Electron Spin Resonance Spectroscopic Investigation of Carbohydrate Radicals. Part 3.[1] Conformation in Deoxypyranosan-2-, -3-, and -4-yl Radicals

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E.s.r. spectra of C-2, -3, and -4 carbohydrate free radicals, generated regiospecifically by halogen abstraction from acylated deoxyhexopyranoses are recorded in benzene solution. Analysis of the hyperfine splittings reveals the retention of the $^4C_1$ chair conformation of the parent compounds in the radicals.

In Part 2[1] the structures of various pyranosyl radicals with the radical centre at the anomeric (C-1) carbon atom have been examined by e.s.r. spectroscopy. In non-aqueous media the pyranos-1-yl radicals exist as planar π-type radicals and their equilibrium conformations strongly depend on the type of carbohydrate. Thus, diastereoselectivities in radical C–C coupling reactions of carbohydrates have to be discussed in terms of carbohydrate conformations[2] rather than in terms of σ-configuration at the radical centre as had been suggested earlier.[3]

Recently, it has been shown that diastereoselective C–C coupling reactions could also be performed at the C-2 position of the carbohydrate backbone, giving 2-deoxy sugars in reasonably good yields.[4] Similarly, radical-induced C–C bond formation is also possible at C-3 and -4 of the pyranosyl rings.[5]

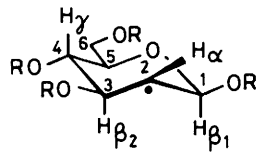
The e.s.r. spectroscopic investigation of C-2, -3, and -4 deoxypyranosanyl radicals, which is presented here, should provide better insight into the dependence of diastereoselectivity on radical conformation. Structurally related radicals have been investigated in the reaction of unprotected sugar derivatives with OH radicals in aqueous solution.[6,7]

Results and Discussion

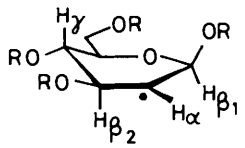
The deoxypyranosanyl radicals (**R1**)—(**R8**) were regiospecifically generated in benzene solution from the corresponding bromo- or iodo-compounds (**1**)—(**8**) by reaction with trimethylstannyl radicals, generated photolytically from hexamethylditin (see Table). The carbohydrates (**1b**), (**2b**), (**3**), and (**6**)—(**8**) are new compounds that were synthesized by standard procedures. The e.s.r. spectra, recorded in the temperature range from −8 to +64 °C, were evaluated manually and the coupling constants were refined by computer simulation. Assignment of the e.s.r. data to the particular carbohydrate radical was unequivocal. In all cases, doublet splittings of *ca.* 2.05—2.25 mT were found, common values for α-hydrogen atoms in unperturbed π-type alkyl radicals.[8] The *g* values of 2.0024—2.0027 are in the range generally found for alkyl radicals and indicate the absence of α-bonded oxygen atoms.[8]

If the pyranosanyl radicals (**R1**)—(**R8**) were generated in THF or toluene solution, only α-tetrahydrofuryl and benzyl radicals, respectively, could be observed. The production of these radicals by hydrogen transfer to pyranosanyl radicals points to the absence of significant thermodynamical stabilization in the carbohydrate radicals with radical centres at C-2, -3, and -4.

(a) *2-Deoxypyranosan-2-yl Radicals.*—The e.s.r. hyperfine splittings of the pyranosan-2-yl radicals (**R1a**)—(**R3**) (see Table) are well interpreted in terms of a $^4C_1$ chair conformation (**A**), possibly slightly distorted at the C-1 end of the carbohydrate ring. This interpretation is supported by the β-hydrogen hyperfine splittings, whose magnitudes are dependent on the configuration of the starting material.



