A CARBON-13 N.M.R. SPECTRAL STUDY OF D-PSICOSE: ANOMERIC AND RING-FORM EQUILIBRIA OF SOLUTIONS OF 2-HEXULOSES

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ABSTRACT

The equilibrium composition of D-psicose in water, as determined from its 13 C n.m.r. spectrum, is 7:2:5:5 α -furanose: β -furanose: α -pyranose: β -pyranose. These data, which are discussed in relation to the anomeric and ring-form equilibria of the other 2-hexuloses, are in general agreement with expectations based on conformational analysis. However, although the 13 C chemical-shift pattern of the β -pyranose is closely consistent with the IC(D) conformation predicted for this anomer, that of the α -pyranose is less readily reconciled with its predicted CI(D) conformation. Usually, carbon-13 nuclei of the furanose rings are substantially less shielded than those of their pyranose counterparts; for 2-hexulopyranoses in general, overall 13 C shielding is close to that of those aldopyranoses expected to have similar conformational free-energies. Spectral data are also reported for several derivatives (glycosides, ethers, and selectively deuterated compounds) that were utilized in analysis of the D-psicose spectrum.

INTRODUCTION

A recent article¹ described the anomeric and ring-form equilibria of various 2-hexuloses and 2-heptuloses, measured for aqueous solutions by ¹³C n.m.r. spectroscopy, and for methyl sulfoxide solutions by hydroxyl p.m.r. spectroscopy. D-Psicose, which is known only as a syrup, produces particularly complex spectra, although, by the aid of data on suitable derivatives of this 2-ketose, its ¹³C spectrum has now been analyzed in detail. The results furnish previously unavailable information about the characteristics of D-psicose in solution.

The equilibrium composition of solutions of D-psicose. — The proton-decoupled, ¹³C spectrum of D-psicose in water¹ contains some 20 individual signals, and their relative intensities make it clear that several signals represent more than one nucleus each. Four well-resolved resonances farthest downfield (see Table I), all attributable to ¹³C-2 nuclei, indicate that both anomers of the pyranose and furanose forms are present. From the peak intensities, and the assignments to be discussed, it was concluded that the preponderant species at equilibrium is the α -furanose (1), and that

TABLE I

Compound	β -Furanose α -Furanose α - and β -Pyranoses				
	¹³ C chemi	cal shift ^a (relat	ive intensity)		
D-Peicose	874(1)	897 (3.5)	946(25)	953(25)	
6- <i>O</i> -methyl-p-psicofuranose	87.1 (1)	89.5 (2.5)	5.10 (215)	5010 (LID)	
5-O-Methyl-D-psicopyranose		,	94.3 (1.3)	94.9 (1)	
Methyl D-psicosides	83.5	87.5	(β) 9	0.4	
Methyl 6-O-methyl-D-psicofuranosides	82.9	87.5			
	OH chemi	cal shift (relation	ve intensity)		
D-Psicose	5.37 (1)	5.11 (3.1)	5.35 (2.2)	5.63 (2.2)	
6-O-Methyl-D-psicofuranose	5.28 (1)	5.07 (2.2)			
5-O-Methyl-D-psicopyranose			5.41 (1.2)	5.72 (1)	

CHEMICAL SHIFTS AND RELATIVE INTENSITIES OF THE C-2 AND OH-2 SIGNALS OF D-PSICOSE AND DERIVATIVES

"In p.p.m. from downfield CS₂; relative intensity in parentheses.

the β -furanose (2) is a minor component, whereas the two pyranoses (3 and 4) have intermediate, equal, populations (see Table I) of different conformations. Related to this situation is the fact that the p.m.r. spectrum of *D*-psicose freshly dissolved in methyl sulfoxide contains four OH-2 singlets, the intensities of which correspond to a composition close to that of the aqueous solution (see Table I).



