PARTIAL METHYLATION OF METHYL 2,6-DIDEOXY-α-D-*xylo*- AND α-D-*lyxo*-HEXOPYRANOSIDE*

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Rate of methylation of the hydroxyl groups in the title glycosides was investigated during their reaction with methyl iodide and sodium hydroxide in acetonitrile. Relative rate constants of the side-reactions and subsequent reactions taking place were calculated. The differences in the reaction rates of methylation of individual hydroxyl groups are discussed in connection with the possible polar and steric effects.

In connection with the methylation analysis of oligo- and polysaccharides[1] it is becoming ever more usual to use direct methylation of suitable derivatives of monosaccharides for the preparation of partially methylated sugars as standards. In the case of 2,6-dideoxyhexoses the corresponding monomethyl ethers were also identified as components of cardiac glycosides[2] and antibiotics[3,4]. In order to utilize optimally the different reactivities of individual hydroxyl groups in the synthesis of partially methylated sugars, its principle must be understood. In this paper which is a continuation of preceding studies[5-8] attention is paid to partial methylation of title methyl glycosides.

Partial methylation of methyl 2,6-dideoxy-α-D-*lyxo*-hexopyranoside (*I*) (Scheme 1) and methyl 2,6-dideoxy-α-D-*xylo*-hexopyranoside (*II*) (Scheme 2) was carried out in the conventional manner with methyl iodide and sodium hydroxide in acetonitrile[5]. Individual components of the reaction mixtures, *i.e.* the starting dihydroxy derivative[9] *I*, methyl 2,6-dideoxy-3-O-methyl-α-D-*lyxo*-hexopyranoside[10] (*III*), methyl 2,6-dideoxy-4-O-methyl-α-D-*lyxo*-hexopyranoside[11-16] (*IV*) and methyl 2,6-dideoxy-3,4-di-O-methyl-α-D-*lyxo*-hexopyranoside[17] (*V*); or dihydroxy derivative[9] *II*, 3-methyl ether *VI*, 4-O-methyl derivative *VII* and 3,4-dimethyl ether *VIII* were identified both by means of mass spectrometry combined with gas chromatography and by using standards.

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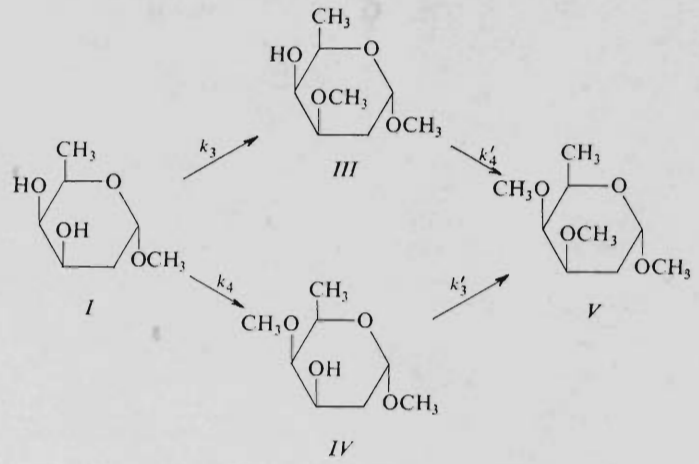
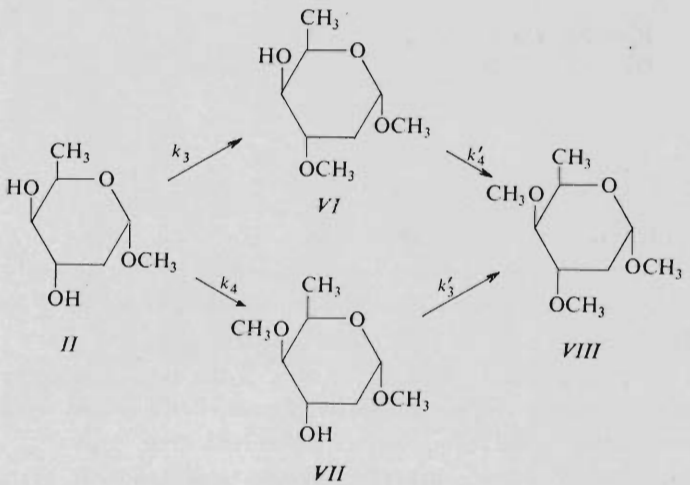
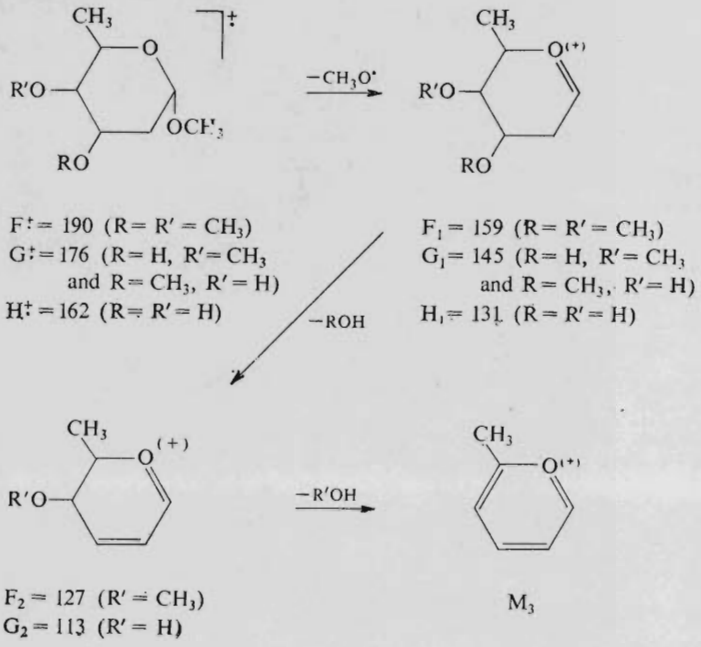


