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^{13}C NMR SPECTRA OF PARENT HEXOPYRANOSES

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UDC 543.422.25:547.455

The first subject for the investigation of carbohydrates by the ^{13}C NMR method included the hexopyranoses most widespread in nature, i.e., D-glucopyranose, D-mannopyranose, and D-galactopyranose [1, 2]. The ^{13}C NMR spectra of the three above-mentioned pyranoses [3, 4], D-allopyranose [3, 4], and D-altopyranose [5] have now been fully interpreted. These are data on the chemical shifts in the ^{13}C NMR spectra of D-talopyranose [6, 7], but fundamental errors were made in the assignment of the signals in these spectra. Thus, exhaustive data on the chemical shifts in the ^{13}C NMR spectra were only available for five of the eight parent hexopyranoses.

The present work was devoted to the investigation and interpretation of the ^{13}C NMR spectra of three hexopyranoses, i.e., α- and β-talopyranose, α- and β-gulopyranose, and α- and β-idopyranose. For a more reliable assignment of the signals in the ^{13}C NMR spectrum of the aqueous solution of L-idose the spectrum of the latter was compared with the spectra of aqueous solutions of structurally related compounds 6-deoxy- and 6-O-methyl-L-idose.

Let us consider the compositions of mutarotating mixtures of D-talose, D-gulose, and D-idose. When D-talose is dissolved in heavy water, the predominating isomer in the initial period is α-D-talopyranose, and this makes it possible to isolate the signals of this isomer both in the PMR spectrum and in the ^{13}C NMR spectrum. Approximately 1 h after dissolution an equilibrium is established between the four forms in the ratios αp:βp:αf:βf ≈ 0.36:0.27:0.21:0.16. The difference in the content of the four forms in the nonequilibrium and equilibrium mixture make it possible to isolate the signals of each of the isomers in the ^{13}C NMR spectra. It is also possible to isolate certain individual signals in the PMR spectrum by homonuclear double resonance (Table 1). As seen from Table 1, the H^3 and H^4 protons of α-D-talopyranose are equivalent in their chemical shifts at 250 MHz, and this does not make it possible to use selective heteronuclear $^{13}C-\{^1H\}$ double resonance for the assignment of the C^3 and C^4 signals in the ^{13}C spectrum. In this connection for the assignment of the C^3 and C^4 signals in the carbon spectrum we made use of the fact that in the α-anomer of D-talopyranose there must be a transoid spin–spin coupling constant for the C^3 atom with the H^1 proton ($^3J_{^1H^1-^{13}C^3}$), if the α-anomer exists in the preferred $^4C^1$ conformation [8]. At the same time the C^4 signal cannot be split from coupling with the H^1 proton, since the $^4H_{^1H^1-^{13}C^4}$ spin–spin coupling constant through four simple bonds is not observed in carbohydrates [9].

Experiments with selective heteronuclear $^{13}C-\{^1H\}$ double resonance with PMR data (Table 1) made it possible, in particular, to assign the C^1, C^2, C^5, and C^6 signals of α-D-talopyranose. The signals at 71.7 and 66.15 ppm were assigned to the C^3 and C^4 atoms of this isomer. From comparison of the spectra of α-D-talopyranose without decoupling from H^1 and with selective irradiation of the H^1 proton (Fig. 1) it is seen that as a result of irradiation of the H^1 proton the comonents of the doublet centered at 66.15 ppm in the carbon spectrum change from pseudoquartet to pseudotriplet. Here the splitting constant of the carbon signal at H^1 (~4.5 Hz), which corresponds in value to the transoid constant $^3J_{^1H-^{13}C}$ in pyranoses [9], disappears. Thus, the signal at 66.15 ppm can only belong to C^3 of α-D-talopyranose.

Similarly, the two closely located signals at 69.45 and 69.6 ppm, which to judge from the intensities belong to the signals of β-D-talopyranose, were assigned to C^3 and C^4. During

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1328-1336, June, 1983. Original article submitted September 21, 1982.

