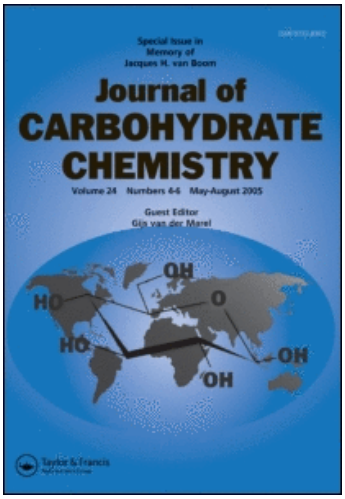

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The Isomeric Composition of *D-ribo*-hexos-3-ulose(3-keto-*D*-glucose) in Aqueous Solution[1]

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THE ISOMERIC COMPOSITION OF D-*RIBO*-HEXOS-3-ULOSE (3-KETO-D-GLUCOSE) IN AQUEOUS SOLUTION[1]

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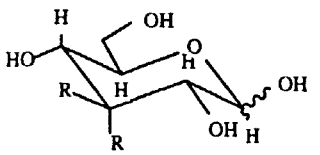
ABSTRACT

1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**2**) prepared by the phase transfer catalyst promoted ruthenium tetraoxide oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**), was partially hydrolyzed to give 1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulose (**3**). The title compound (**4**) was prepared by further acid hydrolysis of **3** or directly from **2**. The anomeric region of the ^{1}H NMR spectrum of freshly prepared **4** showed the presence of at least ten isomeric forms with three forms predominating: α-D-*ribo*-hexofuranos-3-ulose (**4a**, 44%), β-D-*ribo*-hexopyranos-3-ulose (**4b**, 22%) and β-D-*ribo*-hexopyranos-3-ulose hydrate (**4c**, 12%). ^{1}H NMR examination of D_2O solutions of **4** over time showed that the C-2 protons of the various isomeric forms were being exchanged with deuterium.

INTRODUCTION

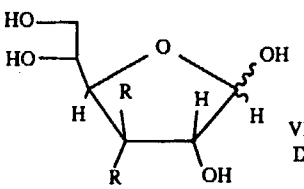
Aldoketoses are monosaccharides that contain both an aldehyde and ketone function. Although a considerable amount of information is available on the composition of simple aldoses and ketoses in aqueous solution,[2] much less is known about the aqueous isomeric composition of aldoketoses.[3-5] Because of the presence of two reactive carbonyl functions in these molecules, their isomeric compositions are quite complex. As part of an ongoing study in this laboratory concerned with the aqueous solution properties of dicarbonyl sugars, it was of interest to see how the aqueous isomeric composition of "3-keto-D-glucose" (D-*ribo*-hexos-3-ulose, **4**) compared with that of the parent D-glucose. Whereas D-glucose exists in aqueous solution (31 °C)[2] as an α and β-pyranose isomeric equilibrium mixture (much less than 1% furanose isomers), an equilibrated aqueous

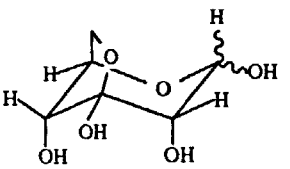
solution of 3-deoxy-D-glucose (3-deoxy-D-*ribo*-hexose) contains about 80% pyranose isomers and about 20% furanose isomers (5% α, 15.5% β at 31 °C).[2] Thus, removal of the C-3 OH group from D-glucose makes the resultant furanose structures more stable due to the lack of crowding between the C-3 OH and the C-5, C-6 branch. A similar trend toward increased furanose composition might be expected for "3-keto-D-glucose" (**4**), if the isomers are not hydrated at C-3. However, the potential isomeric composition of **4** is complicated by the fact that C-3 can also serve as a second anomeric carbon leading to a mixture that could contain a minimum of fourteen simple cyclic forms, six pyranose forms (I - VI) and eight furanose forms (VII - XIV). The preparation and NMR study of the aqueous (D_2O) isomeric composition of the aldoketose "3-keto-D-glucose" (D-*ribo*-hexos-3-ulose, **4**) is the subject of this report.



I, II, (α,β) R = R = O

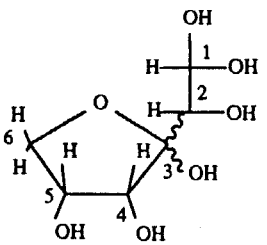
III, IV (α,β)
R = R = OH



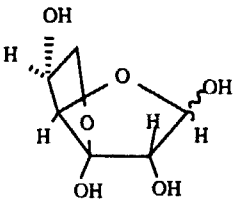


V, VI (α,β)