Assignments for the anomeric ¹³C signals of D-psicose are based on the spectra of several derivatives. Thus, resonances produced by 6-O-methyl-D-psicofuranose have chemical shifts close to those of the two signals at lowest field (see Table I), and also have similar relative intensities. Of the two methyl glycosides synthesized from this ether, the α anomer produces its ¹³C-2 signal upfield from that of the β anomer. Similar values are found for the methyl α - and β -furanosides of D-psicose (see Table I)*. Accordingly, of the two C-2 signals of D-psicofuranose, that at higher field is ascribed to the α anomer; this assignment was also supported by the results of comparison of the optical rotation of 6-O-methyl-D-psicose with those of the methyl furanosides, which indicated that the α anomer is present in the higher proportion.

The comparatively upfield disposition of the two 13 C-2 signals of the pyranose was confirmed by reference to the spectrum of 5-O-methyl-D-psicopyranose (see Table I). As the chemical shifts and intensities are very close to each other in both instances, the individual signals for the pyranoses cannot be specified, although this is of little importance in the present context.

Data for the OH-2 resonances of the 5- and 6-O-methyl derivatives in methyl sulfoxide, also listed in Table I, helped to identify the anomeric hydroxyl signals of the ring forms of D-psicose.

Conformational analysis of equilibria for D-psicose and other 2-hexuloses. — The equilibrium-composition data just reported for D-psicose confirmed various predictions based on the conformational analysis of the different forms of the sugar. Thus, the minimum free-energy values calculated⁵ for α - and β -D-psicopyranose are close to each other, and this is consistent with the fact that these two species are found in equal proportions (see Table II). By analogy with the effects anticipated for interaction

TABLE II

Equilibrium compositions (in percent^{α}) of solutions of the 2-hexuloses in water and in methyl sulfoxide^b

					⊿G ^c		
2-Hexulose	a-Pyranose	β-Pyranose	α-Furanose	β-Furanose	α-Pyranose	β-Pyranose	
D-Psicose	25 (20)	25 (15)	40 (50)	10 (15)	3.90 (<i>C1</i>) 5.35 (<i>1C</i>)	3.55 (<i>IC</i>) 5.09 (<i>C1</i>)	
L-Sorbose	100 (95)	0 (5)			2.30 (1 <i>C</i>) 6.60 (<i>C1</i>)	3.85 (<i>C1</i>) 4.35 (<i>1C</i>)	
D-Tagatose	90 (90)	10 (10)			2.50 (<i>C1</i>) 6.00 (<i>1C</i>)	4.00 (1 <i>C</i>) 4.30 (<i>C</i> 1)	
D-Fructose	<5 (<5)	60 (20)	10 (25)	30 (55)	3.63 (<i>C1</i>) 3.85 (<i>1C</i>)	2.85 (1C) 4.95 (Cl)	

 $a \pm 2-3\%$. ^bIn parentheses. ^cValues from ref. 5; conformation given in parentheses.

between O-3 and C-5 of aldofuranoses^{6,7}, both of the D-psicofuranoses should be energetically favored by the *trans* disposition of the 4-hydroxyl and 5-(hydroxy-methyl) groups. This type of interaction is also possible between C-1 and O-3 of

^{*}It is noteworthy that the downfield displacement of anomeric signals through *O*-methylation is much smaller in these instances, as well as for the β -pyranose, than that (about 7 p.m.m.) observed with aldoses²⁻⁴.

2-ketoses: *i.e.*, they are *cis* in β -D-psicofuranose, but are in the (more stable) *trans* arrangement in the α anomer. Simultaneously, of course, the reverse relationship holds for O-2 and O-3; these are *trans*-disposed in the α anomer, although the latter interaction is surely much less destabilizing than that between *cis*-oriented C-1 and O-3. These characteristics, together with the relative instability of the α - and β -D-psicopyranoses, even in their most favored conformations, undoubtedly account for the preponderance of α -D-psicofuranose in the mixture.