(A)



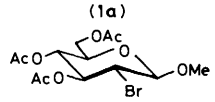
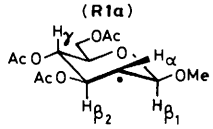
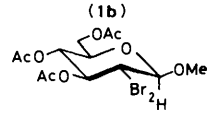
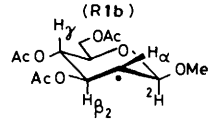
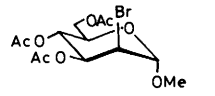
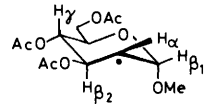
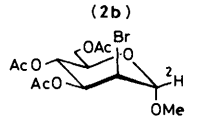
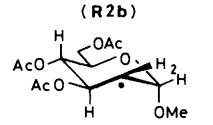
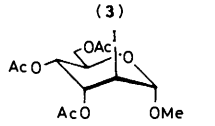
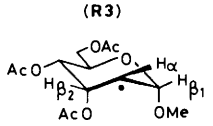
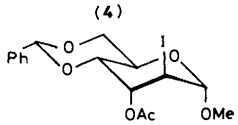
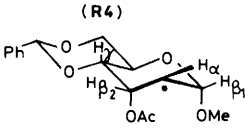
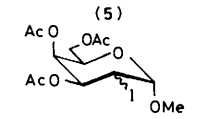
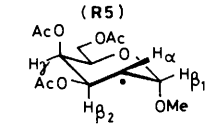
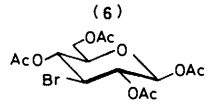
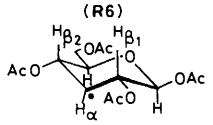
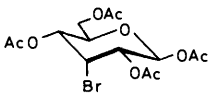
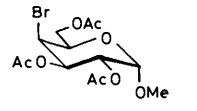
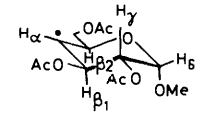
(B)

Radical (**R1a**) displays two large β-H couplings of *ca.* 3.4 and 2.3 mT, in accord with a pseudo-axial arrangement of the two β-CH bonds.[7] The assignment given in the Table is proved by radical (**R1b**), deuteriated at C-1. Here, the smaller of the two β-H couplings is replaced by the corresponding ^{2}H coupling constant (calculated, 0.35; observed, 0.34 mT). The lower value of the β_1-H coupling at C-1 might be interpreted by a flattening of the C-1 side of the six-membered ring, leading to a larger dihedral angle θ between the singly occupied *p*-orbital and the axial β-CH bond. From the $\cos^2\theta$ dependence of the β-hydrogen couplings,[9] a dihedral angle of *ca.* 45° is calculated from the observed coupling constant of 2.3 mT in (**R1**). A dihedral angle of such a magnitude is to a high degree realized in a ^4H half-chair conformation (**B**). On the other hand, electronic interactions can also be responsible for the difference in magnitude of the β-hydrogen splittings. The bonding of C-1 to a second oxygen atom may influence the spin density distribution, resulting in a lower β_1-hydrogen coupling without significantly changing the $^4C_1$ conformation (**A**) of the starting material.

At present, the available data allow no unambiguous distinction between a fully evolved ^4H half-chair conformation (**B**) or a (possibly flattened or twisted) $^4C_1$ chair conformation (**A**).† The e.s.r. data clearly demonstrate that in contrast to the pyranosyl radicals[1] there is no tendency for radicals (**R1**) to convert into a $B_{2,5}$ or $^{1,4}B$ boat conformation in which stabilization by the interaction of the singly occupied *p*-orbital and the adjacent β-C–OR bonds could be achieved. This behaviour supports the assumption that the SOMO energy of

† Half-chair conformations of saturated six-membered rings are normally regarded as maxima (transition states) on the energy hypersurface of ring inversion.