VII, VIII (α,β) R = R = O
IX, X (α,β) R = R = OH



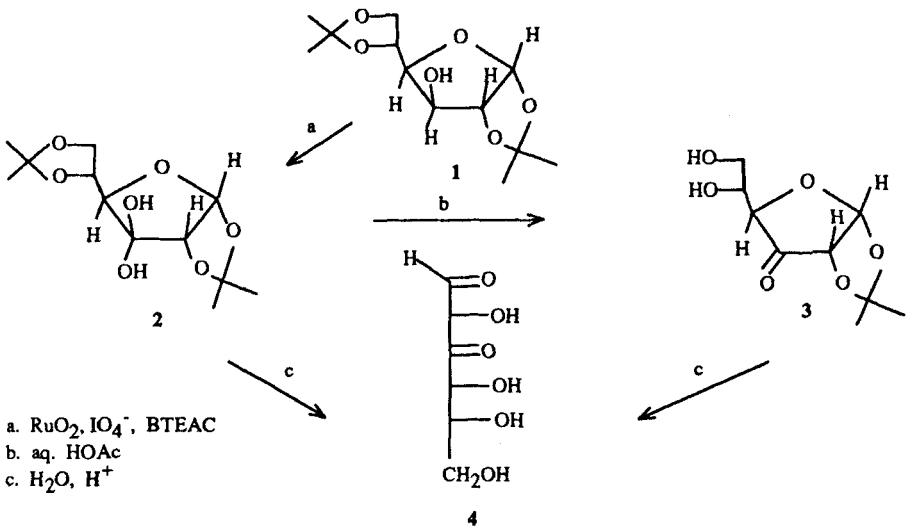
XI, XII (α,β)



XIII, XIV (α,β)

RESULTS AND DISCUSSION

1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**2**), prepared according to Baker et al.,[6] or using a phase transfer catalyst promoted ruthenium tetraoxide oxidation procedure,[7] was selectively deprotected with aqueous acetic acid to give 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**3**) as a syrup. The title compound, D-*ribo*-hexos-3-ulose (**4**,"3-keto-D-glucose") was then generated by further acidic hydrolysis of **3** at 40 °C or directly from **2** using the same procedure. An evaluation of the composition of



SCHEME 1

a freshly prepared sample of syrupy **4** in D_2O (23 °C) was then determined by ^1H NMR spectroscopy (300 MHz). The spectrum (**FIG. 2a**) showed at least ten signals in the anomeric region with four signals predominating. Peak assignments were aided by decoupling and homonuclear correlated chemical shift 2D experiments (COSY),[8] **FIG. 3.** Additional structural information was gleaned from the coupled ^{13}C NMR spectra of **4**, and from heteronuclear correlated 2D (HETCOR[9]) experiments, **FIG. 5.** The assigned structures of the isomeric forms of **4** (except **4d**) are given in **FIG. 1.**, with relative percentages in Table 1. ^1H NMR and ^{13}C NMR spectral data are presented in Tables 2 and 3, respectively.

The principal isomeric form of **4** from a freshly prepared sample is the free keto α-furanose form **4a** (44 %). That the major isomer is a furanose form is clear in that its anomeric proton (5.6 ppm) is the most deshielded which is in keeping with the general trend that furanose anomeric protons are deshielded relative to their pyranose counterparts.[10-12] The $J_{1,2}$ = 4.26 Hz coupling establishes the α-configuration at C-1. The chemical shifts of the H-2, H-4, H-5 and H-6 protons of **4a** have all been assigned, although the H-5 and H-6 protons are embedded in a very congested region of the spectrum (**FIG. 2a**). Additional coupling constants for **4a** are $J_{4,5}$ = 9.8 Hz and $J_{2,4}$ = 1.56 Hz. The second most abundant isomer (22 %) has an anomeric proton doublet at 4.77 ppm ($J_{1,2}$ = 7.93 Hz) and is assigned to the β-pyranose structure **4b**. By comparison, H-1 of β-D-glucopyranose resonates at 4.51 ppm with $J_{1,2}$ = 7.8 Hz.[14] The large $J_{1,2}$

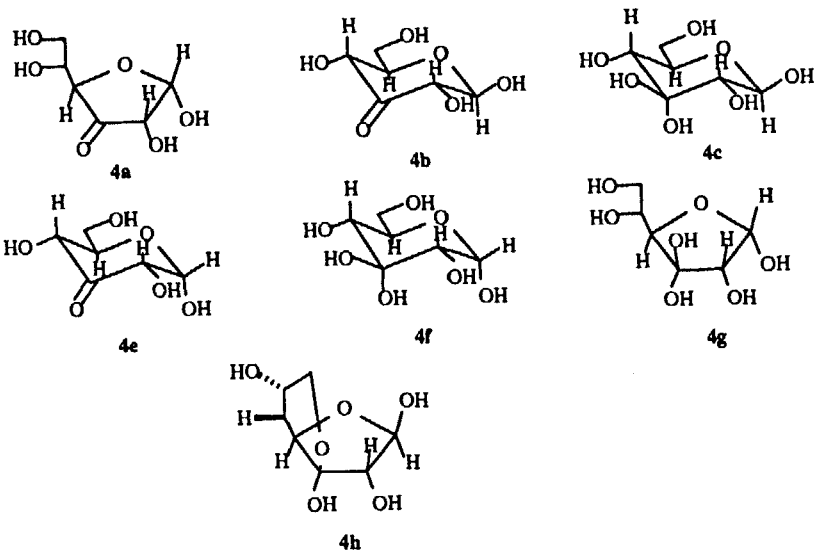


FIG. 1. Structures of the isomeric forms of 4 (except **4d**) in D_2O.

(7.93 Hz) and $J_{4,5}$ (10.3 Hz) values are consistent with the appropriate *trans*-diaxial relationships expected in such a structure. A significant long range coupling was also observed between H-2 and H-4 ($J_{2,4}$ = 1.74 Hz).

