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Preliminary communication

^{13}C-N.m.r. relaxation times and chemical shifts of the *exo* and *endo* isomers of dioxolane-type benzylidene acetals of carbohydrates determination of the absolute configuration

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^{13}C-N.m.r. data published to date[1—3] on the benzylidene acetals of carbohydrates have concerned 4,6-*O*-benzylidenehexopyranosides and the thermodynamically more-stable isomers. No comparable data are available for isomeric 1,3-dioxolane derivatives formed from pyranoid, vicinal *cis*-diols, the absolute configuration of which can be determined by ^{1}H-n.m.r. spectroscopy provided that both isomers are available[4].

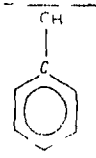
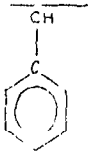
In the stereoselective hydrogenolysis[5,6] of such dioxolane derivatives (with $LiAlH_4$—$AlCl_3$), the reagent attacks[5—8] the axially oriented oxygen atom of the dioxolane ring in the *exo* isomers and yields a product containing an axial hydroxyl group and an equatorial benzyloxy residue. In contrast, the *endo* isomers yield products containing an equatorial hydroxyl group and an axial benzyloxy residue.

We now report ^{13}C-n.m.r. data on isomeric 1,3-dioxolane derivatives in relation to the questions (*a*) are both isomers needed for the determination of the absolute configuration, and (*b*) is the direction of ring cleavage influenced by the motional behaviour of the phenyl groups?

The data for eleven pairs of compounds are listed in Table I and lead to the conclusion that the absolute configuration can be determined on the basis of the following regularities, even if only one of the isomers is available. (*1*) The chemical shift of the acetal carbon (C-7) of the dioxolane ring depends on the steric position of the phenyl group. In the *exo* isomers, C-7 resonates in a range of 102.8—103.4 p.p.m., whereas it is less shielded in the *endo* isomers and its value is between 103.8—104.7 p.p.m., (*2*) *O*-substitution (benzylation, acetylation, or acetalation) of the pyranoside has only a small effect on the chemical shift of C-7, (*3*) the quaternary carbon (member of the aromatic ring) attached to C-7 always resonates at a lower field in the *exo* isomers (139 p.p.m.) than in the *endo* isomers (137.5 p.p.m.), (*4*) the difference ($\Delta\delta$) between the chemical shifts of C-7 and the

TABLE I

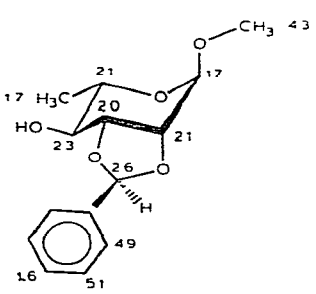
^1H AND ^{13}C NMR DATA [a] FOR THE *exo* AND *endo* ISOMERS OF DIOXOLANE TYPE CARBOHYDRATE BENZYLIDENE ACETALS

Compounds	*exo*						*endo*					
	Dioxane ring		*Dioxolane ring*				*Dioxane ring*		*Dioxolane ring*			
	Ph-C*H*	Ph-C*H*	Ph-C*H*	Ph-C*H*		$\Delta\delta$ [b]	Ph-C*H*	Ph-C*H*	Ph-C*H*	Ph-C*H*		$\Delta\delta$ [b]
Methyl 2,3-*O*-benzylidene-α L-rhamnopyranoside (1)			6 09	102 9	138 8	35 9			5 86	104 1	137 3	33 2
Methyl 4-*O*-benzyl-2,3-*O* benzylidene α L rhamnopyranoside[9] (2)			6 05	102 9	139 0	36 1			5 89	103 9	137 6	33 7
Methyl 4-*O*-acetyl-2,3-*O* benzylidene α L-rhamnopyranoside (3)			6 11	102 8	138 5	35 7			5 80	104 3	136 7	32 4
Benzyl 2,3-*O* benzylidene-α L-rhamnopyranoside (4)			6 13	103 1	138 8	35 7			5 86	104 1	137 2	33 1
Benzyl 4-*O*-benzyl-2,3-*O* benzylidene α L-rhamnopyranoside (5)			6 04	102 9	138 9	36 0			5 87	104 0	137 6	33 6
Benzyl 4-*O*-acetyl-2,3-*O*-benzylidene-α L-rhamnopyranoside (6)			6.19	103 1	138 5	35 4			5 85	104 7	136 7	32 0
Benzyl 3,4-*O*-benzylidene β D-arabinopyranoside (7)			6 18	103 2	139 3	36 1			5 84	103 9	137 4	33 5
Benzyl 2-*O*-benzyl-3,4-*O* benzylidene-β-D-arabinopyranoside (8)			6 02	102 7	138 6	35 9			5 89	103 8	137 6	33 8
Benzyl 2,6-di-*O* benzyl-3,4-*O*-benzylidene β-D-galactopyranoside (9)			5 95	103 4	138 8	35 4			5 85	104 6	137 5	32 9
Benzyl 2,3 4,6-di-*O*-benzylidene-α D-mannopyranoside (10)	5 56	102 0	6 22	102 9	138 9	36 0	5 56	101 6	5 93	103 9	137 2	33 3
Benzyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2,3 4,6-di-*O*-benzylidene-α-D-mannopyranosyl)-α-D-mannopyranoside (11)	5 58 5 60	101 7 102 0	6 25	103 1	139 1	36 0	5 56 5 58	101 8 101 8	6 06	104 1	137 6	33 5

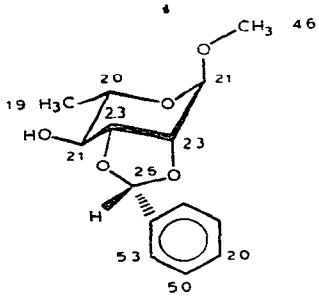
[a] Natural abundance, proton decoupled ^{13}C n m r spectra were obtained with a Varian XL-100-15 F T spectrometer (25 16 MHz), using 8K data points. All spectra were measured at 55° for 25% solutions in CDCl$_3$. [b]

quaternary carbon atom in *exo* isomers is > 35 4 p p m , whereas it is < 33 8 p p m in *endo* isomers, (*5*) the dioxane and the dioxolane rings can be distinguished on the basis of their chemical shifts, the upper limit of the former group usually being 102 p p m

On the other hand, the spin–lattice relaxation times (T_1) of *exo* and *endo* derivatives of **1** (see formulae) indicate that these molecules undergo isotropic tumbling (the dipole–dipole relaxation mechanism being dominant), their motional behaviour is quite similar, so that the high degree of stereoselectivity of ring cleavage cannot be related thereto The results of the measurement can be summarized as follows (*1*) both phenyl



exo-1



endo-1

groups rotate freely around the axis intersecting the para-carbon atom, by an identical ratio $T_1(o,m)/T_1(p) = 2\,8$, (*2*) the free rotation of the methyl group of rhamnose is hindered in both isomers (for a free rotor, we should expect[10] a T_1 value of ~6 sec), (*3*) the T_1 value of C-7, which is a member of the flexible dioxolane ring, is significantly greater than the average value of the sugar ring, 2 15 sec

Spin–lattice relaxation times were measured at 55° for 25% solutions in $CDCl_3$, using the Progressive Saturation method A two-parameter, non-linear, damped least-squares fit[11] was applied for the calculation of individual T_1 values Statistical errors in T_1 data are better than 6% (S/N = 170, NT = 1024)

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