Table. Conformations and e.s.r. data of C-2, -3, and -4 pyranosanyl radicals

Substrate	Conformation	T/°C[a]	g	Hyperfine splittings (mT)[b] a(α-H)	a(β_1-H)	a(β_2-H)	a(γ-H)	a(other)
(1a) 	(R1a) 	+7	2.0024	2.133	2.293	3.462	0.097	
		+23	2.0024	2.107	2.280	3.433	0.095	
(1b) 	(R1b) 	+30	2.0026	2.146		3.408	0.082	0.340 (^{2}H)
(2a) 	(R2a) 	+14	2.002 58	2.162	0.973	3.662	0.085	
		+64		2.150	1.067	3.523	0.077	
(2b) 	(R2b) 	+9	2.002 62	2.168		3.691	0.095	0.141 (^{2}H)
(3) 	(R3) 	−8		2.247	0.281			
		+15	2.002 39	2.252	0.261			
		+31	2.0024	2.247	0.222			
		+55		2.230	0.192			
(4) 	(R4) 	+55	2.0024	2.229	0.689	1.089	0.059	
(5) 	(R5) 	+7	2.0027	2.155	0.630	4.007	0.036	
		+31	2.0027	2.140	0.649	3.945	0.032	
(6) 	(R6) 	+21	2.002 68	2.050	3.305	3.305	0.139	0.079 (γ_1-H)
		+30	2.0026	2.056	3.299	3.299	0.144	0.073 (γ_1-H)
		+43	2.0026	2.057	3.286	3.286	0.168	0.076 (γ_1-H)
(7) 	(R7) ≡ (R6)							
(8) 	(R8) 	+14	2.002 69	2.100	3.588	3.334	0.209	0.047 (γ_2-H, 2 H) 0.087 (δ-H)

[a] ±2 °C. [b] ±0.002—±0.005 mT.

the radical has to be raised by electron donors in order to attain a noticeable interaction with the LUMO of the β-CO bond.[1,2]

The conformation of the above 2-deoxypyranosan-2-yl radicals is not influenced substantially if the methoxy group at C-1 is transposed from the equatorial into the axial position in radical (**R2a**), derived from the 2-deoxymannosyl compound (**2a**). Whereas the β_2-H coupling keeps its value, the β_1-H coupling reduces to *ca.* 1.0 mT, implying a dihedral angle between the β_1-CH bond and the half-filled *p*-orbital of *ca.* 60°. The assignment of the two β-hydrogen couplings here again was

justified by the e.s.r. spectrum of the C-1 deuteriated analogue (**R2b**). The low value of the β_1-H hyperfine splitting largely favours the preservation of the $^4C_1$ conformation (**A**); a ^4H half-chair conformation (**B**) should exhibit a dihedral angle of *ca.* 30°, predicting a much larger β_1-H coupling constant (*ca.* 2.0 mT).

The somewhat surprising observation of only two doublet splittings (2.252 and 0.26 mT at 15 °C) in the e.s.r. spectrum points to a $^4C_1$ chair conformation of radical (**R3**). The 0.26 mT splitting is tentatively assigned to C-1, its magnitude is consistent with a dihedral angle as predicted by a $^4C_1$ chair conformation. The absence of the second β-H coupling at C-3 implies an almost orthogonal arrangement of this C–H bond and the half-filled *p*-orbital.

A significant conformational effect appears in the corresponding 2-deoxyaltrosan-2-yl radical (**R4**), in which the C-4 and -6 positions are connected by a cyclic acetal function. Here, two β-H hyperfine splittings are observed. Their magnitude suggests a fairly undistorted $^4C_1$ chair conformation, fixed by the *trans*-coupling of the rings. The assignment of the two β-H couplings is arbitrary.

The e.s.r. spectra of the 2-deoxygalactosan-2-yl radicals (**R5**) reveal no remarkable difference from the general conformational behaviour of the other pyranosan-2-yl radicals, outlined above. β-H Hyperfine splittings of 4.01 and 0.63 mT are in accord with a $^4C_1$ chair conformation. Worth noticing are the magnitudes of the γ-hydrogen coupling constants at C-4, which are smaller than the corresponding values of radicals (**R1**) and (**R2**). From the mechanism of long-range spin delocalization [10] a reversed order is expected, since (**R4**) displays a better W-like arrangement of the singly occupied *p*-orbital and the γ-CH bond than (**R1**) or (**R2**).