While the ^1H NMR spectrum of **4** clearly shows the dominant α-furanose and β-pyranose structures, the C-3 free keto groups of these isomers were inferred from the ^{13}C NMR spectrum of the isomeric mixture (**FIG. 4**). This spectrum contains two dominant carbonyl resonances, the larger and more deshielded resonance (209.60 ppm) being assigned to C-3 of the α-furanose form **4a**, and the smaller upfield resonance (208.46 ppm) assigned to C-3 of the β-pyranose form **4b**. The assignment of these carbonyl resonances is based upon: 1) comparison of the relative size of these two anomeric resonances with the corresponding ^1H resonances in the ^1H NMR spectrum (α-furanose > β-pyranose), 2) analogy with cyclopentanone carbonyl carbon (less shielded) versus cyclohexanone carbonyl carbon (more shielded) ^{13}C resonances.[13] In an attempt to directly assign these carbonyl carbons by looking for long range C-H coupling, their resonances were examined in the proton coupled ^{13}C spectrum. However, there was no evident long range C-H, C=O coupling, and so direct assignment of the two carbonyl resonances was not possible.

The anomeric proton of the hydrated α-furanose isomer (**4g**, 1.5%) is assigned to the doublet ($J_{1,2}$= 3.85 Hz) at 5.51 ppm, and the anomeric proton of the hydrated β-pyranose

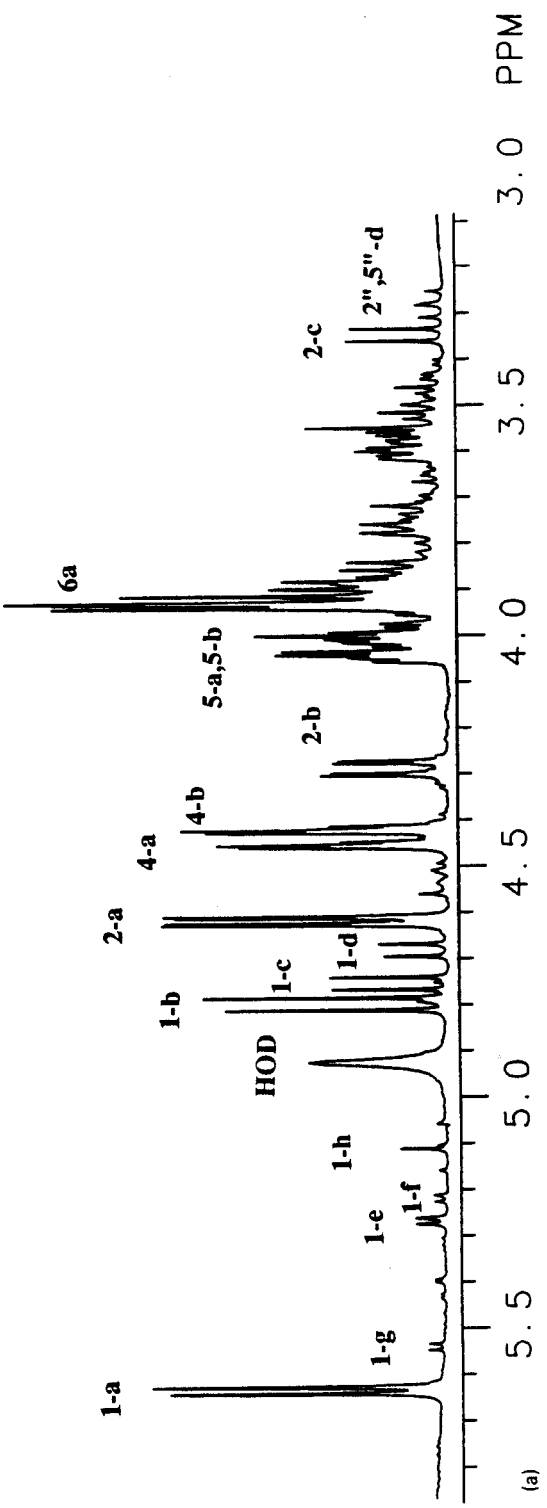


FIG. 2a. ^{1}H NMR spectrum of freshly prepared **4** in D_2O at 300 MHz. Assigned protons (numbers) and isomers (letters) are shone.

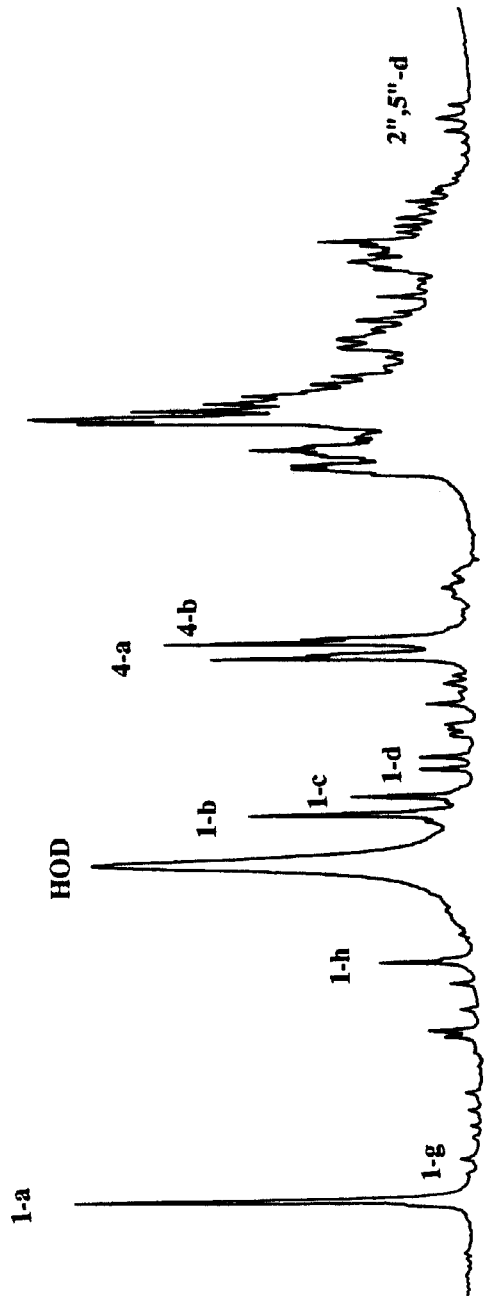


FIG. 2b. The C-2 H deuterium exchanged ^1H NMR spectrum of **4** (3 months) in D_2O at 300 MHz.