SCHEME 1



SCHEME 2

In the interpretation of the mass spectra the presence of fragments is most important, the formation of which can be explained[18] on the basis of Scheme 3. In the case of dihydroxy derivatives *I* and *II* the fragments $H_1 = 131m/z$ and $G_2 = 113m/z$ were found in the mass spectrum, while for dimethyl ether *V* the observed main lines corresponded to the molecular ion $F^{+\cdot} = 190m/z$ and the fragments $F_1 = 159m/z$ and $F_2 = 127m/z$ and analogously, for dimethyl ether *VIII* the fragments $F_1 = 159m/z$ and $F_2 = 127m/z$. For monomethyl ethers *III* and *IV*, as well as *VI* and



SCHEME 3

VII the fragments $G_1 = 145m/z$ were found in the mass spectra of all of them. The differentiation of 3-O-methyl derivatives *III* and *VI* from 4-methyl ethers *IV* and *VII* was carried out on the basis of the presence or the absence of the fragments F_2 and G_2. In the mass spectrum of 3-O-methyl derivatives *III* and *VI* the main line observed corresponded to fragment $G_2 = 113m/z$, while the presence of fragment $F_2 = 127m/z$ could not be observed at all. In contrast to this, in the case of 4-methyl ethers *IV* and *VII* the main line observed in the mass spectrum corresponded to the fragment $F_2 = 127m/z$ while the line at $113m/z$ was completely lacking.

For the preparation of monomethyl ethers *III* and *IV* as standards, partial methylation of diol *I* was made use of. The isolation of individual components was carried out by preparative gas chromatography. Dimethyl ether *V* was also obtained by total methylation of *I* with methyl iodide and sodium hydride in benzene. The structure of monomethyl ethers *III* and *IV* was demonstrated on the basis of ^{1}H-NMR spectra (Table I). In the case of di-O-methyl derivative *V* three singlets were found in its ^{1}H-NMR spectrum, corresponding to nine protons of the methoxyl groups. In the case of protons on the third (H−3) and the fourth (H−4) carbon atom a change of the chemical shift to a higher magnetic field took place simultaneously in comparison with the chemical shifts of these protons in dihydroxy derivative *I*. In the case of monomethyl ethers *III* and *IV* two three-proton singlets of methoxyl groups and