(b) 3-*Deoxypyranosan-3-yl Radicals.*—Bromine abstraction from either 3-bromo-3-deoxyglucopyranose (**6**) or 3-bromo-3-deoxyallopyranose (**7**) leads to formation of the pyranosan-3-yl radical (**R6**). Within the linewidth, the two pseudoaxial β-hydrogen atoms are found to be equivalent, clearly demonstrating a regular $^4C_1$ chair conformation of this radical. Furthermore, influences of the γ-substituents on the radical centre seem to be low. The larger of the two γ-H couplings is tentatively assigned to the axial-bonded hydrogen at C-1.

(c) 4-*Deoxypyranosan-4-yl Radicals.*—The only example of a pyranosan-4-yl radical investigated in this study is (**R8**), generated from methyl 4-bromo-4-deoxygalactoglycoside (**8**). The almost unchanged $^4C_1$ conformation is substantiated by the large coupling constants of 3.6 and 3.3 mT of the axial β-hydrogens. The small triplet splitting of 0.047 mT, reasonably assigned to the exocyclic CH_2 group, indicates entirely free rotation about the C-5—C-6 bond. The two remaining couplings, of 0.209 and 0.087 mT, are tentatively assigned to the γ-H at C-2 and the δ-hydrogen atom at C-1, respectively. Radical (**R8**) is the only example of a pyranosyl radical in which a long-range δ-hyperfine splitting has been observed.

Conclusions.—The analysis of the e.s.r. coupling constants reveals that the carbohydrate radicals derived from positions C-2, -3, and -4 of various deoxypyranosanyl derivatives to a large extent prefer to retain the $^4C_1$ chair conformation of their parent compounds. There is no obvious tendency to transform into a conformation in which the radical *p*-orbital is stabilized by a parallel arrangement with a β-C–OR bond as is observed for some pyranosyl radicals. This is in agreement with the MO perturbational explanation of conformational changes in pyranosyl radicals.[1,2]

Experimental

N.m.r. spectra were observed on a Bruker WM 300 spectrometer, using tetramethylsilane as internal reference. E.s.r. measurements were performed on a Bruker ER-420 X-band spectrometer equipped with a variable-temperature unit. Optical rotations were recorded at 20 °C with a Perkin-Elmer model 141 polarimeter (589 nm). M.p.s were determined with a Büchi SMP 20 apparatus.

Materials.—Methyl 3,4,6-tri-*O*-acetyl-2-bromo-2-deoxy-β-D-glucopyranoside (**1a**),[11] methyl 3,4,6-tri-*O*-acetyl-2-bromo-2-deoxy-α-D-mannopyranoside (**2a**),[11] methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-iodo-α-D-altropyranoside (**4**),[12] and methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-galacto/talopyranoside (**5**)[13] were prepared by literature procedures.

