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PMR STUDY OF THE COMPLEX FORMATION OF ALDITOLS WITH MULTIVALENT CATIONS IN AQUEOUS SOLUTIONS USING PRASEODYMIUM(III) NITRATE AS SHIFT REAGENT

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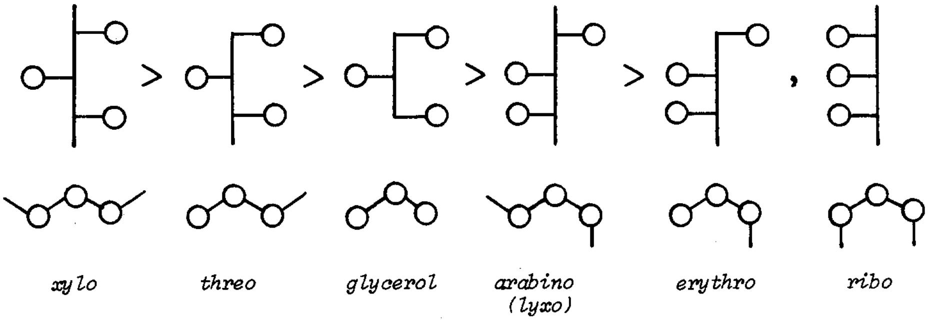
Complexation of multivalent cations with polyoxygen systems is of great biological and technological interest. In particular, complexation phenomena of the calcium(II) ion in aqueous solution have received special attention because of its essential role in the regulation of biological processes[1] and in the search for suitable phosphate substitutes[2]. In this respect, the elucidation of the complexation behaviour of polyhydroxy derivatives[3], in addition to the multidentate macrocyclic compounds[4], is of the utmost importance.

We have investigated the complex formation of ten alditols (see below) with praseodymium(III) nitrate in aqueous solution by 100 MHz PMR spectroscopy. Praseodymium was applied instead of the (isosteric) calcium ion because of the additional advantage of paramagnetically induced shifts. In this way, sufficient information about the relative strengths and the preferred modes of complexation of the alditols was gained. The very recent preliminary communications of Angyal[5] concerning similar PMR studies of some sugars and alditols using europium(III) nitrate has prompted us to report our results at this time.

The complexation equilibrium between the alditols and praseodymium nitrate in deuterium oxide at 30-40°C was found to be fast on the PMR time-scale, *i.e.* averaged spectra of the complexed and uncomplexed species were observed. The praseodymium induced shifts occurred regularly downfield and enabled us to analyse the spectra by general techniques.

The different praseodymium induced shifts point to tridentate complexation by 3 consecutive hydroxyl groups of the alditol. Internal comparison of the various possible tridentate ligand sets present in each alditol with the actual mode of complexation in addition to the order of complex strengths: iditol > sorbitol > (arabitol, galactitol, glycerol, threitol, xylitol) > (erythritol, mannitol, ribitol) reveal the following order of preferential configuration of the various tridentate ligands towards complex formation with praseodymium(III) nitrate in aqueous solutions (O = hydroxyl):



Two major effects are responsible for this complexation sequence: (i) internal hydroxyl groups show better complexation abilities than primary, due to the greater freedom of rotation and the less favourable conformation of the terminal hydroxymethyl group in the uncomplexed state; (ii) the conversion of the *zig-zag* structure into *gauche-* and *cis-*butane conformations upon complexation of the alditol. In most cases, the vicinal coupling constants were not affected by increasing the amount of praseodymium nitrate and were in agreement with a *zig-zag* conformation in both the uncomplexed and complexed alditol. As an exception, $J_{2,3}$ of mannitol varied considerably because of a *gauche*-butane conformation in the complexed species (*arabino* ligand). The complex constant for mannitol is *ca* 0.7 mole^{-1} as obtained from the variation in $J_{2,3}$ as well as the praseodymium induced shifts[6].

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6. Calculated from the induced shifts according to: A.D. Sherry, C. Yoshida, E.R. Birnbaum, and D.W. Darnall, *J. Amer. Chem. Soc.* **95**, 3011 (1973).