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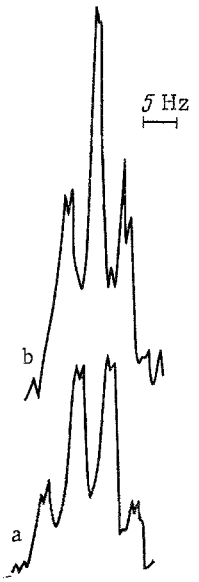

Fig. 1. The form of the bright part of the doublet signal with spin–spin coupling constant $^{1}J_{^{1}H^{3}-^{13}C^{3}}$ = 142 Hz centered at 66.15 ppm: a) in the ^{13}C spectrum of D-talose in D_2O without decoupling from H^1; b) in the spectrum with irradiation at the resonance frequency of the H^1 proton of α-D-talopyranose.

irradiation of the H^1 proton of β-D-talopyranose in the ^{13}C NMR spectrum the cisoid constant of ~1 Hz in the components of the doublet centered at 69.45 ppm disappears.

The remaining signals in the spectrum of the mutarotating mixture of D-talose isomers (Tables 2 and 3) were assigned either by means of selective heteronuclear $^{13}C-\{^{1}H\}$ resonance or from general considerations on the effect of structural factors on the ^{13}C chemical shifts in pyranoses [13] and furanoses [14]. In all cases the difference in the intensities of the lines of the isomers in the nonequilibrium and equilibrium mixture was used to reveal the signals belonging to one of the four series.

Five minutes after dissolution of D-glucose in D_2O the β-D-gulopyranose predominates in the mutarotating mixture of isomers; the signals of α-D-gulopyranose are also noticeable, while the signals of the furanose forms are present as minor components of the spectrum. In the equilibrium mixture the ratios of the isomers are αp:βp:(αf + βf) = 0.17:0.78:0.05. The signals of α- and β-gulopyranose are easily identified in the PMR spectrum (Table 1), and the signals of the pyranose forms in the ^{13}C spectrum were therefore assigned unambiguously by selective heteronuclear $^{13}C-\{^{1}H\}$ double resonance (Table 3).

In a freshly prepared solution of L-idose in D_2O (see the experimental section) 1,6-anhydro-β-L-idopyranose if already present in an appreciable amount, and its signals in the ^{13}C NMR spectra are identical with data taken from [15] (Table 4). In the first hours, however, signals for certain protons of the α- and β-anomers of L-idopyranose can be isolated in the PMR spectrum of the mixture of isomers of L-idose and 1,6-anhydro-β-L-idopyranose (Table 1), and this then makes it possible by heteronuclear $^{13}C-\{^{1}H\}$ double resonance to assign all the key signals in the ^{13}C spectrum of these anomers (Table 4). In the course of the whole period required for the establishment of equilibrium in the mixture it was not possible to observe the signals of the furanose forms in the ^{1}H and ^{13}C NMR spectra. In the equilibrium mixture (one month after dissolution) the ratio of the isomers of L-idopyranose and 1,6-anhydro-β-L-idopyranose was αp:βp:1,6-anhydro-β-L = 0.08:0.07:0.85.

In a solution of 6-O-methyl-L-idose in D_2O after the establishment of equilibrium the following ratios of the isomers were found in the ^{13}C NMR spectra: αp:βp:αf:βf = 0.37:0.34:0.14:0.15. The difference in the intensities of the lines makes is possible to isolate series of signals belonging to the pyranose and furanose forms. The signals of the pyranose series were assigned by comparison of the spectra of the 6-deoxy and 6-O-methyl derivatives and the corresponding parent pyranoses with allowance for the effects of substitution of the CH_2OH group at C^5 by CH_3 in the pyranoses [12] and the effects of methylation at C^6 [13]. The assignment of the signals of the furanose forms was made with due regard to the rela-

TABLE 1. Parameters of the PMR Spectra of D-Talose, D-Glucose, and L-Idose Isomers in D_2O*