Methyl 3,4,6-*Tri*-O-*acetyl*-2-*bromo*-2-*deoxy*-1-*deuterio*-β-D-*glucopyranoside* (**1b**) *and Methyl* 3,4,6-*Tri*-O-*acetyl*-2-*bromo*-2-*deoxy*-1-*deuterio*-α-D-*mannopyranoside* (**2b**).—A solution (methanol, 25 ml) of tri-*O*-acetyl-1-deuterio-D-glucal[14] (1.66 g, 6.05 mmol) was treated for 4 h at 17 °C with *N*-bromosuccinimide (1.60 g, 9.0 mmol). The solution was evaporated under reduced pressure, the resulting oil was dissolved in ether (180 ml), washed with water (50 ml), and dried ($MgSO_4$). Distillation and flash chromatography (pentane–ether–dichloromethane 5:4:1) yields the mannopyranoside (**2b**) (820 mg, 35%; R_F 0.35) and the glucopyranoside (**1b**) (380 mg, 17%; R_F 0.31) (Found: C, 40.6; H, 4.8. Calc. for $C_{13}H_{18}BrDO_8$: C, 40.6; H, 4.7; D, 0.5%). Compound (**1b**) had $[\alpha]_D^{20}$ +22° (*c* 2.0 in $CHCl_3$); $\delta_H(CDCl_3)$ 2.03 (3 H, s), 2.089 (3 H, s), 2.092 (3 H, s), 3.59 (3 H, s), 3.75 (1 H, ddd, *J* 2.4, 4.7, 10.0 Hz), 3.78 (1 H, d, *J* 10.7 Hz), 4.16 (1 H, dd, *J* 2.4, 12.3 Hz), 4.31 (1 H, dd, *J* 4.67, 12.3 Hz), 5.00 (1 H, dd, *J* 9.3, 10.0 Hz), and 5.30 (1 H, dd, *J* 9.3 Hz). Compound (**2b**) had $[\alpha]_D^{20}$ +56° (*c* 1.0 in $CHCl_3$); $\delta_H(CDCl_3)$ 2.06 (3 H, s), 2.09 (3 H, s), 2.11 (3 H, s), 3.43 (3 H, s), 3.99 (1 H, ddd, *J* 2.5, 4.3, 10.0 Hz), 4.15 (1 H, dd, *J* 2.5, 12.2 Hz), 4.25 (1 H, dd, *J* 4.9, 12.2 Hz), 4.44 (1 H, d, *J* 4.0 Hz), and 5.21 (1 H, dd, *J* 4.0, 9.7 Hz).

Methyl 3,4,5-*Tri*-O-*acetyl*-2-*deoxy*-2-*iodo*-α-D-*altropyranoside* (**3**).—A solution (pyridine, 35 ml) of methyl 2-deoxy-2-iodo-α-D-altropyranoside[15] was treated for 14 h at room temperature with acetic anhydride (25 ml). The mixture was dissolved in $CHCl_3$ (100 ml) and washed three times with ice–water (200 ml each), twice with 1M-sulphuric acid (20 ml each), saturated hydrogencarbonate solution (50 ml), and water (50 ml). After drying ($MgSO_4$) and evaporation of the solvent under reduced pressure the *altropyranoside* (**3**) remained as an oil (5.57 g, 98%); $[\alpha]_D^{20}$ +21.7° (*c* 2.0 in $CHCl_3$) (Found: C, 36.3; H, 4.4. $C_{13}H_{19}IO_8$ requires C, 36.3; H, 4.45%); $\delta_H(CDCl_3)$ 2.05 (3 H, s), 2.10 (3 H, s), 2.12 (3 H, s), 3.41 (3 H, s), 4.18—4.42 (3 H, m), 4.27 (1 H, dd, *J* 2.2, 4.9 Hz), 5.03 (1 H, d, *J* 2.2 Hz), 5.33 (1 H, t, *J* 3.3 Hz), and 5.49 (1 H, dd, *J* 4.9, 8.4 Hz).

1,2,4,6-*Tetra*-O-*acetyl*-3-*bromo*-3-*deoxy*-β-D-*glucopyranose* (**6**) *and* 1,2,4,6-*Tetra*-O-*acetyl*-3-*bromo*-3-*deoxy*-β-D-*allopyranose* (**7**).—1,2,4,6-Tetra-*O*-acetyl-3-*O*-tolylsulphonyl-β-D-glucofuranose[16] (3.00 g, 5.97 mmol) was treated for 12 h at 110 °C with LiBr (2.17 g, 25.0 mmol) in DMF (40 ml). The solvent was evaporated under reduced pressure, the residue dissolved in $CHCl_3$ (50 ml), dried (Na_2SO_4), and flash chromatographed (hexane–methyl acetate 6:4). Chromatography yields the allopyranoside (**7**) (710 mg, 29%; R_F 0.32) and the glucopyranose (**6**) (1.20 g, 49%; R_F 0.26). *Compound* (**6**) had m.p. 105 °C; $[\alpha]_D^{20}$ +11.1° (*c* 1.5 in $CHCl_3$) (Found: C, 40.95; H, 4.55. $C_{14}H_{19}BrO_9$ requires C, 40.9; H, 4.7%); $\delta_H(CDCl_3)$ 2.10 (3 H, s), 2.11 (3 H, s), 2.12 (3 H, s), 2.13 (3 H, s), 3.76 (1 H, dd, *J* 8.18, 10.7 Hz), 4.03 (1 H, t, *J* 10.6 Hz), 4.11 (1 H, dd, *J* 2.32, 12.5