Considerations of this kind are also in accord with the equilibrium composition found^{1,8,9} for solutions of D-fructose (see Table II). Both of the furanose forms are favored by the *trans* relationship of O-4 and C-6, but, in the more populous β anomer, C-1 and O-3 are also *trans*. The fact that β -D-fructopyranose, the major constituent, has a lower free-energy than either of the D-psicopyranoses is compensated for (among the respective furanoses) by the absence of a destabilizing, *cis* arrangement of O-3 and O-4 in the D-fructose isomers as compared with the D-psicose isomers. Hence, in solution, there is a comparably high proportion of the furanose forms of each sugar.

β-D-Tagatopyranose-1C

In the foregoing discussion, account has been taken only of interaction between vic substituents on the 5-membered rings. Although cis-1,3 interactions may also be important in furances⁷, they nevertheless probably have little effect on the equilibria described here. The strength of such interactions (as well as cis-1,2 interactions) will naturally be related to the way in which the ring is puckered; for example, it would be anticipated that the α anomers would accommodate quasi-equatorial orientations for the cis 2- and 5-(hydroxymethyl) groups in order to maximize their separation. For simplicity, however, the following possibilities for cis-1,3 interactions between substituents in the four furancess may be noted: α -psicofurances: C-1,C-6

C - D-Tagatopyranose-C1

and O-2,O-4; β -psicofuranose: O-2,C-6 and C-1,O-4; α -fructofuranose: C-1,C-6, O-2,O-4, and O-3,C-6; and β -fructofuranose: O-2,C-6, C-1,O-4, and O-3,C-6.

The intensity of these repulsive interactions should decrease in the order C,C>C,O>O,O. On the assumption that the free-energy contribution of a *cis*-1,3 C,O interaction is about midway between those of the other two interactions, the sums of these various contributions are found to be closely equivalent for α - and β -psicofuranose [C,C+O,O vs. 2 (C,O)], and also for α - and β -fructofuranose [C,C+C,O+O,O vs. 3 (C,O)]. Hence, it is likely that, for both pairs of anomers, the equilibrium ratio is largely determined by the relative disposition of C-1 and O-3.

For L-sorbose or D-tagatose, the α -pyranose form is by far the most stable (see Table II); all four of the furanose forms of these 2-ketoses, essentially absent, would incorporate the unfavorable *cis* O-4,C-6 interaction. Hence, the overwhelming preponderance of α -L-sorbopyranose or of α -D-tagatopyranose at equilibrium¹ in solution is understandable.

The free-energy values listed in Table II afford a generally good prediction of $\alpha:\beta$ pyranose ratios; thus, the percentages of α anomers expected⁵ are: sorbose 92, tagatose 89, psicose 33, and fructose 28. Fructose is the exception, in that the proportion of α -pyranose is very minor, whereas the β -pyranose constitutes 60% of the mixture. It is noteworthy, therefore, that the proportion of the β anomer decreases markedly when the equilibrium is achieved in methyl sulfoxide as solvent, although that of the α appears to remain unaffected (see Table II). This change in composition is accompanied by an increase in the percentages of the D-fructofuranoses, a type of effect already observed^{10.11} with a number of other sugars, including the configurationally related arabinose and galactose. An increase is also found in the relative importance of the furanose forms of D-psicose in methyl sulfoxide. By contrast, there is no sign of furanose forms in the methyl sulfoxide solutions of L-sorbose or D-tagatose, although a small percentage of β -L-sorbopyranose is present, in contrast to zero in its aqueous solution.

These data for the 2-ketoses, therefore, conform to a pattern of behavior (that appears to be general, although as yet unexplained) that relates the equilibrium compositions of solutions of sugars in water to those of their solutions in methyl sulfoxide (and some other organic solvents as well¹²), namely, those sugars which exist to even a small extent as furanose forms in water (or, from stereochemical considerations would be expected to do so) produce a higher proportion of the furanoses in methyl sulfoxide. Other sugars, which appear not to exist as furanoses in water (nor are expected to, on steric grounds) invariably remain as pyranoses in the organic medium, even though the anomeric ratio is commonly altered.