Compound	Chemical shifts, δ, ppm and spin–spin coupling constants J, Hz						
	H^1	H^2	H^3	H^4	H^5	H^6	$H^{6'}$
α-*D*-Talopyranose	5,10 d $J_{1,2}$=1,6	3,67 dd $J_{2,3}$=3,0	3,40–3,47 м		3,93 ddd $J_{5,4}$=1,0	3,62 dd $J_{5,6}$=6,8 $J_{6,6'}$=8,0	3,60 dd $J_{5,6'}$=5,2
β-*D*-Talopyranose	4,63 d $J_{1,2}$=1,0	3,72 dd $J_{2,3}$=3,0					
α-*D*-Talofuranose	5,06 d $J_{1,2}$=1,5	3,81 ddd $J_{2,3}$=4,7	4,15 ddd $J_{3,4}$=6,8	$J_{2,4}$=0,5	$J_{3,5}$=0,4		
β-*D*-Talofuranose	5,19 d $J_{1,2}$=3,6	3,95 dd $J_{2,3}$=5,0	4,00 dd $J_{3,4}$=5,2				
α-*D*-Gulopyranose	5,00 dd $J_{1,2}$=3,6	3,74 dd $J_{2,3}$=3,3	~3,8 $J_{1,3}$=0,8	3,75 dd $J_{4,3}$=3,5	4,08 td $J_{4,5}$=1,4	~3,55 $^1/_2(J_{5,6}+J_{5,6'})$=5,8	
β-*D*-Gulopyranose	4,70 d $J_{1,2}$=8,4	3,44 ddd $J_{2,3}$=3,5	3,88 t $J_{3,4}$=3,5	3,64 ddd $J_{4,2}$=0,5	3,82 td $J_{5,4}$=1,3	~3,55 $^1/_2(J_{5,6}+J_{5,6'})$=5,8	
α-*L*-Idopyranose	5,01 d $J_{1,2}$=5,6	3,46 dd $J_{2,3}$=7,5	3,70 t $J_{3,4}$=7,5				
β-*L*-Idopyranose	5,08 d $J_{1,2}$=1,4	3,68 dd $J_{2,3}$=3,3	4,09 t $J_{3,4}$=3,3	3,60 dd $J_{4,5}$=1,6	4,02 ddd $J_{5,6}$=4,5	3,8–3,9 m $J_{5,6'}$=8,5	

*The spectra were measured at 25°C with acetone as internal standard (2.08 ppm from TMS), and the chemical shifts are given with reference to TMS.

TABLE 2. The ^{13}C Chemical Shifts of α- and β-D-Talofuranose*

Compound	Chemical shifts, δ, ppm ($^1J_{H^1-C^1}$, Hz)					
	C^1	C^2	C^3	C^4	C^5	C^6
α-*D*-Talofuranose†	102,0 (173)	76,2	71,6	83,1	72,7	63,8
β-*D*-Talofuranose	97,45 (173)	71,6	71,7	83,5	72,1	63,9

*The chemical shifts were measured in D_2O at 25°C with methanol as internal standard (50.15 ppm from TMS) and are given with reference to TMS.
†The ^{13}C chemical shifts of α- and β-D-talopyranose are given in Table 3.

TABLE 3. The ^{13}C Chemical Shifts of the Parent Pyrans

Compound	^{13}C chemical shifts δ, ppm ($^1J_{H^1-C^1}$, Hz)*						Reference
	C^1	C^2	C^3	C^4	C^5	C^6	
α-*D*-Glucopyranose	92,7 (169,5)	72,15	73,45	70,4	72,1	61,3	[12]
β-*D*-Glucopyranose	96,5 (160)	74,8	76,4	70,3	76,6	61,5	[12]
α-*D*-Mannopyranose	95,0 (170)	71,7	71,3	68,0	73,4	62,1	[12]
β-*D*-Mannopyranose	94,6 (160)	72,3	74,1	67,8	77,2	62,1	[12]
α-*D*-Allopyranose	93,4 (170)	67,6	72,3	66,7	67,5	61,35	[4]
β-*D*-Allopyranose	94,0 (162)	71,9	71,75	67,4	74,2	61,8	[4]
α-*D*-Galactopyranose	93,6 (169,5)	69,8	70,5	70,6	71,7	62,5	[12]
β-*D*-Galactopyranose	97,7 (159,5)	73,3	74,2	70,1	76,3	62,3	[12]
α-*D*-Altropyranose	94,7 (168)	71,2	71,1	66,0	72,0	61,4	[5]
β-*D*-Altropyranose	92,6 (162)	71,6	71,3	65,2	75,0	62,5	[5]
α-*D*-Talopyranose	95,6 (170,5)	71,1	66,15	70,6	72,1	62,4	
β-*D*-Talopyranose	95,1 (160,5)	72,5	69,45	69,6	76,55	62,2	
α-*D*-Gulopyranose	94,05 (169,2)	66,0	72,1	70,7	67,7	62,1	
β-*D*-Gulopyranose	95,1 (162,8)	70,4	72,4	70,7	74,9	62,2	
α-*D*(*L*)-Idopyranose	93,55 (163,7)	73,5	73,3	71,5	76,45	60,35	
β-*D*(*L*)-Idopyranose	94,6 (165,5)	71,05	70,95	69,25	75,8	62,5	

