated: 36.06% C, 3.38% H, 43.61% F; found: 36.25% C, 3.53% H, 43.73% F.

2,4-O-Ethylidene-1-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-erythritol (**8**, a mixture of diastereoisomers ≈1 : 1) (353 mg, 27%) was obtained from 2,4-*O*-ethylidene-D-erythritol (**4**) (Table I, entry 8) by column chromatography (65 g of silica gel, S3) as colorless syrup (TLC, S3: R_F 0.37). IR ($CHCl_3$): 3 447, 3 024, 2 957, 2 870, 1 467, 1 410, 1 365, 1 374, 1 317, 1 243. ^{1}H NMR: 4.69 q, 2 H, *J* = 4.9 (H-5AB); 4.30 bs, 2 H (H-2′AB); 4.13 dd, 2 H, *J* = 5.2, 10.7 (H-4*e*AB); 3.85 dd, 1 H, *J* = 4.7, 10.5 (H-1aA); 3.84 dd, 1 H, *J* = 5.7, 10.2 (H-1aB); 3.77 dd, 1 H, *J* = 3.6, 10.5 (H-1bA); 3.76 m, 2 H (H-3AB); 3.75 dd, 1 H, *J* = 3.7, 10.2 (H-1bB); 3.67 dd, 1 H, *J* = 3.2, 10.2 (H-1′aA); 3.65 dd, 1 H, *J* = 3.1, 10.2 (H-1′aB); 3.55 m, 2 H (H-2AB); 3.54 dd, 1 H, *J* = 6.3, 10.2 (H-1′bA); 3.49 dd, 1 H, *J* = 7, 10.2 (H-1′bB); 3.41 t, *J* = 10.5 (H-4*a*A); 3.40 t, *J* = 10.5 (H-4*a*B); 3.39 bs, 1 H (OH-2′A); 3.25 bs, 2 H (OH-3AB); 3.245 d, 1 H, *J* = 3.8 (OH-2′B); 2.43–2.16 m, 4 H (H-3′a, H-3′bAB); 1.34, 1.33 2 × s, 2 × 6 H (H-6AB). ^{13}C NMR: *120.6–108.3* 6 × m (C-4′–C-9′AB); 99.1 (C-5AB); 79.7 (C-2AB); *75.3* (C-1′A); *74.9* (C-1′B); *71.9* (C-1A); *71.6* (C-1B); *70.5* (C-4AB); 64.4 (C-2′AB); 63.1 (C-3A); 62.9 (C-3B); *34.7–34.3* (C-3′AB); 20.4 (C-6AB). ^{19}F NMR: Table II. For $C_{15}H_{17}F_{13}O_5$ (524.3) calculated: 34.36% C, 3.27% H, 47.11% F; found: 33.93% C, 3.38% H, 47.36% F.

2,4-O-Ethylidene-1,3-di-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-erythritol (**9**, a mixture of diastereoisomers) (50 mg**,** 3%) was obtained from 2,4-*O*-ethylidene-D-erythritol (**4**) (Table I, entry 9) as a colorless syrup. ^{1}H NMR: broad unsplitted signals at 4.24, 4.0–3.3, 2.5–2.15, 1.6, 1.34. ^{13}C NMR: broad signals at *120–108*, 99, 80, *76*, *75*, *71*, *69*, *68*, 65–63, *35–33*. ^{19}F NMR: Table II. For $C_{24}H_{22}F_{26}O_6$ (900.4) calculated: 32.02% C, 2.46% H, 54.86% F; found: 31.65% C, 2.39% H, 55.22% F.