a single-proton signal of the hydroxyl group were found in both cases. The differentiation of compounds *III* and *IV* was carried out on the basis of the differences in chemical shifts of protons H−3 and H−4. In 4-O-methyl derivative *IV* the chemical shift H−3 had the same chemical shift as H−3 in diol *I*. However, the chemical shift of H−4 displayed a change in δ towards a higher magnetic field in comparison with substance *I*. The observed δ-value corresponds to the chemical shift of H−4 in dimethyl ether *V*. Contrary to this, in the case of 3-O-methyl derivative *III* a change of the chemical shift of H−3 from δ = 3·99 for dihydroxy derivative *I* to the value δ = 3·62 took place. This value δ also corresponds to the chemical shift of H−3 in dimethyl ether *V* (δ = 3·63).

Quantitative analyses of the reaction mixtures from partial methylation of diol *I* were carried out by gas chromatography. The results of the analyses were evaluated

TABLE I

^{1}H-NMR spectra of the compounds studied

Parameter	*I*[a]	*III*[b]	*IV*[c]	*V*[d]	*II*[e]	*II*[e,f]
			Chemical shifts (δ, ppm)			
H_1	m 4·77	m 4·84	m 4·78	m 4·83	q 4·77	q 4·84
H'_2	m 1·82	m 1·77	m 1·57	m 1·77	dt 2·14	dt 2·18
H_2	m 1·82	2·14	2·09	2·15	m 1·79	o 1·76
H_3	m 3·99	m 3·62	m 4·00	m 3·63	m 3·86	m 3·77
H_4	d 3·62	d 3·79	d 3·24	m 3·21—3·45	q 3·46	q 3·42
H_5	q 3·89	m 3·85	q 3·87	q 3·80	o 4·22	o 4·23
H_6	d 1·27	d 1·31	d 1·31	d 1·28	d 1·27	d 1·26
	a	b	c	d	e	e
			Coupling constants (Hz)			
1,2′	2·5	2·5	2·5	2·5	3·4	3·4
1,2	1·5	2·0	2·0	2·0	1·5	2·0
2′,3	10·0	10·0	10·0	10·0	3·4	3·4
2,3	7·0	7·0	6·5	7·0	2·5	2·4
3,4	3·0	3·0	3·0	3·0	3·5	3·4
4·5	<1·5	<2·0	<2·0	<2·0	≦2·0	≦1·5
5,6	7·0	6·8	6·8	6·8	6·8	6·8
2,2′	—	—	—	—	15·0	15·1

[a] s 3·11 OH, s 3·33 OCH_3; [b] s 2·02 OH, s 3·34 OCH_3, s 3·40 OCH_3; [c] m 2·12 OH, s 3·32 OCH_3, s 3·63 OCH_3; [d] s 3·33 OCH_3, s 3·40 OCH_3, s 3·60 OCH_3; [e] s 3·37 OCH_3; [f] measured in CD_3CN.

graphically as dependence of the content of monomethyl ethers *III* and *IV* on the amount of the starting diol *I* (Fig. 1*a*). This graph alone shows that the reactivity of the hydroxyl group on $C_{(3)}$ is higher in dihydroxy derivative *I* than the rate of methylation of the hydroxyl group in position 4. In this context the finding is interesting that at a higher degree of conversion of diol *I* the 3-O-methyl derivative *III* disappears from the reaction mixture at a much higher rate than the 4-methyl ether *IV*. This fact indicates a higher reactivity of the hydroxyl group on $C_{(4)}$ in monomethyl ether *III* in comparison with the reactivity of the OH group on $C_{(3)}$ in 4-O-methyl derivative *IV*.