Carbon-13 chemical shifts of D-psicose and derivatives. — Turning now to a fuller analysis of the ¹³C spectrum of D-psicose (see Table III), other data obtained for the O-methyl derivatives already mentioned, as well as from ¹³C n.m.r. spectra of D-psicose-3-d and D-psicose-3,4-d₂, permit a definitive identification of most of the signals produced by the various anomeric and ring forms of D-psicose. As noted ¹³ for other sugars and derivatives, ¹³C nuclei of the furanoid rings* are here, also, found to be generally deshielded relative to those of their pyranoid counterparts, a difference that appears to be accounted for largely by differences in diamagnetic contributions to the chemical shift¹³.

TABLE III

¹³C CHEMICAL SHIFTS⁴ OF D-PSICOSE AND SOME DERIVATIVES

Carbon atom number	D-Psice	ose			Methyl	D-psicosi	ides	Methyl 6-0-me D-psico	l ethyl- osides
	α-f ^b	β-f	α-p	<i>β</i> -p	α-f	<i>β</i> -f	<i>β</i> -p	α-f	β-f
1	129.5	130.4	128.7	128.7	132.3	135.5	127.6	132.1	133.6
2	89.7	87.4	94.5	95.2	87.5	83.5	90.4	87.5	82.9
3	122.5	118.1	127.3	122.5	120.3	118.1	123.2	120.4	118.3
4	121.1	121.8	127.8	122.5	122.0	120.9	122.9	121.8	120.3
5	109.4	109.4	123.8	127.0	108.0	109.1	127.2	110.1	110.8
6	129.5	130.1	131.5	134.8	130.6	129.3	135.0	120.0	118.3
1-OMe	<u> </u>	¹	<u> </u>		143.5	144.1	·	143.5	143.2
6-0Me	·	·	-	·			<u> </u>	133.5	135.2

"In p.p.m. from CS_2 , ^bf = furanose; p = pyranose.

By empirically allowing for appropriate configurational and conformational features, good agreement has been obtained between ¹³C chemical shifts observed and calculated for aldoses^{3,4}, 2-ketoses¹, and cyclitols¹⁴. Analogous use of these shielding parameters for α - and β -D-psicopyranose furnished the data given in Table IV. Interconversions were visualized starting from α -D(or L)-sorbopyranose, the most conformationally stable of the 2-hexuloses; differences in the pattern of interactions for the various species were taken into account (column 4), and the associated changes in chemical shift anticipated (column 5) were then computed. Reference to the experimental values shows that C-3 and C-4 are particularly strongly shielded, and this discrepancy also holds if α -D-tagatopyranose or β -L-fructopyranose is used as the basis for comparison. As interconversions of this kind among the other 2-hexuloses lead to generally close agreement¹, these results imply that the conformation of α -D-psicopyranose departs significantly from that associated with α -D-sorbopyranose. By contrast, the values calculated for β -D-psicopyranose correspond quite well to the chemical shifts observed, implying the CI(D) conformation for this isomer.

In comparing diastereoisomers, it had been noted^{4,15} that the "total" ${}^{13}C$ chemical shifts, as a measure of overall shielding of the molecules, tend to vary as their

^{*}A good correlation has been found¹³ between the ${}^{13}C$ chemical shifts of the furanosides (see Table III) and calculated values of the charge densities of these carbon atoms.

