

**EPR Studies of Spin Trap Adducts of Carbohydrate Radicals: Recognition of Adduct Isomerism and Chirality.**

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The nitrogen substituents of glycosamines (amides, sulfonamides and amines) react with hypochlorite (HOCl) to form long-lived N-chloro derivatives (chloramides, N-chlorosulfo-namides and chloramines) that are decomposed to nitro-gen-centred radicals (amidyl, sulfo-namidyl and aminyl radicals) via one-electron reduction. These radicals rearrange via intramolecular hydrogen abstraction to yield carbon-centred radicals that form persistent adducts with the spin traps 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and/or 2-methyl-2-nitrosopropane (MNP). The EPR spectra of some of these adducts are unexpectedly complex, with this shown to be due to isomerism or chirality effects. Thus isomeric adducts formed via trapping of C-2 carbon-centred radicals located on reducing residues interconvert via muta-otation of the C-1 hemiacetal function as evidenced by time-dependent changes in adduct concentrations. Structurally analogous C-2 carbon-centred radicals formed on non-reducing residues do not form interconvertible adduct isomers. The MNP adducts of methylene radicals formed on the glycosidic groups of N-acetylglucosamine  $\alpha$ - and  $\beta$ -methyl glycosides ( $t\text{Bu-NO}^{\bullet}\text{-CH}_2\text{-O-sugar}$ ) give EPR signals with non-equivalent  $\beta$ -hydrogen hyperfine split-tings. Observation of a difference in the magnetic environment of these hydrogens (i.e. chiral recognition) is ascribed primarily to interac-tions between the nitroxide function and the (chiral) sugar moiety that restrict the rotation of the nitroxide  $\alpha$ -C-N bond.