For the determination of quantitative relationhips the relative rate constants in the Scheme 1, *i.e.* $k_3/k_4 = 2{\cdot}11$, $k'_3/k'_4 = 0{\cdot}11$, $k_3/k'_3 = 30{\cdot}59$ and $k_4/k'_4 = 1{\cdot}60$ were calculated in a modified way[19], which permit the following statements: When glycoside *I* is methylated 3-O-methyl derivative *III* is formed at approximately twice the formation rate of 4-methyl ether *IV*. In the subsequent step 3-O-methyl derivative *III* reacts almost ten times faster than 4-O-methyl derivative *IV*. The hydroxyl group on the third carbon atom reacts after methylation of the vicinal hydroxyl on $C_{(4)}$ about thirty times more slowly, while the hydroxyl group on $C_{(4)}$ is substantially less affected by substitution on $C_{(3)}$—OH, *i.e.* after methylation of $C_{(3)}$—OH the rate of methylation of the hydroxyl on $C_{(4)}$ is decreased about 1·5 times.

In the case of partial methylation of glycoside *II* the results of the analyses were evaluated graphically as a dependence of the constant of monomethyl ethers *VI* and

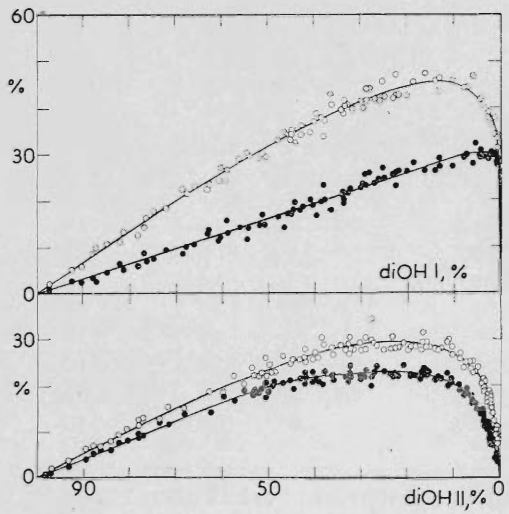


FIG. 1

a Regression curves of partial methylation of methyl 2,6-dideoxy-α-D-*lyxo*-hexopyranoside (*I*). ○ 3-O-Me *III*, ● 4-O-Me *IV*. *b* Regression curves of partial methylation of methyl 2,6-dideoxy-α-D-*xylo*-hexopyranoside (*II*). ○ 3-O-Me *VI*, ● 4-O-Me *VII*

VII on the amount of the unreacted starting compound, *II* (Fig. 1*b*). Analogously[19], the values of the relative rate constants $k_3/k_4 = 1{\cdot}27$, $k'_3/k'_4 = 1{\cdot}12$, $k_3/k'_3 = 1{\cdot}16$ and $k_4/k'_4 = 1{\cdot}03$ in Scheme 2 were calculated. On the basis of these values it can be concluded that in partial methylation of compound *II* the OH group on $C_{(3)}$ reacts somewhat more rapidly than the OH group on $C_{(4)}$ ($k_3/k_4 = 1{\cdot}27$). In the methylation to the second degree the preference of the hydroxyl group on $C_{(3)}$ in 4-O-methyl derivative *VII* is still less distinct ($k'_3/k'_4 = 1{\cdot}12$) in comparison with the methylation rate of $C_{(4)}$—OH in 3-methyl ether *VI*. When the reactivities of the hydroxyl group on $C_{(3)}$ in the unsubstituted and the monosubstituted derivatives are compared, it may be observed that the reactivity of 4-O-methyl derivative *VII* is decreased negligibly in comparison with diol *II* ($k_3/k'_3 = 1{\cdot}16$). The substitution of the hydroxyl group on $C_{(3)}$ has almost no effect on the reactivity of the OH group on $C_{(4)}$ either ($k_4/k'_4 = 1{\cdot}03$).

