THERMODYNAMIC AND SPECTROSCOPIC PROPERTIES OF 2-DEOXY-SUGARS IN WATER.
COMPARISON WITH THE CRYSTAL STRUCTURES.

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ABSTRACT

The excess enthalpies, free energies and entropies of aqueous solution of some 2-deoxy-sugars have been determined at 298.15 K by microcalorimetric and isopiestic measurements. The differences between the thermodynamic properties of these 2-deoxy-derivatives resemble those that characterize the parent monosaccharides and seem to depend on the solute stereochemistry. In order to obtain information about the conformational analogies between the deoxy-derivatives and their parent monosaccharides, a crystallographic study and nmr investigation in solution are also in advance on these compounds.

THERMODYNAMICS

It is well known that the excess thermodynamic functions are a measure of the deviations from the ideal behaviour of the solutions and their values are determined by the intermolecular interaction occuring in the mixture. Using the molality scale, an excess properties of a binary solution, containing m moles of solute per kg of solvent, can be defined as:

$$Y^E(m) = Y(m) - Y^\circ_w - m\bar{Y}^\circ_x - Y^{ID} \qquad (1)$$

where $Y(m)$ is the corresponding absolute function of the solution, Y°_w is the standard property of one kg of pure water and $\bar{Y}^\circ_x$ is the standard partial molar property of the solute x, Y^{ID} is the ideal part intrinsically null in the case of the enthalpy. According to the Friedman extension (ref.1) of the McMillan-Mayer theory (ref.2) to the solution of non electrolytes, each excess thermodynamic property can be represented by a power expansion series of the molality. For the excess Gibbs free energy, enthalpy and entropy, it results respectively:

$$G^E(m) = g_{xx}m^2 + g_{xxx}m^3 + \ldots \qquad (2)$$
$$H^E(m) = h_{xx}m^2 + h_{xxx}m^3 + \ldots \qquad (3)$$
$$TS^E(m) = Ts_{xx}m^2 + Ts_{xxx}m^3 + \ldots \qquad (4)$$

where the virial coefficientes g_{xx}, g_{xxx} etc. assume a statistical mechanical significance, as they can be considered a measure of the intermolecular interactions of pairs, triplets and higher numbers of solute particles. However these coefficients account implicitely also for the changes (with the concentration) in the solvent-solvent and solute-solvent interactions (refs.3-5). For non electrolytes, in particular for their aqueous solutions, these changes can be more remarkable than solute-solute contributions.

The excess free energy coefficients can be obtained from isopiestic measuraments (ref.5) and the enthalpic ones from flow microcalorimetry (refs.1,3,4,6). The entropies were calculated from the preceding data.

TABLE 1

Coefficients of the virial expansions of the excess Gibbs free energies, enthalpies and entropies of 2-deoxy-D-sugars and their parent monosaccharides at 298.15 K, with confidence limits at 95% in parentheses.

	g_{xx}	h_{xx}	Ts_{xx}	h_{xxx}
	(J kg mol^{-2})			(J kg^2 mol^{-3})
2-deoxy-D-galactose	58(7)	442(22)[a]	384	-21(15)[a]
2-deoxy-D-ribose	80(5)	468(12)[a]	388	-21(8)[a]
2-deoxy-D-glucose	88(8)	592(17)[a]	504	-36(12)[a]
D-galactose	65(12)	133(8)[b]	68	-[b]
D-ribose	20(5)[c]	202(8)[a]	182	-6(5)[a]
D-glucose	92	343(10)[d]	251	-13[d]

[a]ref.4, [b]ref.6, [c]ref.7, [d]ref.8.

The values of the h_{xx} and Ts_{xx} coefficients of 2-deoxy-derivatives are all higher than those of the corresponding sugars (Table 1). The g_{xx} values, viceversa, do not differ appeciably; they are generally much more small, due to the enthalpy-entropy compensation phenomenon. The higher values of enthalpies and entropies of the 2-deoxy-sugars, respect to those of the parent monosaccharides, can be attributed to the loss of a hydroxyl group (refs.4-6). The g_{xx} of D-ribose do not follow the sequence in the values shown by other coefficients.