1,3-O-Ethylidene-4-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-threitol (**10**, a mixture of diastereoisomers ≈1 : 1) (50 mg, 4%) was obtained from 1,3-*O*-ethylidene-D-threitol (**5**) (Table I, entry 10) by column chromatography (70 g of silica gel, S3) as the colorless syrup (TLC, S2: R_F 0.34). ^{1}H NMR: 5.21, 5.20 2 × q, 2 H, *J* = 4.7 (H-5AB); 4.29 m, 4 H (H-1*a*, H-1*e*AB); 4.07 m, 1 H (H-2′A); 3.93 m, 1 H (H-2′B); 3.88–3.59 m, 8 H (H-2AB, H-3AB, H-4aAB, H-4bAB); 3.55 d, 1 H, *J* = 9.5 (OH-2); 2.81 dd, 1 H, *J* = 3.0, 12.2 (H-1′aA); 2.73 dd, 1 H, *J* = 3.0, 12.2 (H-1′aB); 2.30 m, 4 H (H-3′a, H-3′bAB); 2.00 dd, 1 H, *J* = 12.2, 11.9 (H-1′bA); 1.95 dd, 1 H, *J* = 12.2, 11.9 (H-1′bB); 1.39 d, 6 H, *J* = 4.7 (3 × H-6AB). ^{13}C NMR: *120–108* 6 × m (C-9′–C-4′AB); 101.8 (C-5AB); 79.4 (C-2AB); 78.5 (C-2′AB); *75.2* (C-4AB); *72.1*, *71.7* (C-1′A, C-1′B); 64.4 (C-3AB); *62.5* (C-1AB); *34.6* (C-3′AB); 20.0 (C-6AB). ^{19}F NMR:

Table II. For $C_{15}H_{17}F_{13}O_5$ (524.3) calculated: 34.36% C, 3.27% H, 47.11% F; found: 34.63% C, 3.45% H, 47.39% F.

1,3-O-Ethylidene-2,4-di-O-((RS)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonyl)-D-threitol (**11**, a mixture of diastereoisomers) (270 mg, 12%) was obtained from 1,3-*O*-ethylidene-D-threitol (**5**) (Table I, entry 11) by column chromatography (80 g of silica gel, S3) as a colorless syrup (TLC, S2: R_F 0.36). ^{1}H NMR: 5.21, 5.20 2 × q, 2 H, J = 4.7 (H-5AB); broad unsplitted signals at 4.28, 4.23, 3.71–3.51, 2.9, 2.28, 1.39 d, 6 H, J = 4.7 (H-6AB). ^{13}C NMR: *120–108* (signals separated with difficulty from noise), 101.8, 90.9, 78.1, *75.4*, *74.9*, *72.0*, *71.8*, *71.7*, 64.3, *34.6*, *29.7*, 19.9. ^{19}F NMR: Table II. For $C_{24}H_{22}F_{13}O_6$ (900.4) calculated: 32.02% C, 2.71% H, 54.86% F; found: 31.77% C, 2.71% H, 55.14% F.

The Stability of 1,2-*O*-Isopropylidene-α-D-xylofuranose (**3**) and 1,2-*O*-Isopropylidene-α-D-glukofuranose (**15**) under the Attack of $BF_3{\cdot}Et_2O$. General Procedure

A solution of **3** or **15** (1 mmol) in appropriate solvent (Tables III and IV) was stirred with 40–80 μmol of $BF_3{\cdot}Et_2O$ at the selected temperature with absence of moisture. After designated time, the precipitated and liquid parts were separated by filtration. The precipitate was washed with the used solvent (2 × 5 ml) and with chloroform (2 × 5 ml), dried in vacuum and analyzed by help of spectral measurement, HPLC and elemental analysis. Acid hydrolysis of precipitate from **3** or **15** (50–70 mg) proceeded in water (2 ml) by stirring with Dowex 50W (H^+) (1 ml) or in HCl (2 ml, 1 M water solution) at room temperature, with HPLC analysis of the hydrolyzate. The liquid part (an original filtrate combined with the washing solvents) was evaporated and the residue was chromatographed on silica gel, using stepwise elution with ethyl acetate–petroleum ether 1 : 1 → ethyl acetate → ethanol for separation of mixture from **3** and chloroform–methanol 20 : 1 → chloroform–methanol 10 : 1 → ethanol for separation of mixture from **15**. The separated compounds (Tables III and IV) were identified by comparison with standards by means of the NMR spectroscopy or HPLC.