In the discussion of the reactivity of the hydroxyl groups of the compounds studied we also considered, similarly as in the preceding studies[5–8], in addition to steric and polar effects the possibilities of the methylation rate being affected by the formation of intramolecular hydrogen bonds. Therefore infrared spectra were measured in the 3 000 – 3 800 cm^{-1} region of dihydroxy derivatives and corresponding monomethyl ethers isolated. In the case of 4-O-methyl derivative *IV* the absorption band $\nu(OH) = 3\,580\ cm^{-1}$ was found, corresponding to the intramolecular hydrogen bond $O_{(3)}$=H...$O_{(4)}$. In 3-O-methyl derivative *III* the observed absorption band $\nu(OH) = 3\,585\ cm^{-1}$ indicates the formation of the intramolecular hydrogen bond $O_{(4)}$—H...$O_{(3)}$. For the second theoretically possible hydrogen bond $O_{(4)}$—H...$O_{(5)}$ it may be expected with the greatest probability that absorption would occur at 3 590 – 3 600 cm^{-1}. For the analogous hydrogen bond in 3-hydroxytetrahydropyran the values $\nu(OH) = 3\,590$ and $3\,604\ cm^{-1}$ were found[20,21], and similarly the value $\nu(OH) = 3\,595\ cm^{-1}$ was observed in ethyl 2,3,6-trideoxy-α-D-*threo*-hexopyranoside[22]. In view of the stronger hydrogen bonds with a vicinal *cis*-diol arrangement* it may be assumed that the formation of the hydrogen bond $O_{(4)}$—H...$O_{(3)}$ will be preferred in compound *III*. In the IR spectrum of diol *I* an intensive absorption band $\nu(OH) = 3\,576\ cm^{-1}$ was observed. The existence of this band is explicable by the formation of a „double bridge"[27] $O_{(3)}$—H...$O_{(4)}$—H...$O_{(5)}$.

In the case of glycoside *II* the minor absorption band in the IR spectrum, $\nu(OH) = 3\,635\ cm^{-1}$, corresponding to the free hydroxyl group was accompanied by two absorption bands, $\nu(OH) = 3\,598\ cm^{-1}$ and $\nu(OH) = 3\,550\ cm^{-1}$. The last mentioned band with the lowest wave-number value corresponds to a strong intramolecular

* In *cis*-2-methoxy-3-hydroxytetrahydropyran the value[21] $\nu(OH) = 3\,588\ cm^{-1}$ was measured and similarly $\nu(OH) = 3\,586\ cm^{-1}$ in *cis*-1-methoxy-2-hydroxycyclohexane[23], $\nu(OH) = 3\,583\ cm^{-1}$ in 1,5-anhydro-2-deoxy-D-erythropentitol[24], and $\nu(OH) = 3\,587\ cm^{-1}$ and $3\,585\ cm^{-1}$ in *cis*-1,2-cyclohexanediol[25,26] itself.

hydrogen bond, $O_{(3)}$—H...$O_{(1)}$, with a 1,3-diaxial arrangement, ** similarly as in methyl 2,6-dideoxy-4-O-methyl-α-D-*ribo*-hexopyranoside[6] and methyl 2,4,6-trideoxy-α-D-erythro-hexopyranoside[32]. Analogously, for *cis*-cyclohexane-1,3-diol the value $\nu(OH) = 3\,544\ cm^{-1}$ was measured[25] for the bonded OH group, and the value $\nu(OH) = 3\,548\ cm^{-1}$ for this group in 5-phenylcyclohexane-1,3-diol[33]. The existence of the absorption band $\nu(OH) = 3\,598\ cm^{-1}$ is explicable by a slightly weaker hydrogen bond $O_{(4)}$—H...$O_{(5)}$. The value of the observed vibration is in agreement with the values obtained in compounds with a similar steric arrangement[20-22]. On the basis of the results of the IR spectra the experimental measurements may be explained. 1. In the case of dihydroxy derivative *II* with two axial OH groups a somewhat higher reactivity of the hydroxyl group on $C_{(4)}$ may be expected on the basis of the inductive effect of the oxygen atom of the pyranoside ring. However, this effect is most probably compensated by the formation of a very strong intramolecular hydrogen bond $O_{(3)}$—H...$O_{(1)}$ (in comparison with the hydrogen bond $O_{(4)}$—H...$O_{(5)}$) to such an extent that the nucleophilicity of the oxygen atom on $C_{(3)}$, and hence the reactivity of this hydroxyl group as well, is higher than of the OH group on $C_{(4)}$. In view of the fact that in the case of glucoside *II* a *trans*-diaxial arrangement of the OH groups is involved, it may be assumed that the substitution of the hydroxyl group hydrogen by a methyl group will have small effect on the formation of the intramolecular hydrogen bonds in monomethyl ethers *VI* and *VII*. The measured values of the relative rate constants for methylation of the same hydroxyl group on the unsubstituted and monosubstituted derivatives indicated the correctness of this assumption, since these values were practically equal to one for both OH groups. Hence, the higher reactivity of the hydroxyl group on $C_{(3)}$ in 4-O-methyl derivative *VII* in comparison with the OH group on $C_{(4)}$ in 3-methyl ether *VI* may be explained in an analogous manner as in the cases of diol *II*.

