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A CONFORMATIONAL STUDY OF DIOXOLANE-TYPE ACETALS OF SOME CARBOHYDRATE DERIVATIVES BY N.M.R. SPECTROSCOPY

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ABSTRACT

The conformation of the methylene, isopropylidene, benzylidene, and 1-phenylethylidene acetals of some rhamnopyranoside and arabinopyranoside derivatives has been investigated by n.m.r. spectroscopy. In each series, the pyranoside ring adopts a distorted chair conformation. For the benzylidene acetals, the pyranoside ring is more distorted in the *endo*-phenyl isomers, and these isomers are compared to the methylene and isopropylidene acetals. For the 1,3-dioxolane ring, only the coupling constant of the acetal carbon atom with the axial bridgehead proton is measurable; for the benzylidene acetals, it is larger in the *exo*-phenyl isomer. For the other types of acetals, the coupling constant depends on the nature of the *endo* substituent at the acetal carbon atom. If it is bulky, the coupling constant and the conformation of the dioxolane ring are similar to those of the corresponding *endo*-phenyl benzylidene derivative.

INTRODUCTION

Acetal protecting-groups are important in carbohydrate chemistry in the synthesis of oligosaccharides. Benzylidene acetals can be prepared easily and, on regioselective reductive ring-cleavage, provide benzyl ethers containing a free hydroxyl group, the position of which is dependent on the configuration at the parent acetal carbon atom[1–5]. This reaction offers a route to partially protected monosaccharide derivatives of value in the synthesis of oligosaccharides[6–9].

On searching for the reasons for the regioselectivity of the reductive ring-opening of benzylidene acetals, electronic factors were excluded since the reaction of the *exo*- and *endo*-phenyl isomers of 1,2-*O*-benzylidene-α-D-glucopyranose followed the rule recognised earlier, although the electron density of the two oxygen atoms involved in the dioxolane ring was not equivalent[10]. The reductive ring-cleavage is also regioselective in ethylidene and isopropylidene acetals[11] and it is possible that the decisive factor is steric.

Prior to investigating possible steric factors, a knowledge of the stereochemistry and conformation of individual acetal derivatives is necessary. The conformation of the pyranoid ring can be studied by using the Karplus expression[12] for

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the measured $^3J_{H,H}$ values; for 1,3-dioxolane rings, the $^3J_{C,H}$ values for the acetal carbon atom and bridgehead protons may give information about the conformation since they are also dependent on the dihedral angle[13]. The conformation in the crystal may not be the same as that in solution, but a comparison of the results for X-ray and n.m.r. methods may give valuable information about conformation.

We now report on conformational studies of a series of acetal derivatives using ^{1}H- and ^{13}C-n.m.r. spectroscopy.

RESULTS AND DISCUSSION

Dioxolane-type cyclic acetals *cis*-fused to pyranoside rings deform the initial, usually chair, conformation[14–16] of the latter ring. This can be demonstrated, for example, by the $^3J_{H,H}$ values[17] for methyl 2,3-*O*-benzylidene-α-L-rhamnopyranoside and methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside derivatives (see Tables I and II), which suggest that the pyranoside ring of each *endo*-phenyl isomer is even more distorted than that of the corresponding *exo*-phenyl isomer. The ^3J values for the bridgehead protons are always larger for the *endo* isomers than for the *exo* compounds, *i.e.*, the dihedral angle of these protons decreases from 60° in the chair conformation to ~30° and this angle is smaller for the *endo* isomers. Also, a bulky substituent vicinal to the benzylidene ring decreases the deviation from the chair conformation, and thus the values of the coupling constants are closer to those for an ideal chair conformation.

The distortion of the pyranoid ring, however, cannot be unequivocally correlated with the conformation of the dioxolane ring, and therefore the couplings of the acetal carbon atom with the bridgehead protons were measured for several derivatives. For the *cis*-fused benzylidene acetals, it was recognised that the acetal carbon is coupled only with the *axial* proton. Although the coupling is different for