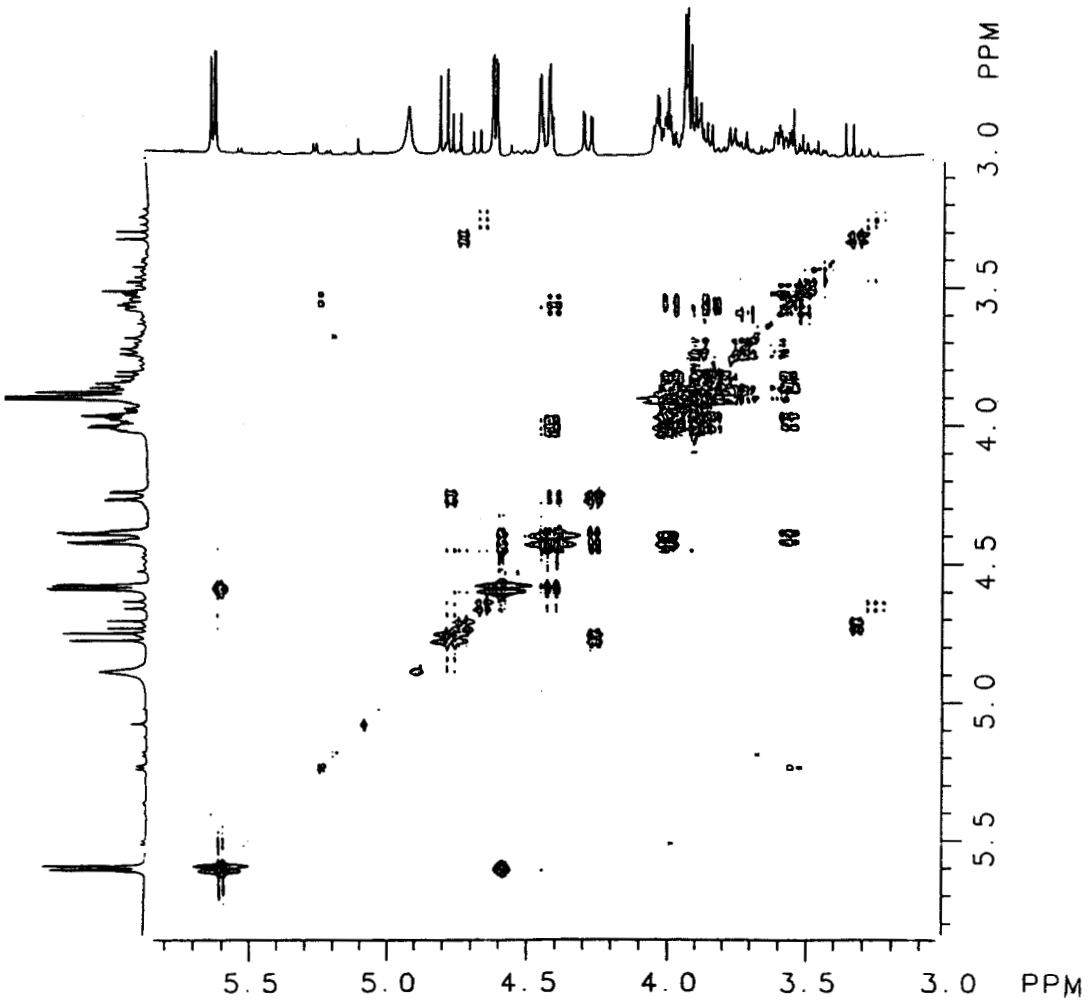


FIG. 3. Contour plot of the 2D COSY ^{1}H NMR spectrum of freshly prepared **4** in D_2O at 300 MHz.

isomer (**4c**, 12%) to the doublet ($J_{1,2}$ = 8.07 Hz) at 4.72 ppm. Interestingly, the anomeric protons of **4g** and **4c** are slightly upfield to their free carbonyl counterparts.