2. In the case of compound *I* with a *lyxo* configuration, *i.e.* with a *cis*-diol arrangement the equatorial hydroxyl group on the third carbon atom reacts preferentially in comparison with the axial OH group on $C_{(4)}$. The higher reactivity of the equatorial OH group on $C_{(3)}$, as opposed to the axial OH group on $C_{(4)}$, was also described for compound *I* in the case[11] of acylation with acetic anhydride in pyridine at $-10°C$, and similarly also in the case of the corresponding antipode during the benzoylation with benzoyl chloride[34]. However, in the benzoylation with N-benzoylimidazole

** Of all methyl 2,6-dideoxy-α-D-hexopyranosides the greatest doubt may arise about the existence of the $^4C_1$ (D) conformation just in the case of compound *II* with three axial substituents on the basis of Reeves factors of instability[28,29]. Therefore the $^4C_1$ (D) conformation of this compound was proved both by means of the ^{1}H-NMR spectra ($J_{1,2a} = 3{\cdot}4$, $J_{1,2e} \leqq 2{\cdot}0$, see Table I) and by means of the ^{13}C-NMR spectra. In the ^{13}C-NMR spectrum of this compound the presence of an axial methoxyl group was proved[30,31] on the first carbon atom on the basis of the observed coupling constant $^1J(C_{(1)}—H) = 170{\cdot}3$ Hz, which in the case of α-anomer means a $^4C_1$ (D) conformation.

in chloroform almost the same amount[34] of both monobenzoyl derivatives was formed. The difference observed in the reactivity of the hydroxyl groups is explained by the authors on the basis of the difference in conformational equilibrium under the conditions used. This explanation, however, is improbable, taking into consideration a later study of benzoylation with N-benzoylimidazole[35] in which the migration of the benzoyl group, leading to the predominant formation of the thermodynamicall more stable isomer, was proved. In addition to a more favourable steric position the higher reactivity of the equatorial OH group on $C_{(3)}$ is probably also affected by the formation of the intramolecular hydrogen bond $O_{(3)}$—H...$O_{(5)}$. In contrast to diol *I* a higher reactivity of the hydroxyl group on $C_{(4)}$ in 3-O-methyl derivative *III* was also observed in the case of the methylation of monomethyl ether *III* and *IV*. In actual fact this value of the relative rate constant of methylation to the second degree is probably due to the anomalously low reactivity of the hydroxyl group on $C_{(3)}$ in 4-O-methyl derivative *IV* as may be deduced from the comparison with the rate of methylation of this OH group in diol *I*.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. The optical rotation values were measured on a photoelectric polarimeter Opton at 20°C. The solvents were evaporated on a rotatory evaporator in a water pump vacuum at 40°C. The infrared spectra were measured in tetrachloromethane on a Perkin–Elmer 325 instrument in 20 mm quartz cells (slit width 1·2 cm^{-1} at 3 400 cm^{-1}). The mass spectra were measured on an LKB 9000 spectrometer. The ^{1}H-NMR spectra were measured in deuteriochloroform (deuterioacetonitrile) on a Varian XL-100-15 instrument, using tetramethylsilane as internal standard. The chemical shifts are given in ppm, δ-scale, the coupling constants in Hz. The ^{13}C-NMR spectra were measured in deuterioacetonitrile on a Jeol FX-60 instrument (at a 15·03 MHz frequency), using tetramethylsilane as internal standard. Gas chromatography was carried out on Varian-Aerograph 2 100 in combination with a Hewlett-Packard 3 380 A integrator, using flame-ionization detector and helium as carrier gas. Preparative gas chromatography was carried out on a Chrom 3 apparatus (Laboratory apparatus, Prague) using hydrogen as carrier gas, in combination with a catharometer for detection. For quantitative analysis of the reaction mixture after partial methylation of diol *I* the content of individual components, *I*, *III*, *IV*, and *V*, was read from the integration records of gas chromatography and it was calculated by means of relative responses of the detector. The responses were determined on the basis of analyses of mixtures of known composition which were prepared from standards. In the case of methyl ethers of compound *II* an effective separation could not be achieved by preparative gas chromatography and therefore the results of the analyses were evaluated without the relative responses of the detector. In view of the small differences in retention times and the ensuing comparable residual absorption on the stationary phase of the column it may be assumed that the error of the determination will not be large. Methyl 2,6-dideoxy-α-D-hexopyranosides *I* and *II* were synthetized using the procedure described in our preceding paper[9].