Inversion ^a	C	δA (exptl. ^b)	Interaction ^c	48	§B (calc.)	δB (exptl. ^b)
or T						
HO					•	
 문		127.9	0	0	127,9	128.7
Q-D-S	3	94.3	+0//0-4, -0//H-4	-0.5	93.8	94.6
(A)	3	121.1	+adj. 4	+2.5	123.6	127.3
	4	117.7	+ax. 0, +0//0-2, -FI//0-2, +0//H6	+4.5	122.2	127.8
	5	122.3	+ adj. 4	+2.5	124.8	123.9
HO CH ² OH	9	130.0	+H//0-4	+2.5	132.5	131.5
- 연 - 어				-	· · ·,	
Q-0-P						
HO						
	•					•
HO HO HO	•					
- E	-	127.9	0	0	127.9	128.7
(۵) ۲-۲-۵	2	94.3	+adj. 3, -0/0-3	0	94.3	95.3
i —	ŝ	121.1	+ax. 0, +0//0-5, -0/0-2	+2.0	123.1	122.5
, HO	4	117.7	+ adj. 3, + adj. 5	+5.0	122.7	122.5
- O - CHOH	5	122.3	+ax. 0, 0//0-3	+4.5	126.8	127.0
	Q	130.0	+adj. S	+2.5	132.5	134.8
HO HO			· · · · · · · · · · · · · · · · · · ·			- -
Ø-0-P		-		-	•	
(8)						
"The change of compound A-+com Values from ref. 4: ax., C bears a	apound B represents an axial substituent	an inversion at ((+2.5 p.p.m.); i	C-3 (upper) or at C-2 and C-4 (lower); S = so adj., adjacent C bears an axial substituent (rbose; P = (+2.5 p.p.n	psicose. ^b P.I n.); 0/O =	o.m. from CS ₂ . gauche oxygen
atoms $(+2.5 \text{ p.p.m.})$; $O//O = syn$	·1,3 0,0 (+2.0 р.р.п	H = H/0 put (.)	<i>syn</i> -1,3 O,H (+2.5 p.p.m.).			

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TABLE IV. ¹³C SHIELDING DIFFERENCES BETWEEN ISOMERS

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free energies. The same relationship is clearly evident among the 2-hexuloses (see Table V); *i.e.*, α -D-sorbopyranose is the most stable of the series, and possesses, overall, the least shielded ¹³C nuclei. Similarly, the D-psicopyranoses produce spectral signals that, on the average, are upfield of those of the other 2-ketoses, and that also have high, calculated conformational free-energies. Also noteworthy (see Table V) is the fact that these summed chemical-shift values are very close to the total ¹³C chemical shifts of those aldopyranoses that would be expected⁵ to have approximately the same conformational free-energies as the related 2-ketoses under discussion. This agreement may accordingly be taken as support for the validity of the energy correlations that have been made⁵ between pyranoses of the 2-keto- and aldo-hexose series.

TABLE V

COMPARISON BETWEEN TOTAL ¹³C CHEMICAL-SHIFT AND FREE ENERGY

2-Ketohexose	$\Sigma \delta^a$	⊿F⁵	Aldohexose	<i>Σδ</i> °
α-L-Sorbopyranose	713.3	2.40	α-D-Glucopyranose	716.2
α-D-Tagatopyranose	717.6	2.55	α-D-Mannopyranose	715.5
β -D-Fructopyranose	723.1	2.85	α-D-Galactopyranose	724.0
β -D-Tagatopyranose	724.1	4.00		
β -D-Psicopyranose	730.7	3.55		
α-D-Psicopyranose	733.6	3.90		

^aSum of ¹³C chemical shifts for the six carbon atoms (in p.p.m. from CS₂). ^bSee ref. 5. ^cSee ref. 4.

It may be noted that, although the observed equilibrium of ~1:1 ratio for the anomers of D-psicopyranose accords well with the free energies calculated for these sugars, substantial differences have been observed¹⁶ with some derivatives. Thus, the anomers of 3-O-methyl-D-psicopyranose equilibrate* in water to give a ratio of 1:3 (their respective configurational designations are as yet uncertain), and treatment of D-psicose with methanol-hydrogen chloride has afforded methyl β -D-psicopyranoside but not the α anomer. In both instances, the two furanose forms were prominently represented. These, and related, characteristics of D-psicose derivatives will be described elsewhere.

EXPERIMENTAL

Carbon-13 spectra. — Measurements were made at a frequency of 25.15 MHz, with proton-decoupling at 100 MHz, by means of a Varian HA-100 spectrometer (cw mode) or a Varian XL-100 spectrometer (Ft mode); in the former mode, methyl- ^{13}C iodide was used as the internal, reference lock-signal, whereas a deuterium lock was employed for the Fourier-transform experiments.