Whereas H-2 of **4g** was too small to be assigned, H-2 of **4c** was clearly seen as a doublet at 3.31 ppm. This value is close to the reported chemical shift of β-D-glucopyranose H-2 (δ = 3.13 ppm).[14] The hydrated β-pyranose isomer **4c**, unlike the free carbonyl isomer **4b**, shows no H-2, H-4 long range coupling. A good model system for the observed relative amounts of free carbonyl form **4b** and hydrated form **4c** is that

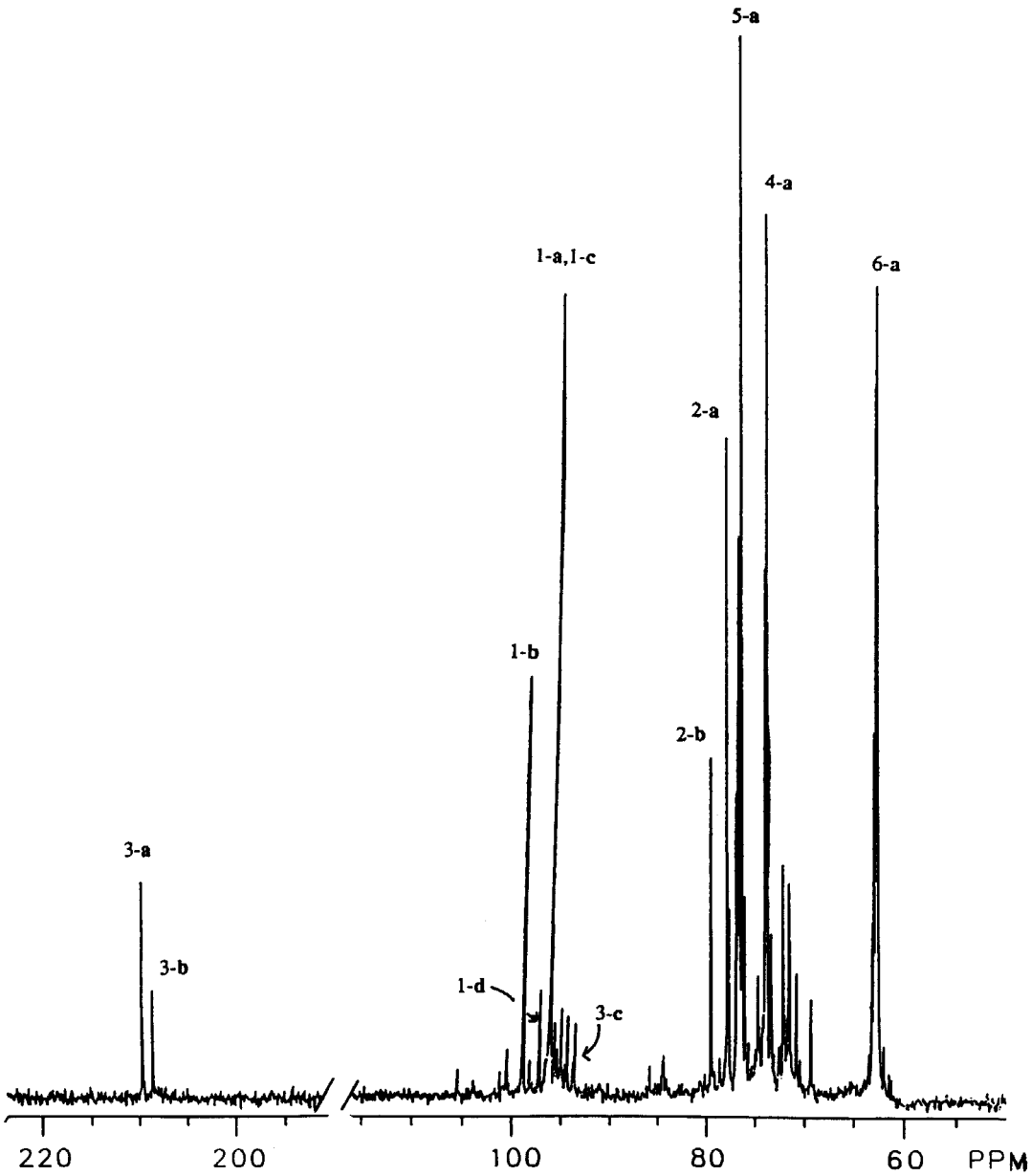


FIG. 4. Fully decoupled ^{13}C NMR spectrum of freshly prepared 4 in D_2O at 75.4 MHz. Assigned carbons (numbers) and isomers (letters) are shown.