Hz), 4.26 (1 H, dd, *J* 4.6, 12.5 Hz), 5.28 (1 H, t, *J* 10.0 Hz), 5.29 (1 H, dd, *J* 8.2, 10.7 Hz), and 5.63 (1 H, d, *J* 8.2 Hz). *Compound* (**7**) had $[\alpha]_D^{20}$ −14.1° (*c* 1.6 in $CHCl_3$) (Found: C, 40.65; H, 4.5%); $\delta_H(CDCl_3)$ 2.09 (3 H, s), 2.10 (3 H, s), 2.12 (3 H, s), 2.13 (3 H, s), 4.14—4.24 (1 H, m), 4.29—4.39 (2 H, m), 4.85 (1 H, dd, *J* 3.7, 8.1 Hz), 4.86 (1 H, dd, *J* 3.5, 8.1 Hz), 5.04 (1 H, t, *J* 3.5 Hz), and 6.10 (1 H, dd, *J* 0.3, 8.1 Hz).

Methyl 2,3,6-*Tri*-O-*acetyl*-4-*bromo*-4-*deoxy*-α-D-*galacto*-*pyranoside* (**8**).—A mixture of methyl 2,3,6-tri-*O*-acetyl-α-D-galactopyranoside[17] (1.45 g, 4.53 mmol), triphenylphosphine (3.43 g, 13.1 mmol), tribromoimidazole (2.66 g, 8.74 mmol), and imidazole (0.59 g, 8.74 mmol) in toluene (50 ml) was stirred under reflux for 45 min. After the solution had cooled to room temperature, saturated aqueous sodium hydrogencarbonate solution (50 ml) was added, the mixture stirred for 5 min, and iodine added portionwise until the organic phase remained iodine-coloured. After the mixture had been stirred for 10 min, aqueous sodium thiosulphate solution was added to remove the excess of iodine. The organic phase was washed three times with water (20 ml each), dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography (ether–pentane 3:1) yields the galactopyranoside (**8**) (1.25 g, 72%), m.p. 89 °C (crystallized from ether–pentane), $[\alpha]_D^{22}$ +170° (*c* 0.73, $CHCl_3$) (Found: C, 40.65; H, 5.0. $C_{13}H_{19}BrO_8$ requires C, 40.75; H, 5.0%); $\delta_H(CDCl_3)$ 2.10 (3 H, s), 2.12 (3 H, s), 2.13 (3 H, s), 2.40 (3 H, s), 4.10—4.25 (2 H, m), 4.29 (1 H, dd, *J* 6.1, 10.5 Hz), 4.64 (1 H, dd, *J* 1.1, 3.7 Hz), 5.00 (1 H, d, *J* 3.6 Hz), 5.14 (1 H, dd, *J* 3.7, 10.6 Hz), and 5.24 (1 H, dd, *J* 3.6, 10.6 Hz).

E.s.r. Measurements.—Radicals were generated by u.v. irradiation of the solutions in sealed Suprasil quartz tubes (outer diameter 4.0 mm) with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp. The e.s.r. solutions were composed of the sugar derivative (*ca.* 50 mg), dry benzene (0.2 ml), and hexamethylditin (0.2 ml). The addition of di-t-butyl peroxide (0.02 ml) in some cases gave increased signal intensities. Oxygen was removed from the solutions by purging with dry nitrogen for 30 min.

E.s.r. hyperfine coupling constants were refined by simulation of the manually evaluated e.s.r. spectra on a PDP-11/34 computer. *g* Values were determined with the aid of a microprocessor-controlled device, using the digital output of a microwave frequency counter and a n.m.r. field-measuring unit.

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