The precipitate from **3**: M.p. 165–195 °C. ^{1}H NMR: continuous spectrum with broad peaks at δ-values: 5.90, 5.05, 4.60, 4.50, 4.08, 3.70, 3.50, 3.38, 1.39, 1.30, 1.26. ^{13}C NMR: 103.7, 99.1, 97.8, 92.4, 79.5, 76.7, 74.7, 73.2, 72.4, 69.7, *65.7*, *62.1*, 26.1. MS (the most abundant ions): 345.2, 477.3, 609.3, 741.4, 873.5, 1 005.6, 1 137.6, 1 269.7, 1 401.8, 1 533.8, 1 665.9, 1 798.0, 1 930.0, corresponding with quasi-molecular sodium cationized ions of general formula $[C_{13}H_{22}NaO_9 + (C_5H_8O_4)_n]^+$ for n = 0–12. HPLC: 5 peaks with the capacity factors k' = 0.0 (90.6%), 0.05 (2.5%), 0.09 (2.0%), 0.14 (1.7%), 0.44 (3.2%). HPLC of the hydrolyzate: D-xylose (capacity factor k' = 0.44). Elemental analysis: Found: 44.83% C, 6.80% H.

The precipitate from **15**: M.p. 120–130 °C. MS (the most abundant ions): 405.2, 567.3, 729.4, 891.5, 1 053.6, 1 215.7, 1 377.7, corresponding with quasi-molecular sodium cationized ions of general formula $[C_{15}H_{26}NaO_{11} + (C_6H_{10}O_5)_n]^+$, for n = 0–6. HPLC: 5 peaks with the capacity factors k' = 0.0 (33%), 0.09 (16%), 0.16 (16%), 0.21 (7%), 0.35 (28%). HPLC of the hydrolyzate: D-glukose (capacity factor k' = 0.35). Elemental analysis: Found: 42.06% C, 6.13% H.

Results of experiments are summarized in Tables III and IV.

Behavior of 2,4-*O*-Ethylidene-D-erythritol (**4**) in Presence of $BF_3 \cdot Et_2O$

A solution of derivative **4** (1 020 mg, 6.85 mmol) in diisopropyl ether (30 ml) was stirred with $BF_3 \cdot Et_2O$ (40 µl, 0.3 mmol) at the bath temperature 80 °C. After 5 h, the reaction mixture was evaporated and the residue was extracted with CH_2Cl_2 (8 × 50 ml). From the column chromatography of the extract, 1,3:2,4-di-*O*-ethylideneerythritol (**17**; 240 mg, 1.4 mmol, 20%) and 2,4-*O*-ethylidene-D-erythritol (**4**; 490 mg, 48%) were obtained. Spectral and other data of the isolated compounds **17** and **4** were in accordance with data of the standard samples.

The residue non-extractable with CH_2Cl_2 (a crude erythritol **18a**, 202 mg) was solved in pyridine (10 ml) and esterified with benzoyl chloride (1 ml) to *1,2,3,4-tetra-O-benzoyl erythritol* (**18b**) in the yield 780 mg (1.45 mmol, 21% to **4**). After recrystallization from ethanol it exhibited m.p. 190 °C; ref.[27] gives m.p. 188–189 °C. ^{1}H NMR: 8.0 dd, 8 H; 7.55 m, 4 H; 7.42 q, 8 H (arom.); 5.97 m, 2 H (H-2, H-3); 4.89 dd, 2 H, J = 2.4, 12.2 (H-1, H-4); 4.65 dd, 2 H, J = 5.2, 12.2 (H-1′, H-4′). ^{13}C NMR: *166.0*, *165.4* (C=O); 133.4, 133.2, 129.8, 129.7, *129.4*, *129.3*, 128.5, 128.4 (arom.); 70.1 (C-2, C-3); *62.7* (C-1, C-4). For $C_{32}H_{26}O_8$ (538.6) calculated: 71.37% C, 4.87% H; found: 71.47% C, 5.01% H.