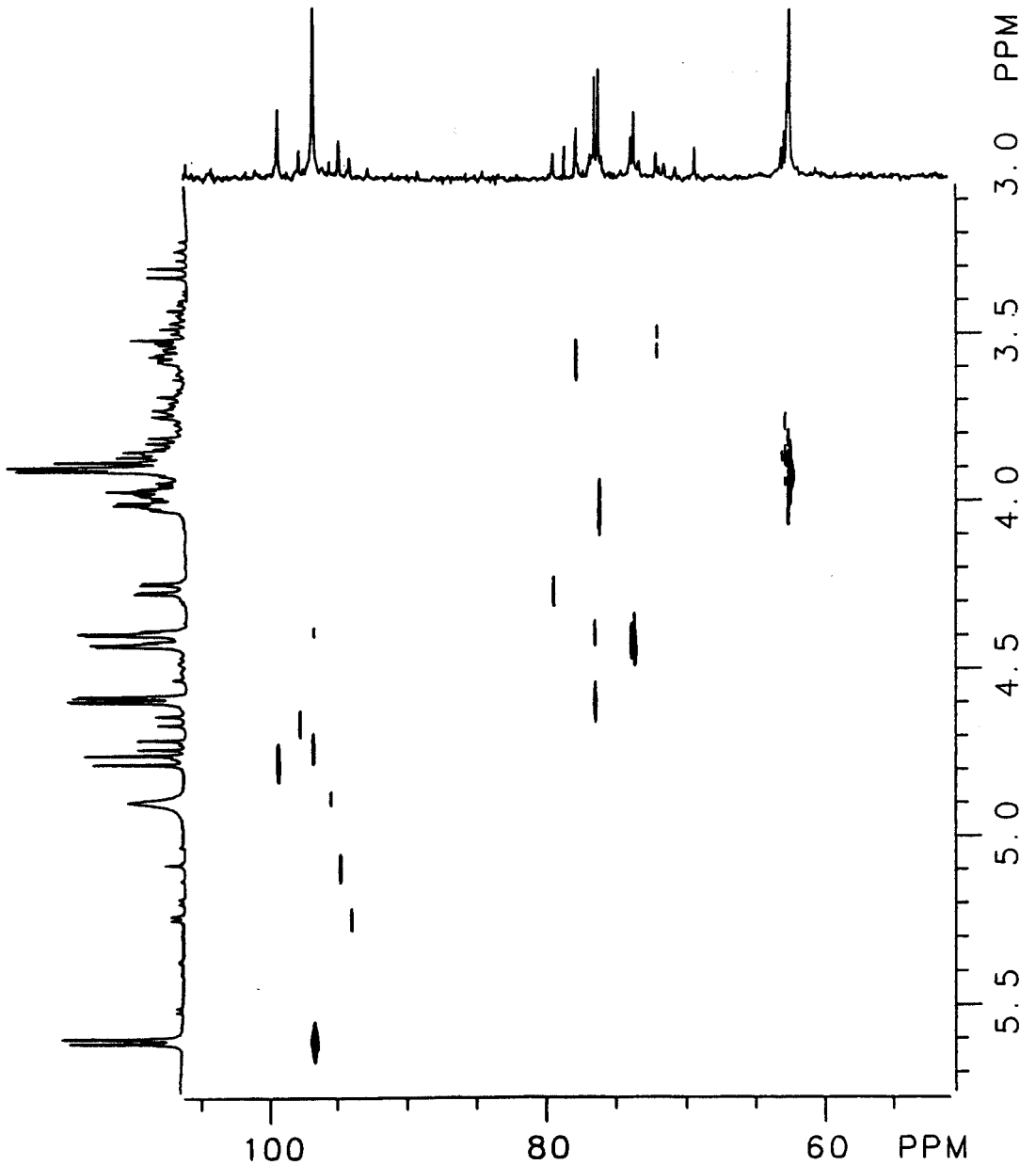


FIG. 5. Heteronuclear correlated 2D (HETCOR) spectrum of freshly prepared 4 at 300 MHz.

TABLE 1. Percentages - Isomeric Forms of 4

4a	4b	4c	4d	4e	4f	4g	4h
44	22	12	8	5	2	1.5	1

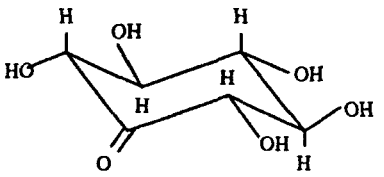
TABLE 2. ^{1}H NMR Spectral Data (D_2O) For Isomeric Forms of 4

Compound	H-1 ($J_{1,2}$)	H-2 ($J_{2,4}$)	H-4 ($J_{4,5}$)	H-5	H-6a,b
4a	5.67 d (4.26)	4.59 dd (1.56)	4.40 dd (9.8)	≈4.0m	≈3.9m
4b	4.77 d (7.93)	4.25 d (1.74)	4.40 dd (10.3)	≈4.0m	
4c	4.72 d (8.07)	3.31 d			
4d	4.65 d (7.93, 3" and 6")	3.26 d, 3.32 d (7.93, 2",5" or reverse)			
4e	5.23 d (3.77)				
4f	5.19 d (4.12)				
4g	5.51 d (3.85)				
4h	5.13 s	4.60 s			

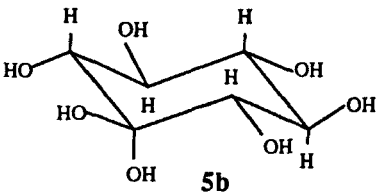
TABLE 3. ^{13}C NMR Chemical Shifts (D_2O) for Isomeric Forms of 4

Compound	C-1	C-2	C-3	C-4	C-5	C-6
4a	96.64	76.44	209.60	73.59	76.14	62.41
4b	99.31	79.42	208.46	73.80		62.6
4c	96.64	75.93	92.30			
4d	97.8					
4e	94.70					
4f	----					
4g	----					
4h	95.70					

reported for the equilibrium between *scyllo*-inosose (**5a**) and its hydrate (**5b**).[15] As with **4b** and **4c**, all non-keto ring substituents of **5a** and **5b** are equatorial. A strong correlation between the C-3 carbonyl ^{13}C NMR chemical shift values and the relative percentages of **4b** : **4c** versus **5a** : **5b** was observed: **5a** C=0 at 206-207 ppm,[15] **5b** hydrated carbonyl at 95.3 ppm[15] with **5a** : **5b** = 63 : 27; **4b** C=0 at 208.46 ppm, **4c** hydrated carbonyl at 92.30 ppm with **4b** : **4c** = 65 : 25. The hydrated C-3 of **4c** was identified as a singlet in both the proton coupled and decoupled ^{13}C NMR spectra of **4**.