*The chemical shifts are given with reference to TMS, and some of the chemical shifts given in the cited papers were rounded off with an accuracy of up to 0.05 ppm.
†The spin–spin coupling constants for D-gluco-, D-manno-, and D-galactopyranose were taken from [10], and those for α-D-allopyranose were taken from [11]. On account of the absence of data on the spin–spin coupling constants for β-D-allopyranose the constant for 2-deoxy-β-D-allopyranose [11] is given. According to [11], the constants for the α-anomers of D-allopyranose and 2-deoxy-D-allopyranose coincide.

tionships governing the effect of structural factors on the ^{13}C chemical shifts in furanoses [14] and by comparison of the spectra of the furanose isomers of 6-O-methyl- and 6-deoxy-L-idose.

According to ^{13}C NMR spectroscopy, the equilibrium mutarotating mixture of isomers of 6-deoxy-L-idose has the following composition: αp:βp:αf:βf = 0.41:0.33:0.13:0.13. The difference in the line intensities makes it possible to isolate three series of signals: α-pyranose, β-pyranose, and furanose forms. The assignment of the signals within the series was made as described above for the isomers of 6-O-methyl-L-idose.

DISCUSSION OF RESULTS

The parameters of the ^{13}C NMR spectra of the whole series of related hexopyranoses are given in Table 3. In view of the total identity of the spectra of the pyranoses of the D and L series in achiral solvents the parameters of the ^{13}C NMR spectra obtained for α- and β-L-idopyranose in Table 3 were assigned to the corresponding pyranoses with the absolute D configuration for the purpose of generality in the subsequent presentation.

During comparison of the chemical shifts of the carbon atoms for all eight hexopyranoses it is difficult to find any common relationships in their variation during the transition from one epimer or anomer to the other. For the case of α,β-D-gluco-, α,β-D-manno-, and α,β-D-galactopyranose in [12] the groundlessness of attempts at the empirical calculation of the ^{13}C NMR spectra of pyranoses by additive increments corresponding to the α, β, and γ effects of epimerization and anomerization was demonstrated. The criticism of such attempts was based on the fact that the "long-ranging" effects (in the terminology used in [12]) of epimerization and anomerization are not compatible in magnitude with inversion of the configuration of the substituents at the various carbon atoms in the asymmetric pyranose ring. Thus, inversion of the configuration at C^3 (cf. the corresponding anomers of gluco- and allopyranose) gives rise to a substantial change in the chemical shifts of C^3 (the α effect of epimerization), C^2 and C^4 (the β effects), C^5 in both anomers, and C^1 in the β-anomer (γ effects). The inversion of the configuration of the substituents at C^4 (cf. the corresponding anomers of gluco- and galactopyranose) does not give rise to substantial changes in the chemical shift of C^4 (the absence of the α effect of epimerization) and C^5 (the absence of the β effect).