*Some effects of O-methylation on sugar equilibria have already been noted^{11,17}.

1,2:4,5-Di-O-isopropylidene- β -D-fructopyranose. — This compound was prepared according to Brauns and Frush¹⁸, although recrystallization of the crude reaction-product from ethanol was found more satisfactory than from ligroin, because this greatly minimized the co-crystallization of admixed 2,3:4,5-di-Oisopropylidene- β -D-fructopyranose*; the product had m.p. 118.5–119°, $[\alpha]_D - 145°$ (c 1, chloroform); lit.¹⁹ m.p. 119°, $[\alpha]_D^{25} - 145°$ (in chloroform).

1,2:4,5-Di-O-isopropylidene- β -D-erythro-2,3-hexodiulo-2,6-pyranose²⁰⁻²³ and its 4-deuterio analog. — 1,2:4,5-Di-O-isopropylidene- β -D-fructopyranose (80 g) in chloroform (500 ml) was oxidized with ruthenium dioxide²⁴ (600 mg, hydrated) in the presence of an aqueous suspension (500 ml) of potassium periodate²⁵ (150 g), potassium carbonate (15 g), and potassium hydrogen carbonate (15 g), with efficient stirring. After 6 days at room temperature, the reaction was complete; the excess of the oxidant was reduced with isopropyl alcohol, and the title compound was isolated from the water-washed chloroform layer (yield, 66 g), and recrystallized from hexane; m.p. 101–102°, $[\alpha]_D - 108°$ (c 1, ethanol); lit.²³ m.p. 102–103°, $[\alpha]_D^{25} - 113.5°$ (in ethanol).

A solution of the diketone diacetal (2.6 g) in pyridine (25 ml) and deuterium oxide (25 ml) was heated²² for 15 min at 95°, the solvent was evaporated off, and the residue was recrystallized; m.p. 100–102°. The p.m.r. spectrum of this product, as compared with that of undeuterated diketone diacetal, showed the absence of the H-4 doublet and a less complex H-5 signal.

1,2:4,5-Di-O-isopropylidene- β -D-psicopyranose, -3-d, and -3,4-d₂. — A solution of the diketone diacetal (50 g) in tetrahydrofuran (500 ml) was added to a slurry of lithium aluminum hydride (15 g) in tetrahydrofuran during 1 h. One hour later, the reaction mixture was processed, and the product was recrystallized from hexane (yield, 45.5 g); m.p. 65–66°, $[\alpha]_D - 126^\circ$ (c 1.1, chloroform); lit.²³ m.p. 68–69°, $[\alpha]_D^{25} - 120.7^\circ$ (in chloroform).

The diacetal-3-d was prepared by the same procedure, but with lithium aluminum deuteride as the reducing agent; for preparation of the $3,4-d_2$ analog, the 4-deuterio diketone (see previous section) was reduced with lithium aluminum deuteride.

D-Psicose, -3-d, and -3,4-d₂. — All three title compounds were prepared by hydrolysis of the appropriate sample of the di-O-isopropylidene- β -D-psicopyranose. Typically, a solution of nondeuterated diacetal (10 g) in water (250 ml) containing Amberlite IR-120 (H⁺) resin (50 ml) was heated for 5 h at 70°; by chromatographic examination, the reaction was shown to be complete. The resin was filtered off and washed, and the solution was evaporated to a clear, colorless syrup (7.8 g); $[\alpha]_D + 4.9^\circ$ (c 1.5, water); lit.²⁶ $[\alpha]_D^{25} + 4.7^\circ$ (in water).

Other reference compounds. — Syntheses of the O-methyl derivatives and methyl glycosides used as reference compounds have been described¹⁶.

^{*}An improved method¹⁹ for preparation of the title compound almost completely eliminates formation of the 2,3:4,5-diacetal.

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