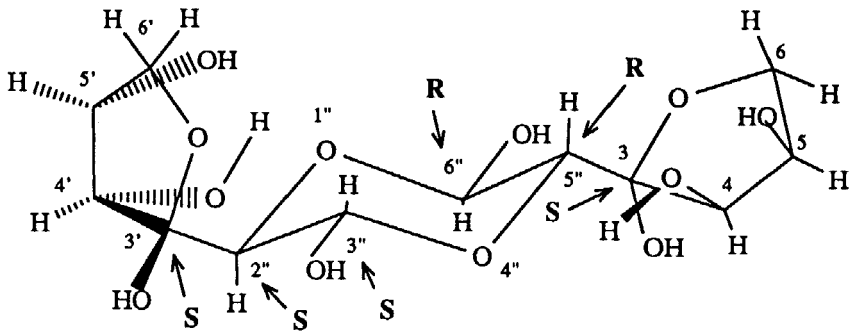
5a



5b

Two small anomeric proton doublets at 5.23 ppm ($J_{1,2}$ = 3.77 Hz) and 5.19 ppm ($J_{1,2}$ = 4.12 Hz) are assigned to free carbonyl α-pyranose isomer **4e** (5%) and the hydrated α-pyranose isomer **4f** (2%), respectively. The α-pyranose structure for these isomers is based upon comparison of the observed H-1 chemical shifts and H-1, H-2 couplings with those reported for α-D-glucopyranose (H-1, δ 5.09 ppm, $J_{1,2}$ = 3.6 Hz).[14] Assignment of free carbonyl **4e** as the more abundant isomer is based upon analogy with β-pyranose isomers **4b** and **4c**, but the **4e**/**4f** assignments may be reversed.

The remaining anomeric doublet at δ 4.65 ($J_{1,2}$ = 7.93 Hz), 8%, was more difficult to assign. The large coupling suggested a six-membered ring with the anomeric proton in a 1,2-*trans* diaxial (*anti*) relationship with H-2. This downfield doublet was coupled with two adjacent upfield doublets (3.26 and 3.32 ppm), each of which was half the intensity of the downfield doublet. These observations suggested a dimeric structure for this isomer with two magnetically equivalent anomeric protons and two magnetically nonequivalent adjacent protons. A likely structure for this isomer is the disubstituted 1,4-dioxolane, **4d**. This dimer can be formed by linking C-1 and HO-2 of one monomer (**4**) with HO-2 and C-1 of a second monomer, the large equatorial substituents being furanoid rings formed between C-3, C-6. Isomer **4d** is not symmetrical, its asymmetry coming from attachment of the two furanoid rings of identical chirality (C-3 and C-3' of the *S*-configuration) with the C-2" and C-5" dioxolane carbons of opposite chirality (*S* and *R* respectively). In spite of this overall molecular asymmetry the **4d** dioxolane anomeric protons H-3" and H-6" appear to be magnetically identical due to the symmetry of the dioxolane ring itself. This is not the case with H-2" and H-5" which are clearly



4d

diastereomeric protons. An alternate dimeric form that would also account for these results would have C-3 and C-3' with *R* stereochemistry. It is of interest that a 6,3-furanoid ring system as proposed for the dimer **4d** has previously been reported as a methyl ketal produced by treating the title compound **4** or its isopropylidene precursor **1** with methanolic HCl.[16] In addition, dimeric forms of trioses and tetroses have been previously observed using both ^1H NMR and ^{13}C NMR techniques.[17]

The spectral data and structural assignments given thus far were gleaned from D_2O solutions of freshly prepared **4**, some of which were observed to be stable for several days. However, eventually all of the samples studied began to give different, but reproducible ^1H and ^{13}C NMR spectra. Spectral changes at room temperature were slow but appeared to be complete after three months. Initially these changes were considered to be due to slow equilibration of isomeric forms[1] but a suggestion that the changes came about as a result of exchange of the doubly activated C-2 protons with deuterium provided a more plausible explanation.[18] The ^1H NMR spectrum of deuterium exchanged **4** (**FIG. 2b.**) is dominated by anomeric singlets in place of the anomeric doublets of **4a**, **4b**, and **4c**. The deuterated isomeric forms of **4** were shown to be convertible to their protiated precursors by exchange in H_2O with H^+ resin as the catalyst. It is interesting to note that the protons assigned to C-2 of the dimer **4d** were not exchanged nor were the singly activated C-4 protons of the various isomers.

One final signal for which an assignment has been made is a singlet (5.13 ppm), overlapping another resonance. The chemical shift and singlet nature of this signal suggest a β-furanose isomer. A second singlet which may correspond to H-2 of this isomer is observed at ≈ 4.56 ppm. Reasonable assignments for these singlets are the C-1 and C-2 protons of the β-furanose bicyclic structure **4h**. Precedence for this particular ring form is the already mentioned dimethyl acetal form of **4h** produced by methanolysis

of **2** or **4**.[16] The ^1H NMR spectra of freshly prepared **4** still show several very small doublets signals in the anomeric region which have not as yet been assigned. Although it is conjecture, these very minor isomeric forms may include the 6,3-anhydro forms (V, VI), the β-furanose isomers VIII and X and the ketofuranose forms (XI, XII).

SUMMARY

Acidic hydrolytic deprotection of the isopropylidene derivatives **2** or **3** produces a mixture composed of at least ten isomeric forms. Structural assignments have been made for eight of these forms, of which the α-furanose and β-pyranose C-3 free carbonyl isomers are major contributors. These non-hydrated isomers are reasonable in that hydration of the C-3 carbonyl introduces an additional destabilizing axial substituent in pyranose structures and C-3 OH, C-5,C-6 branch *cis*-interactions in furanose structures. It was surprising to not find significant amounts of β-furanose forms in the equilibrium mixture.