Partial Methylation of Compound *I*

Powdered sodium hydroxide (in a molar ratio of 0·2—1·8 to the diol *I*) was added to a stirred solution of 200 mg (1·23 mmol) of compound *I* in 50 ml of acetonitrile and 1 ml of methyl iodide and the mixture was stirred at 20°C. The mixture was analysed by means of gas chromatography on a 1 800 × 2 mm column packed with 5% Versamide 900 on Chromosorb T, at 170°C and 20 ml/min flow-rate of helium; retention times: *V* 102 s, *III* 182 s, *IV* 238 s and *I* 661 s. The reaction mixtures of individual kinetic measurements were evaporated, combined and redissolved in chloroform. The solution was washed with water, dried over magnesium sulfate, filtered and evaporated. The components were separated by preparative gas chromatography under identical conditions on a 500 × 1 cm column, using hydrogen as carrier gas.

Methyl 2,6-*dideoxy*-3-O-*methyl*-α-D-lyxo-*hexopyranoside* (III) was obtained as a syrup with $[\alpha]_D^{20} = 173°$ (*c* 0·4; chloroform). Mass spectrometry *m/z* (%): 145 (21), 118 (45), 113 (32), 101 (19), 87 (26), 85 (17), 75 (87), 74 (90), 73 (13), 71 (48), 69 (23), 61 (15), 59 (100), 58 (71), 57 (42), 55 (22). ^{1}H-NMR spectrum see Table I. Literature[10] gives a syrup with $[\alpha]_D^{20}$ 81·4 ± 2° (*c* 1·6; acetone).

Methyl 2,6-*dideoxy*-4-O-*methyl*-α-D-*lyxo*-*hexopyranoside* (IV), m.p. 95—96°C, $[\alpha]_D^{20} = 168°$ (*c* 0·6; chloroform). Mass spectrometry, *m/z* (%): 145 (12), 132 (13), 127 (42), 118 (61), 88 (12), 87 (18), 75 (35), 74 (100), 73 (58), 72 (74), 71 (48), 69 (14), 61 (26), 59 (100), 58 (32), 57 (39), 55 (18). ^{1}H-NMR spectrum see Table I. Literature[12] gives m.p. 98°C, $[\alpha]_D^{26} = 150°$ (*c* 0·4; ethanol), lit[13] m.p. 92°C, $[\alpha]_D^{22} = 122°$ (*c* 1; ethanol), lit.[11] m.p. 95—96°C, $[\alpha]_D^{22}$ 164° (*c* 1; chloroform), lit[14] m.p. 96—97°C, $[\alpha]_D^{20}$ 174° (*c* 1·2; ethanol), lit.[15] m.p. 97—98°C, $[\alpha]_D^{22}$ 160° (*c* 0·5; ethanol) and lit.[16] m.p. 92°C, $[\alpha]_D^{22}$ 122° (*c* 1; ethanol). Mass spectrometry of dihydroxy derivative *I*, *m/z* (%): 131 (29), 118 (12), 113 (29), 104 (74), 87 (15), 85 (18), 74 (17), 73 (23), 71 (29), 69 (15), 67 (11), 61 (39), 60 (93), 59 (100), 58 (90), 57 (61), 56 (13), 55 (32).