During examination of the whole series of hexopyranoses it is seen that the irregularity of the α, β, and γ effects is not the only reason for the difficulties in the search for empirical relationships governing the variations of the chemical shifts of carbon in the epimeric pyranoses. For some pyranoses the position of the conformational equilibrium $^4C_1 \rightleftarrows {}^1C_4$ plays a no less important role in the formation of the ^{13}C NMR spectrum. The shift of the conformational equilibrium can be followed from the variation of the $^1J_{^1H^1-^{13}C^1}$ spin–spin coupling constant, which depends on the orientation of the substituents at C^1 in relation to the unshared electron pairs of the oxygen at C^5 [10]. For D-pyranoses with one axial hydroxy at C^2, C^3, or C^4 (in the $^4C_1$ conformation) $^1J_{^1H^1-^{13}C^1}$ amounts to ~170 Hz for the α-anomers and ~160 or ~162 Hz for the β anomers with the equatorial (e) or axial (*a*) substituent at C^3, respectively. As shown by calculations and experimental data [8], all these pyranoses do in fact exist in the preferred $^4C_1$ conformation. From this standpoint β-D-altro-, α- and β-D-talo-, and α- and β-D-gulopyranoses have the "normal" values of the constants for the $^4C_1$ conformation (Table 3), and the conformational equilibrium in them is consequently shifted toward this conformation. The PMR data and the calculated data [8] agree with this suggestion. For α-D-altropyranose the constant (168 Hz) is appreciably reduced in comparison with the normal value for α-D-pyranoses in the $^4C_1$ conformation (~170 Hz), and this makes it possible to suppose an appreciable contrfibution from the $^1C_4$ conformation in this case. However, the deviation from the normal values of the constants for the α- and β-D(L)-idopyranoses is particularly noticeable. The anomalously high value of the constant for the β-anomer of D-idopyranose (165.5 Hz) means that for this pyranose ring the lifetime in the $^1C_4$ conformation is already comparable with the lifetime in the $^4C_1$ conformation. The anomalously low value of the constant for the α-anomer of D-idopyranose (163.7 Hz) makes it possible to state that the $^1C_4$ conformation is already predominant for this isomer. The proton spin–spin coupling constants in the PMR spectrum of α-L-idopyranose (Table 1) conform the last suggestion. (In order to avoid misunderstandings we emphasize that the statements concerning the conformation of the rings of pyranoses of the L series will be opposite to those which were given above for the pyranoses of the D series; in particular, the predominating conformation for the α-L-idopyranose must be $^4C_1$.)

Analysis of the data given in Table 3 shows that an indication of the shift of the equilibrium $^4C_1 \leftrightarrow {}^1C_4$ toward the last conformer (for pyranoses of the D series) can also be provided by the magnitude of the chemical shift of the C^5 carbon atoms or the difference between the chemical shifts of C^5 in the α- and β-anomers. As indicated above, the chemical shift of C^5 is practically independent of the configuration of the substituents at C^4 but is dependent on the presence or absence of steric interaction between the proton at C^5 and the hydroxyl groups at C^1 and C^3. For β-D-pyranoses with the preferred $^4C_1$ conformation the chemical shift of C^5 lies in the range of 76.3-77.2 ppm (if C^3 carries an e-OH) or about 74.2 ppm for pyranoses with an *a*-OH at C^3 (to judge from the chemical shift of C^5 in β-D-allopyranose).

TABLE 4. The ^{13}C Chemical Shifts of the Isomers of L-Idose and Some Related Compounds*

Compound	Chemical shifts δ, ppm						
	C^1	C^2	C^3	C^4	C^5	C^6	6-OMe
α-*L*-Idopyranose	93,55	73,5	73,3	71,5	76,45	60,35	
β-*L*-Idopyranose	94,6	71,05	70,95	69,25	75,8	62,5	
1,6-Anhydro-β-L-idopyranose	102,5	75,4	75,4	72,0	76,3	65,9	
6-O-Methyl-α-L-idopyranose	93,4	72,95	71,2	71,2	72,95	70,6	59,6 †
6-O-Methyl-β-L-idopyranose	94,85	71,0	70,7	69,3	73,8	72,5	59,5 †
6-O-Methyl-α-L-idofuranose	102,9	82,0	77,5	82,25	70,0	74,35	59,6 †
6-O-Methyl-β-L-idofuranose	96,7	76,6	76,5	78,6	69,5	74,5	59,5 †
6-Deoxy-α-L-idopyranose	93,5	72,8	70,1	74,6	72,6	13,95	
6-Deoxy-β-L-idopyranose	93,35	70,95 ‡	70,75 ‡	71,3	71,3	16,8	
6-Deoxy-α-L-idofuranose	103,1	81,9	77,5	86,6	68,0	19,4 **	
6-Deoxy-β-L-idofuranose	97,0	76,7	76,25	83,2	67,3	19,6 **	

*For the measurement conditions of the spectra, see Table 1.
†The assignment of the signals is not conclusive.
‡The assignments in the line may be reversed.
**The assignments of the signals may be reversed.