CRYSTAL STRUCTURE DETERMINATION AND NMR STUDY

It is known that in water D-galactose and D-glucose are essentially a mixture (~2:1) of β- and α-anomers of the pyranose form in $^4C_1$ conformation. D-ribose is present also as furanose (~20%). Nothing is known about the 2-deoxy-derivatives.

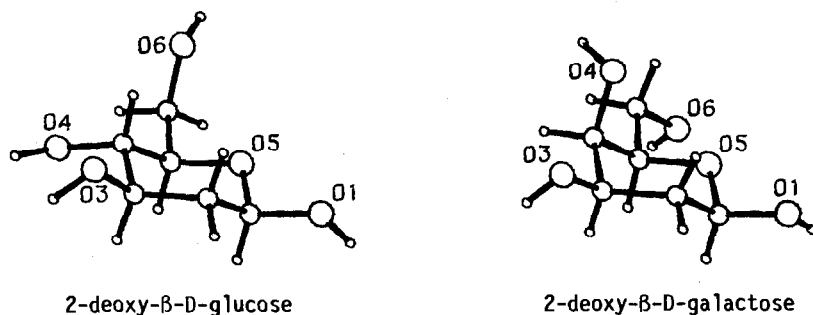We have carried-on a X-ray investigation on crystals of 2-deoxy-D-galactose

2-deoxy-ß-D-glucose   2-deoxy-ß-D-galactose

Fig. 1. Conformation of the molecules in the solid state.

and 2-deoxy-D-glucose (from ethanol). The results show that both compounds cry-
stallize as ß-pyranose form and the molecules assume the $^{4}C_{1}$ conformation (Fig.
1). Moreover the primary hydroxyl group is in the gauche-gauche conformation
(respect to the C5-O5 and C5-C4 bonds), for the 2-deoxy-glucose, while is in the
gauche-trans conformation for the 2-deoxy-galactose. Details on the crystallogra-
phic analysis are in press (ref.9).

The crystals, upon dissolving in heavy water, show the mutarotation, that was
monitored by the change in the intensities of the proton nuclear relaxation si-
gnals. The preliminary assignment indicates the presence, in all cases, of both
α- and ß-pyranose forms, the last one being prevailing even after several hours
but more abundant in the freshly prepared solutions. In the 2-deoxy-D-ribose spe-
ctra however there are no evidences for a remarkable presence of furanose form.
In conclusion these studies support the hypothesis that the thermodynamic proper-
ties reflect analogies in the distibution of the population of conformers and,
ultimately, their stereochemistry. Then the lower value of g_{xx} of D-ribose, res-
pect to those of the other sugars here considered, could be due to the presence,
only in this case, of the furanose isomeric forms.

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REFERENCES

1 H.L. Friedman and C.V. Krishnan, J. Solution Chem., 2 (1973) 119-138.
2 W.G. McMillan Jr. and J.E. Mayer, J. Chem. Phys., 13 (1945) 276-305.
3 F. Franks, M. Pedley and D.S. Reid, J. Chem. Soc., Faraday Trans. 1, 72 (1976) 359-367.
4 G. Barone, G. Castronuovo, D. Doucas, V. Elia and C.A. Mattia, J. Phys. Chem., 87 (1983) 1931-1937.
5 G. Barone, G. Castronuovo, V. Elia and V. Savino, J. Solution Chem., 13 (1984) 209-219.
6 G. Barone, P. Cacace, G. Castronuovo and V. Elia, Carbohydr. Res., 91 (1981) 101-111
7 R.H. Stokes and R.A. Robinson, J. Phys. Chem., 70 (1966) 2126-2130.
8 J.J. Savage and R.H. Wood, J. Solution Chem., 5 (1976) 733-750.
9 R. Puliti, C.A. Mattia and G. Barone, Carbohydr. Res., (1984) in press.