TABLE I

^{1}H-N.M.R. DATA FOR SOME 2,3-ACETAL DERIVATIVES OF METHYL α-L-RHAMNOPYRANOSIDE

Compound	*Chemical shifts (p.p.m.)*						*Coupling constants (Hz)*					*Ref*
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	
1	4.90	4.08	4.38	3.48	3.69	1.31	0.6	5.5	6.6	9.5	6.0	17
2	4.95	4.20	4.23	3.43	7.66	1.25	0.1	6.6	6.5	8.5	6.3	
3	4.95	4.13	4.47	5.01	3.78	1.22	<1.0	5.2	7.7	10.0	6.3	17
4	4.99	4.20	6.34	4.94	3.78	1.18	<1.0	6.1	6.9	10.0	6.3	17
5	4.89	4.11	4.59	3.33	3.74	1.34	<1.0	5.4	6.9	9.7	6.1	17
6	4.98	4.20	4.40	3.24	3.75	1.26	<1.0	6.3	6.6	9.8	6.2	17
7	4.90	3.88	4.33	3.13	3.70	1.28	<1.0	5.7	6.9	9.9	6.1	
8	4.90	4.18	4.18	4.86	3.70	1.17	<1.0	5.4	7.9	10.0	6.3	
9	4.97	4.27	4.19	3.04	3.60	1.12	0.5	5.5	7.5	9.6	6.2	
10	4.91	3.82	4.10	3.53	4.69	1.35	0.5	6.1	6.9	9.0	6.2	
11	4.92	3.82	4.18	4.98	3.71	1.19	<1.0	6.9	7.5	10.0	6.3	

TABLE II

^{1}H-N.M R. DATA FOR SOME 3,4-ACETAL DERIVATIVES OF METHYL AND BENZYL β-L-ARABINOPYRANOSIDE

Compound	*Chemical shifts (p.p.m.)*						*Coupling constants (Hz)*					*Ref.*
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	
12	4.79	3.93	4.42	4.19	3.95	3.95	3.6	7.1	5.5	1.9	1.9	17
13	4.70	3.83	4.32	4.24	3.99	3.99	3.7	5.6	6.2	1.6	1.6	17
14	4.95	5.13	4.65	4.28	4.13	3.91	3.6	8.0	5.5	0.8	2.2	17
15	4.86	4.98	4.46	4.30	4.15	3.95	3.4	7.4	6.1	0.9	2.4	17
16	4.98	3.52	4.54	4.16	4.03	3.86	3.4	7.7	5.5	0.8	2.2	17
17	4.79	3.54	4.39	4.26	4.10	3.94	3.3	6.9	6.1	1.0	1.9	17
18	4.79	3.29	4.20	4.08	4.01	3.89	3.3	7.5	6.2	2.9	1.0	
19	4.85	4.98	4.29	3.90	4.02	3.82	3.4	7.9	5.9	1.0	3.0	
20	4.69	4.52	4.47	4.40	4.07	3.91	2.8	7.7	4.5	1.0	2.6	
21	4.94	3.69	4.68	4.16	3.95	3 95	3.5	7.9	5.6	1.7	1.7	
22	4.84	3.58	4.52	4.25	4.04	4.04	3.4	7.4	6.1	1.8	1.8	
23	4.82	3.50	4.36	4.20	3.96	3.88	3.4	7.6	5.6	2.5	1.6	

TABLE III

$^3J_{C,H}$ HETERONUCLEAR COUPLING CONSTANTS (Hz) OF THE ACETAL CARBON ATOM AND H-3

Methyl 2,3-O-benzylidene-α-L-rhamnopyranoside		
4-*O*-Acetyl *exo*-phenyl	(**3**)	5.9
4-*O*-Acetyl *endo*-phenyl	(**4**)	4.2
4-*O*-Benzyl *exo*-phenyl	(**5**)	6.0
4-*O*-Benzyl *endo*-phenyl	(**6**)	4.2
Benzyl 3,4-O-benzylidene-β-L-arabinopyranoside		
2-*O*-Acetyl *exo*-phenyl	(**24**)	5.2
2-*O*-Acetyl *endo*-phenyl	(**25**)	4.4
2-*O*-Benzyl *exo*-phenyl	(**21**)	5.2
2-*O*-Benzyl *endo*-phenyl	(**22**)	4.4
Non-benzylidene acetals of methyl α-L-rhamnopyranoside		
Methylene	(**7**)	5.6
Isopropylidene	(**8**)	4.3
exo-Phenyl 1-phenylethylidene	(**11**)	4.2
Non-benzylidene acetals of methyl β-L-arabinopyranoside		
endo-Methyl ethylidene	(**18**)	4.2
Isopropylidene	(**23**)	5.2

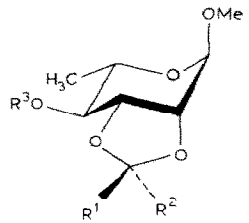
the *exo*- and *endo*-phenyl isomers, it is not influenced by the substituents vicinal to the dioxolane group (Table III).