The chemical shifts of C^5 in the three β-D-pyranoses and β-D-altropyranose investigated in the present work correspond to those for pyranoses with the authentic $^4C_1$ conformation.

For α-D-pyranoses with the preferred $^4C_1$ conformation the chemical shift of the C^5 lies in the range of 71.7-73.4 ppm (if C^3 carries an e-OH) or about 67.5 ppm (α-D-allopyranose). From the data in Table 3 it is seen that the chemical shift of C^5 in α-D-altropyranose (72.0 ppm) lies in an abnormally downfield region for pyranoses with an *a*-substituent at C^3, and this indicates appreciable shift of the equilibrium $^4C_1 \leftrightarrow {}^1C_4$ toward the last conformer. As far as α-D-idopyranoses are concerned, the chemical shift of C^5 in the spectrum lies in the region of the resonance of C^5 in β-D-pyranoses with an e-substituent at C^3, for which steric interaction between the proton at C^5 and the OH groups at C^1 and C^3 is absent. For α-D-idopyranose such a situation arises for the $^1C_4$ conformation, where only the substituent at C^5 is axial. In the cyclohexane derivatives the appearance of the *a*-group (e.g., CH_3) instead of the e-group usually gives rise to an upfield shift of the signal for the carbon carrying these groups. The anomalous downfield shift of C^5 in α-D-idopyranose can therefore only be explained by the predominance of the $^1C_4$ isomer (or, for α-L-idopyranose, the $^4C_1$ isomer). Further evidence in favor of this is provided by the upfield shifts of the C^6 signals in the spectra of α-L-idopyranose (Table 3) and 6-deoxy-α-L-idopyranose (Table 4), which clearly indicates the *a*-orientation of the CH_2OH and CH_3 groups, respectively, in these compounds.

The difference in the chemical shifts of C^5 in the α- and β-anomers of the pyranoses can also provide a test for the position of the equilibrium $^4C_1 \leftrightarrow {}^1C_4$. If both anomers of the D-pyranoses exist in the preferred $^4C_1$ conformation, it amounts to ~4 ppm in pyranoses with the e-substituent at C^3 or ~7 ppm for pyranoses with the *a*-substituent at C^3. The decrease of the difference to 3 ppm in D-altropyranoses, for example, indicates a shift of the equilibrium $^4C_1 \leftrightarrow {}^1C_4$ (mainly, as seen from the foregoing, in the α-anomer) toward the last conformer.

The dependence of the chemical shifts of the C atoms in the pyranoses on the lifetime (statistical weight) of the $^1C_4$ and $^4C_1$ conformers (and, possibly, other conformers) imposes certain limitations on the possibility of calculating the ^{13}C NMR spectra of derivatives of pyranoses which differ from the parent in the nature of the substituents at the ring carbon atoms but not in the configuration. On the basis of the ^{13}C NMR spectra of D-gluco-, D-manno-, and D-galactopyranoses it is possible to calculate the spectra of some of their derivatives (uronic acids, 6-deoxypyranoses, pentopyranoses with the same configuration of the substituents at C^1—C^4) from the additive constants [12]. Thus, substitution of the CH_2OH group by CH_3 at C^5 gives rise to more or less standard changes in the chemical shifts for only the closest C^5 and C^4 atoms (the "soft-ranging effect" in the terminology in [12]). We

add that the effects of substitution of the OH group by NHAc can be included among the short-ranging effects and it is thus possible to calculate the spectra of sugar acetamides from the spectra of the corresponding parent pyranoses. However, the dependence of the chemical shifts of pyranoses on the conformational equilibrium gives rise to the need for independent control of the composition of the conformational equilibrium in pyranoses, since the possibility of shift to one or the other side during substitution of one functional group by another is not ruled out. This control can be realized experimentally by means of the spin–spin coupling constants in the PMR spectra or from the indications in ^{13}C NMR spectra described above.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument at 250 MHz for protons and 62.89 MHz for carbon (solutions in D_2O, 25°C). The D-talose was the standard product from Chemapol, while D-gulose was the standard product from Sigma. The L-idose was synthesized from diacetone-D-glucose according to data in [16]. L-Iditol hexaacetate, mp 118-120°, $[\alpha]_D^{20}$ −24.7° (C 1.0, $CHCl_3$); cf. [16]. 6-Deoxy-L-idose was synthesized according to data in [17]; $[\alpha]_D^{20}$ + 25.4° (C 3.1, H_2O), cf. [17].