Behavior of 1,3-*O*-Ethylidene-D-threitol (**5**) in Presence of $BF_3 \cdot Et_2O$

A solution of derivative **5** (136 mg, 0.91 mmol) in diisopropyl ether (5 ml) was stirred with $BF_3 \cdot Et_2O$ (5 µl, 40 µmol) at the bath temperature 70 °C. After 5 h, reaction mixture was evaporated and the residue was treated as in the precedent experiment. The combined dichloromethane parts were evaporated and the residue (122 mg) was chromatographed on silica gel (15 g) column. *1,3:2,4-Di-O-ethylidene-D-threitol* (**19**; 41 mg, 0.24 mmol) and the starting **5** (64 mg, 0.43 mmol) were eluted with benzene–ethanol 50 : 1 and toluene–ethanol 50 : 1, respectively. Inseparable compounds with R_F close to **19** found in some minor fractions (Σ ≈12 mg) are as isomers of the **19** considered[22]. The derivative **19** showed m.p. 123–124 °C, $[\alpha]_D^{20}$ –39 (*c* 1, $CHCl_3$). ^{1}H NMR: 4.77 q, 2 × 1 H, J = 5.2 (H-5, H-5′); 4.11 d, 2 × 1 H, J = 12.6, 1 (H-1*e*, H-4*e*); 3.84 dd, 2 × 1 H (H-1*a*, H-4*a*); 3.56 m, 2 × 1 H (H-2, H-3); 1.41 d, 2 × 3 H (H-6, H-6′). ^{13}C NMR: 98.8 (C-5, C-5′); *69.54* (C-1, C-4); 69.35 (C-2, C-3); 21.0 (C-6, C-6′). NMR data corresponded to the described[22] ones of the racemic form. MS: 175 $(M + 1)^+$. For $C_8H_{14}O_4$ (174.2) calculated: 55.16% C, 8.10% H; found: 55.04% C, 8.21% H.

The part insoluble in CH_2Cl_2, which was assumed to be D-threitol (**20a**; 26 mg, 0.21 mmol) was solved in pyridine (5 ml) and stirred with benzoyl chloride (150 µl, 1.3 mmol) at room temperature for 12 h (TLC, S3: starting compound, R_F 0.0; product, R_F 0.86). After a usual treatment, the product was recrystallized from ethanol (0.7 ml). *1,2,3,4-Tetra-O-benzoyl-D-threitol* (**20b**) was obtained in the yield 101 mg (88%), m.p. 96–97 °C, $[\alpha]_D^{25}$ –6 (*c* 1, $CHCl_3$); ref.[28] gives m.p. 97 °C, $[\alpha]_D^{25}$ –4.2 (*c* 1, $CHCl_3$). ^{1}H NMR: 8.02 dd, 8 H; 7.54 m, 4 H; 7.41 q, 8 H (arom.); 5.99 m, 2 H (H-2, H-3); 4.78 dd, 2 H, J = 3.8, 12.0 (H-1, H-4); 4.68 dd, 2 H, J = 5.8, 12.0 (H-1′, H-4′). ^{13}C NMR: *166.0*, *165.6* (C=O); 133.5, 133.3, 129.9, 129.8, *129.4*, *129.3*, 128.5, 128.4 (arom.); 70.1 (C-2, C-3); *62.8* (C-1, C-4). For $C_{32}H_{26}O_8$ (538.6) calculated: 71.37% C, 4.87% H; found: 71.13% C, 4.69% H.

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