Examination of molecular models suggested that measurable coupling was to be expected only between one of the bridgehead protons and the acetal carbon atom. The dihedral angle between this carbon and the *axial* proton is 150–170°, whereas for the *equatorial* proton it is in the range 70–90° where the Karplus-type

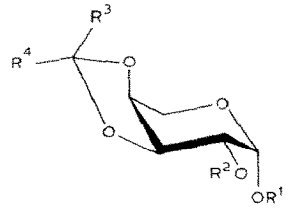
curve has a minimum. As shown by the data in Table III, the $^3J_{C,H}$ values are larger for the *exo*-phenyl isomers, and therefore the C–O–C–H dihedral angle must be greater than in the *endo*-phenyl compound.

Since the above comparison involves individual pairs of *exo*- and *endo*-phenyl isomers, it is reasonable to assume that the different coupling constants reflect different conformations because the pattern of substituents remains constant. Also, in considering the coupling constants involving the bridgehead protons, the changes due to the electronegativity and bond-altering effect of the substituent vicinal to the dioxolane ring were neglected.

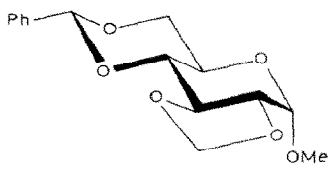
The $^3J_{H,H}$ values of several dioxolane-type cyclic acetals have been compared with the data for some benzylidene acetal analogues. In Tables I and II, the ^{1}H-n.m.r. data for several derivatives of methyl α-L-rhamnopyranoside and methyl β-L-arabinopyranoside, respectively, are summarised.



1 R^1 = Ph, R^2 = R^3 = H
2 R^1 = R^3 = H, R^2 = Ph
3 R^1 = Ph, R^2 = H, R^3 = Ac
4 R^1 = H, R^2 = Ph, R^3 = Ac
5 R^1 = Ph, R^2 = H, R^3 = Bzl
6 R^1 = H, R^2 = Ph, R^3 = Bzl
7 R^1 = R^2 = H, R^3 = Bzl
8 R^1 = R^2 = Me, R^3 = Ac
9 R^1 = Ph, R^2 = Me, R^3 = H
10 R^1 = Me, R^2 = Ph, R^3 = H
11 R^1 = Ph, R^2 = Me, R^3 = Ac



12 R^1 = Me, R^2 = R^3 = H, R^4 = Ph
13 R^1 = Me, R^2 = R^4 = H, R^3 = Ph
14 R^1 = Me, R^2 = Ac, R^3 = H, R^4 = Ph
15 R^1 = Me, R^2 = Ac, R^3 = Ph, R^4 = H
16 R^1 = R^2 = Me, R^3 = H, R^4 = Ph
17 R^1 = R^2 = Me, R^3 = Ph, R^4 = H
18 R^1 = R^2 = R^3 = Me, R^4 = H
19 R^1 = R^3 = Me, R^2 = Ac, R^4 = Ph
20 R^1 = R^4 = Me, R^2 = Ac, R^3 = Ph
21 R^1 = R^2 = Bzl, R^3 = H, R^4 = Ph
22 R^1 = R^2 = Bzl, R^3 = Ph, R^4 = H
23 R^1 = R^2 = Bzl, R^3 = R^4 = Me
24 R^1 = Bzl, R^2 = Ac, R^3 = H, R^4 = Ph
25 R^1 = Bzl, R^2 = Ac, R^3 = Ph, R^4 = H