EXPERIMENTAL

General procedures. All chemicals and solvents were analytical grade and were used without further purification. Melting points were determined on a Fisher-Johns melting point apparatus and are reported uncorrected. Thin-layer chromatographic (TLC) analysis was performed using precoated 250 μm silica gel on glass plates from Analtech, Inc. Chromatograms were visualized by spraying with concd H_2SO_4 spray followed by heating. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a GE widebore spectrometer (NT series) equipped with a 1180e computer and 293c pulse programmer. Resonance frequencies for ^1H NMR and ^{13}C NMR were 300.1 and 75.4 MHz, respectively. ^1H and ^{13}C spectra were referenced to acetone (2.07 and 28.9 ppm) or *t*-butyl alcohol (1.30 and 31.3 ppm) and were obtained in D_2O at ambient (23 °C) temperatures. The ^1H chemical shift assignments were obtained from 2D homonuclear-correlated spectroscopy, COSY, which utilized the following pulse sequence:[8] (π/2)-(t1)-(π/2)-(FID,t2). Quadrature phase detection was employed and the transmitter was placed at 4.4. The spectral width in the F1 and F2 domains was 838 Hz and contained 1K data points. Two hundred and fifty-six spectra were acquired in 5 h. Processing involved sine multiplication in each dimension and zero filling to yield a 512 × 512 data set. The π/2 pulse was 8 μsec.

The ^{13}C chemical shift assignments were obtained from the proton decoupled spectra and proton coupled spectra and were confirmed with a 2D heteronuclear-correlated experiment (HETCOR) which ultilized the following pulse sequence:[9] ($\pi/2$,^1H)-(t1/2)-($\pi/2$,^1H)-(1/2J)-(π,^1H;π,^{13}C)-(1/2J)-($\pi/2$,^1H)-(t1/2)-(Δ_1)-($\pi/2$,^1H;$\pi/2$,^{13}C)-(Δ_2)-(FID, decoupling). Thirty two spectra were acquired in 10 h. The spectral width in the proton and carbon domains were 838 and 4166 Hz, respectively. Processing involved exponential multiplication in the F2 domain and sine multiplication and zero filling in the F2 domain. This produced a 1K x 64 point data set. The $\pi/2$ proton and carbon pulses were 34 and 32 μsec, respectively. Infrared (IR) spectra were recorded on a Beckman Acculab spectrophotometer as nujol mulls. Nafion® membrane was obtained from the Aldrich Chemical Company and is a product of Dupont. Elemental analyses were performed by Atlantic Microlab, Atlanta, Georgia.

1,2-*O*-Isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (3). 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulose hydrate (**2**, 1.0 g, 3.6 mmol) prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) by the method of Morris and Kiely[7] or Baker and co-workers[6] was stirred at room temperature for 6 h with glacial acetic acid (10 mL) and H_2O (2 mL). TLC (1 : 1 Et_2O-$CHCl_3$) showed complete conversion of **2** to the lower running diol **3**. The solvent was removed by freeze-drying to give 700 mg (2.9 mmol, 82%) of **3** as a thick straw colored syrup: IR (neat) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS) δ 6.01 (d, $J_{1,2}$ = 3.68 Hz, 1H, H-1), 4.58 (d, $J_{1,2}$ = 3.68 Hz, 1H, H-2), 4.47 (d, $J_{4,5}$ = 3.91 Hz, 1H, H-4), 4.62 (m, $J_{4,5}$ = 3.91 Hz, 1H, H-5), 4.32 and 3.76 (m, 2H, H-6a and H-6b).

Anal. Calcd for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.67; H, 6.53.

D-*Ribo*-hexos-3-ulose (4).

a) From **3**: The diol **3** (250 mg, 1.0 mmol) was dissolved in D_2O (5 mL) and placed in a vial containing a 2 cm x 2 cm piece of prepared Nafion® membrane and held at 40 °C for 8 h. The Nafion® membrane was prepared in the following manner. Holes were placed 1 cm apart in two rows with a needle on a piece of membrane 2 cm long x 2 cm wide. The membrane was then soaked in 2 N H_2SO_4 for 4 h and washed well with deionized H_2O. The membrane was stored in D_2O until used. TLC (1:1 Et_2O-$CHCl_3$) showed complete conversion of **3** to **4** as a spot at the origin. The D_2O was removed by freeze-drying to give a straw-colored glass. The sample was prepared for ^1H NMR by dissolving it in D_2O (99.8%) followed by freeze-drying three times.

b) From **2**: The 3-ulose hydrate **2** (1.0 g, 3.6 mmol) was held at 40 °C in D_2O (5 mL) for 10 h with prepared Nafion® membrane. TLC (1:1 Et_2O-$CHCl_3$) showed complete conversion of **2** to **4**. Removal of the D_2O by freeze-drying gave a straw-colored glass which was further prepared for analysis by freeze drying it three times from D_2O.

Samples of **4** for NMR analysis were prepared by dissolving the monosaccharide from procedures **a** or **b** in 0.5 mL D_2O for ^1H analysis and 1.5 mL D_2O for ^{13}C NMR analysis. Freshly prepared samples were run within an hour of dissolving **4** in D_2O and the selectively deuterated samples were prepared by allowing the samples to set at ambient temperature for 3 months.

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