Synthesis of 6-O-Methyl-L-idose. A 2.92-g sample (10 mmole) of 1,2-O-isopropylidene-3-O-benzyl-5,6-anhydro-α-L-idofuranose [16] [^{13}C NMR spectrum (δ, ppm): 105.4 (C^1), 83.0 (C^2), 82.6 (C^3), 82.2 (C^4), 50.2 (C^5), 43.0 (C^6), 72.0 (CH_2Ph), 26.3, 26.8, 111.8 (CMe_2), 137.4, 128.4, 127.8, 127.5 (Ph)] was dissolved in 20 ml of 1 N sodium methoxide solution. The mixture was kept at ∿20°C until the initial compound had disappeared (TLC, ∿2 h). The mixture was diluted with 30 ml of water and extracted with chloroform (3 × 50 ml). The chloroform layer was washed with water (2 × 50 ml), dried with sodium sulfate, filtered, and evaporated. The residue was chromatographed on silica gel (gradient benzene–ether). The yield of 1,2-O-isopropylidene-3-O-benzyl-L-idofuranose (I) was 2.3 g (70%); $[\alpha]_D^{20}$ −60° (C 5.0, $CHCl_3$). ^{13}C NMR spectrum (δ, ppm): 104.8 (C^1), 82.8 (C^2), 82.5 (C^3), 80.2 (C^4), 73.5 (C^5), 69.1 (C^6), 59.0 (OMe), 71.8 (CH_2Ph) 26.3, 26.8, 111.7 (CMe_2), 137.0, 128.4, 128.0, 127.8 (Ph).

A 2.3-g sample (7 mmole) of (I) was dissolved in 30 ml of methanol, and 10 g of Raney nickel was added. The mixture was hydrogenized at atmospheric pressure until the initial compound had disappeared (TLC). The mixture was then filtered through a layer of silica gel. The precipitate was washed on the filter with methanol (3 × 30 ml), and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel (gradient benzene–ether). The yield of 1,2-O-isopropylidene-6-O-methyl-L-idofuranose (II) was 1.31 g (80%); $[\alpha]_D^{20}$ −0.6° (C 1.0, $CHCl_3$). ^{13}C NMR spectrum (δ, ppm): 104.7 (C^1), 85.5 (C^2), 76.0 (C^3), 80.8 (C^4), 74.0 (C^5), 69.1 (C^6), 59.1 (OMe), 26.8, 26.2, 111.6 (CMe_2).

A 1.31-g sample (5.6 mmole) of (II) was dissolved in 20 ml of 0.1 N sulfuric acid and heated at 45°C for 1 h. The mixture was then cooled, neutralized with barium carbonate, and filtered. The precipitate was washed with water (2×10 ml), and the filtrate was evaporated to dryness. The yield of 6-O-methyl-L-idose was 1.07 g (98%). The compound was chromatographically uniform according to paper chromatography in the 6:4:3 pyridine–1-butanol–water system, R_f 1.2 (in relation to D-glucose). The ^{13}C NMR spectrum is given in Table 4.

The author conveys his gratitude to A. F. Sviridov for the synthesis of L-idose and its derivatives.

CONCLUSIONS

1. The ^{13}C NMR spectra were obtained and interpreted for aqueous solutions of three parent hexoses: D-talose, D-gulose, and L-idose. The parameters of the PMR spectra for solutions of these compounds in D_2O are given.

2. The ^{13}C NMR spectra of the L-idose derivatives in aqueous solutions were interpreted for 6-deoxy- and 6-O-methyl-L-idose.

3. The dependence of the ^{13}C chemical shifts and $^{1}J_{^{1}H^{1}-^{13}C^{1}}$ spin–spin coupling constants in eight parent hexopyranoses on the position of the conformational equilibrium of the pyranose rings in solutions is discussed.

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