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In the rhamnoside series, comparison of the data for the methylene derivative **7** with those for the 4-*O*-benzyl-2,3-*O*-benzylidene acetals (**5** and **6**) showed that the value of $J_{2,3}$ (*i.e.*, for the bridgehead protons) is between those for the corresponding *exo*- and *endo*-benzylidene acetals. The value of $J_{2,3}$ for the isopropylidene derivative **8** is closer to that of the *exo*-phenyl benzylidene derivative **3**. All other couplings in both compounds are similar to those of the *exo*-phenyl benzylidene analogues. For the 1-phenylethylidene derivatives[11] **9** and **10**, the couplings are more similar to those for the *exo*- and *endo*-phenyl benzylidene isomers having the appropriately oriented phenyl group. The value of $J_{2,3}$ for the 4-acetate[11] **11** of the 2,3-*O*-*exo*-phenyl 1-phenylethylidene (*S*) acetal is near to that of the corresponding *endo*-phenyl benzylidene acetal; the value of $J_{3,4}$ is similar to that of the *exo*-phenyl benzylidene derivative.

Similar conclusions can be drawn by comparing the data for the arabinoside acetals. The isopropylidene acetal **23** shows couplings similar to those of the *exo*-phenyl benzylidene acetal **21**, whereas the data for the *endo*-methyl ethylidene isomer **18** are similar to those of the *endo*-phenyl benzylidene derivative **17**. The couplings of the 1-phenylethylidene acetals **19** and **20** are closer to those of the corresponding benzylidene compounds **14** and **15**.

Assuming that the substituents at the acetal carbon atom (and also the substituent vicinal to the dioxolane ring) do not significantly affect the couplings between the ring protons, the change of these values must be due mainly to alterations in conformation and it is concluded that systems possessing similar coupling constants represent similar conformational (*exo*- or *endo*-phenyl benzylidene-type) properties.

The couplings of the acetal carbon atom with the *axial* bridgehead proton for non-benzylidene acetals are shown in Table III. From these data, it is seen that, in the rhamnopyranoside series, the methylene acetal **7** and the isopropylidene acetal **8** possess couplings close to those of the *exo*- and *endo*-phenyl benzylidene derivatives, respectively. At the same time, the *exo*-phenyl 1-phenylethylidene derivative **11** has a $^3J_{C,H}$ value which is similar to that of the *endo*-phenyl benzylidene compound **4**.

In the arabinopyranoside series, the couplings for the *endo*-methyl ethylidene (**18**) and the *endo*-phenyl benzylidene (**22**) derivatives are equivalent, but, in contrast to the rhamnopyranoside series, the isopropylidene derivative (**23**) and the *exo*-phenyl benzylidene acetal (**21**) possess nearly the same heteronuclear coupling.

If it is accepted that the presence of a substituent vicinal to the dioxolane ring does not cause change in the $^3J_{C,H}$ value and that its alteration is due to changes in conformation, the similarity of the heteronuclear couplings means that the conformations of the acetal rings are similar. Thus, in the rhamnoside series, the conformation of the acetal ring of the isopropylidene and *exo*-phenyl 1-phenylethylidene derivatives is of the *endo*-phenyl benzylidene type, whereas it is of the *exo*-phenyl benzylidene type in the methylene acetal. In the arabinopyranoside series, the *endo*-methyl ethylidene compound has the *endo*-type and the isopropylidene de-

rivative the *exo*-type conformation. Thus, it is assumed that, for the *endo*-phenyl benzylidene derivatives, the phenyl group and the *axial* hydrogen (H-4 in the rhamnopyranoside and H-2 in the arabinopyranoside derivatives, respectively) are in close proximity; in order to minimise the interaction, the conformation probably adopted is $^{2}T_{O\text{-}2}$ in the rhamnopyranoside series and $^{4}T_{O\text{-}4}$ in the arabinopyranoside series. For the *exo*-phenyl benzylidene isomers, the most probable conformation of the dioxolane ring is $^{O\text{-}3}T_{3}$. The experimental data concerning the regioselectivity of the reductive ring-cleavage reaction accord well with the above conformational properties. When the heteronuclear couplings suggest the *endo*-type conformation of the dioxolane ring, the formation of the product with *axial* ether and *equatorial* hydroxyl groups is usually more favoured, whereas the acetal with *exo*-type couplings usually gives a higher proportion of the product with the ether group *equatorial*[11].

The acetal carbon atom of cyclic dioxolane-type acetals shows heteronuclear coupling with the bridgehead protons only in the *cis*-fused series. In the *trans*-fused series, no such heteronuclear coupling can be detected. For the methyl 2,3-*O*-methyleneglucoside[11,18,19], besides the $^{2}J_{C,H}$ coupling (t, J 170 Hz), no additional coupling can be detected.