Methyl 2,6-Dideoxy-3,4-di-O-methyl-α-D-*lyxo*-hexopyranoside (*V*)

Sodium hydride (about 100 mg) was added to a solution of 162 mg (1 mmol) of diol *I* in 50 ml of benzene, the mixture was stirred for 1 h and 1·5 ml of methyl iodide was then added to it. When all compound *I* and the corresponding monomethyl ethers *III* and *IV* had reacted (GLC) methanol was added. The solvents were evaporated and the residue extracted with chloroform. The combined extracts were washed with water, dried over magnesium sulfate and filtered. After evaporation of chloroform 165 mg (86·8%) of syrupy *V* were obtained, $[\alpha]_D^{20} = 149°$ (*c* 0·7; ethanol). Mass spectrometry, *m/z* (%): 190 (1), 159 (6), 132 (10), 127 (35), 101 (12), 89 (29), 88 (100), 87 (15), 75 (87), 73 (81), 72 (61), 71 (39), 67 (14), 59 (42), 58 (13), 57 (23), 55 (15). ^{1}H-NMR spectrum, see Table I. Literature[17] for compound *V* gives $[\alpha]_D^{23}$ 115° (*c* 1; ethanol), or $[\alpha]_D^{23}$ 133° (*c* 0·6; ethanol).

Partial Methylation of Compound *II*

Powdered sodium hydroxide was added to a stirred solution of 40 mg (0·25 mmol) of compound *II* in 10 ml of acetonitrile and 0·2 ml methyl iodide and the mixture was stirred at 20°C. Analyses were carried out on a column identical to that used in the case of partial methylation of compound *I*, at 150—170°C, using a temperature gradient of 1°C/min and a 30 ml/min flow-rate of helium. Under these conditions the following retention times were measured for individual components: *VIII* 214 s, *VII* 268 s, *VI* 467 s, *II* 858 s. The reaction mixtures of individual kinetic measurements were worked up in the same manner as in the case of partial

methylation of compound *I*. However, in preparative gas chromatography of compounds *II*, *VI—VIII* the required resolution of individual components was not achieved and therefore the structure of compounds *VI—VIII* was proved on the basis of mass spectra only: *VI*, *m/z* (%): 145 (11), 144 (5), 118 (14), 113 (13), 101 (8), 87 (13), 85 (7), 75 (52), 74 (100), 73 (6), 71 (22), 69 (6), 61 (8), 59 (81), 58 (39), 57 (20), 55 (11); *VII*, *m/z* (%): 145 (6), 132 (3), 127 (3), 118 (13), 88 (19), 87 (4), 75 (10), 74 (100), 73 (19), 72 (39), 71 (13), 69 (3), 61 (6), 59 (39), 58 (5), 57 (10), 55 (3); *VIII*, *m/z* (%): 159 (8), 132 (3), 127 (8), 119 (4), 115 (4), 101 (7), 99 (5), 89 (14), 88 (100), 87 (6), 85 (7), 75 (52), 74 (3), 73 (38), 72 (32), 71 (18), 69 (3), 67 (7), 59 (30), 58 (5), 57 (10), 55 (6). *II*, *m/z* (%): 131 (13), 118 (6), 113 (8), 105 (5), 104 (30), 87 (5), 85 (7), 73 (12), 71 (12), 69 (5), 60 (97), 59 (100), 58 (78), 57 (30), 55 (8). ^{1}H-NMR spectrum see Table I and lit.[9], ^{13}C-NMR spectrum (CD_3CN): 14·9 (q, C—6); 29·4 (t, C—2); 53·4 (q, OCH_3); 60·8 (d, C—5); 67·1 (d, C—4); 69·7 (d, C—3); 97·9 (d, $^1J_{C_1-H} = 170{\cdot}3$, C—1).

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