The structure of the *exo*-phenyl isomer of methyl 4-*O*-acetyl-2,3-*O*-(1-phenylethylidene)-α-L-rhamnopyranoside in the crystalline state is known from X-ray measurements[20]. The values of dihedral angles thus determined and the corresponding coupling constants for H-2,3 and the acetal carbon atom for the compound in solution are as follows: $J_{2,3}$ 6 Hz ($\varphi_{2,3}$ 31°), $J_{2,C}$ 0 Hz ($\varphi_{2,C}$ 79°), and $J_{3,C}$ 4.2 Hz ($\varphi_{3,C}$ 149°). Since the dihedral angle between the acetal carbon atom and the equatorial proton (H-2) is 79°, no heteronuclear coupling is to be expected for this proton. It should be emphasised that the coupling constants and dihedral angles relate to the solution and crystalline state, respectively.

The ^{13}C-n.m.r. data of arabinopyranoside benzylidene acetals are given in Table IV, which shows that the chemical shift of the signal for C-3 of the *endo*-

TABLE IV

^{13}C-N M R DATA[a] FOR SOME 3,4-ACETAL DERIVATIVES OF METHYL AND BENZYL β-L-ARABINOPYRANOSIDE

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-ac*	*Other signals*
18	97.7	80.5	74.9	75.4	58 5	101.8	21.0, CH-CH_3; 58.5, 55.5, 2 OCH_3
19	97.2	72.9	73.2	73 6	58.4	109.4	29.4, CH_3-C-Ph; 55.6, OCH_3; 21.1, $COCH_3$
20	96.9	73.4	71.0	74.0	58.3	109.3	28.4, CH_3-C-Ph; 55.3, OCH_3; 20.6, $COCH_3$
21	96.0	74.2	76.8	73.6	59.0	102.7	72.3, 69.4, 2 CH_2-Ph
22	95.9	77.3	75 5	76.1	59 0	103.9	72.1, 69.4, 2 CH_2-Ph
23	96 2	77.0	75.6	73.6	59.2	108 8	28.2, 26.3, $C(CH_3)_2$; 72.2, 69.4, 2 CH_2-Ph
24	95 2	69.5	74 2	73.4	58.8	102.8	69.7, CH_2-Ph
25	95 2	72 8	73.0	75.8	58.9	104.4	69.8, CH_2-Ph

[a]Chemical shifts in p.p.m

phenyl isomer is decreased by 1–1.5 p.p.m. as compared to that of the *exo*-phenyl isomer, whereas the shift of the signal for C-4 is increased by 2–2.5 p.p.m. Similar changes in chemical shifts have been observed for the benzylidene acetals of rhamnosides[6], where the shift of the C-3 signal for the *endo*-phenyl isomer is lower by 1.2–2.1 p.p.m. than for the *exo*-phenyl isomer, whereas that of the signal of C-2 for the latter is higher by 2.5–3 p.p.m. than for the *endo*-phenyl isomer. Thus, the chemical shift of the signal of the carbon atom bearing the *axial* oxygen is higher by 2–3 p.p.m. and the shift of the signal of those having the *equatorial* substituent is lower by 1–2 p.p.m. in the *endo*-phenyl benzylidene acetals as compared to the respective *exo*-phenyl isomers. Similar effects have been observed also for benzyl and methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranosides[6]. Corresponding, but smaller, differences in chemical shifts have been detected for the *exo*- and *endo*-phenyl isomers of 1-phenylethylidene acetals (see Table IV). These data may be important in assigning the configuration at an acetal carbon atom. Whereas the difference in the shift of the signal of the acetal carbon is usually small (0.1–0.3 p.p.m.) and, in several instances, the difference in the chemical shifts of the signals of the anomeric carbons is insignificant, the chemical shift of the bridgehead carbon atom of the dioxolane ring changes by 0.5–2 p.p.m. in the examples studied in comparison with the data for the *exo*- and *endo*-phenyl 1-phenylethylidene derivatives.

EXPERIMENTAL

N.m.r. measurements were carried out with a Bruker WP 200 SY spectrometer, using the pulse technique. ^{1}H-N.m.r. spectra were recorded for solutions (10–20 mg/mL) in $CDCl_3$ (internal Me_4Si; pulse length, 3 μs; number of scans, 16–32; digital resolution after Fourier transformation, 0.125 Hz/point) and were assigned by first-order analysis. The ^{13}C-n.m.r. spectra were assigned by using heterocorrelated 2D experiments based on proton-assignments[21] in which only the range of the skeleton protons and carbon atoms was applied as the spectral width. The measurements were performed with 512 or 1024 scans, and they took 45–90 min together with the Fourier transformation and plot.

The couplings of the acetal carbon atoms with the bridgehead protons were measured with a spectral width of 400–800 Hz and, for the elimination of the undesired couplings, the aromatic or methyl protons were saturated with 0.4–0.8 mW intensity. The resulting spectra contained only the signals of the acetal carbon atoms, with digital resolution of 0.1 Hz/point after Fourier transformation. The off-resonance effect of this decoupling on the actual coupling constant was <0.1 Hz. The measurements necessitated 10,000–80,000 scans. When the acetal carbon atom carried a proton, relaxation was forced in the intervals of the pulses with the gated-decoupling technique and the pulse length was 8–12 μs. When the acetal carbon atom did not carry a proton, a pulse length of 3 μs was applied without relaxation delay and the measurements took 8–12 h.

REFERENCES

1 A LIPTAK, *Tetrahedron Lett.*, (1976) 3551–3554.
2 A. LIPTÁK, P. FUGEDI, AND P. NANÁSI, *Carbohydr. Res.*, 51 (1976) c19–c21
3 A. LIPTÁK, Á. BOBAK, AND P. NÁNÁSI, *Acta Chim. Acad. Sci. Hung*, 94 (1977) 291–296.
4 A. LIPTÁK, I. CZÉGÉNY, J. HARANGI, AND P NANASI, *Carbohydr Res.*, 73 (1979) 327–331.
5 A LIPTAK, *Carbohydr. Res.*, 63 (1978) 69–75
6 A. LIPTAK, P. FUGEDI, P. NÁNÁSI, AND A. NESZMÉLYI, *Tetrahedron*, 35 (1979) 1111–1119.
7 A. LIPTAK, P. NANÁSI, A. NESZMÉLYI, AND H. WAGNER, *Tetrahedron*, 36 (1980) 1261–1268.
8 A. LIPTÁK, Z. SZURMAI, P. NÁNASI, AND A NESZMÉLYI, *Carbohydr. Res.*, 99 (1982) 13–21.
9 A. LIPTAK, J. IMRE, AND P. NÁNASI, *Carbohydr. Res.*, 114 (1983) 35–41
10 A. LIPTAK, J. IMRE, J. HARANGI, AND P. NÁNÁSI, *Carbohydr. Res.*, 116 (1983) 217–225.
11 A LIPTÁK, Z. SZURMAI, V A OLÁH, J. HARANGI, L. SZABO AND P NANASI, *Carbohydr. Res.*, in press.
12 M. KARPLUS, *J Am. Chem Soc.*, 85 (1963) 2870.
13 R U. LEMIEUX, T. L. NAGABHUSHAN, AND B. PAUL, *Can J. Chem*, 50 (1972) 773–776
14 C. PECIAR, J. ALFOLDI, R. PALOVCIK, AND P KOVAC, *Chem. Zvesti*, 27 (1973) 90–93
15 P. M. COLLINS AND N. N. OPARAECHE, *Carbohydr Res.*, 33 (1974) 35–46.
16 K. G. R. PACHLER, E. B. RATHBONE, G. R. WOOLARD, AND M. WOUDENBERG, *Carbohydr Res.*, 79 (1980) 29–37.
17 J. HARANGI, A. LIPTÁK, V. A OLAH, AND P. NANASI, *Carbohydr. Res.*, 98 (1981) 165–171
18 J. S. BRIMACOMBE, A. B. FOSTER, B. D. JONES, AND J. J. WILLARD, *J Chem Soc.*, (1967) 2404–2407.
19 K S. KIM AND W. A. SZAREK, *Synthesis*, (1978) 48–50
20 H. LOTTER AND A. LIPTAK, *Z. Naturforsch., Teil B*, 36 (1981) 997–999
21 A BAX, *J. Magn Reson.*, 53 (1983) 517–520.