The Composition of Keto Aldoses in Aqueous Solution as Determined by NMR Spectroscopy

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Keto aldoses usually form complex mixtures of equilibrating isomers in solution. This is due to the two different positions that may be used for ring closure in dicarbonyl sugars. The composition of various 2-keto aldoses **1**–**5** and **8**, the 3-keto aldose 2-deoxy-D-*erythro*-hexos-3-ulose (**9**), and the ketose 1-deoxy-D-ribulose (**10**) in aqueous solution has been determined by NMR spectroscopy. The investigated keto aldoses form equilibria containing three to fifteen isomers. Among various furanose and pyranose ring structures stemming from 1,4-, 1,5-, 2,5-, and 2,6-cyclization, bicyclic forms were also found in several cases. The 2-keto aldoses mainly exist as hydrated isomers in H_2O. Therefore, these forms and their proportions were compared to forms found in two homomorphous aldoses and one homomorphous ketose as model compounds. Besides the NMR data, also the composition of the 2-keto aldoses agreed with the average of forms found in the model compounds, a finding that might eventually be useful for deducing the composition of other keto aldoses.

1. Introduction. – The composition of carbohydrates in solution is of major importance for their chemical, physical, and biological properties. Common reducing and nonreducing sugars have been studied extensively by NMR spectroscopy, and their equilibria in H_2O are well-documented [1][2]. Aldoses and ketoses mainly form two pyranose and two furanose anomers, which are rarely accompanied by open-chain or other forms. The analysis of the NMR spectra of these common sugars is, therefore, relatively straightforward. This is not the case for carbohydrates that have a second C=O function. In keto aldoses, ring closure can take place at two different positions, and, accordingly, these compounds exist as complex mixtures of isomeric forms. For this reason, the composition of keto aldoses has been analyzed thoroughly in only a few cases [3–14].

Keto aldoses are important intermediates in biological and chemical processes. In mammals, the keto aldose D-glucosone (**1**) is believed to be formed by auto-oxidation of glucose [15] or by other processes [16], and 3-deoxy-D-glucosone (**5**) occurs in blood and urine [17] in concentrations that are elevated in diabetic patients [18]. The hexosulose **5** also plays an important role in the *Maillard* reaction [19]. The chemical interest in keto aldoses stems from the fact that they combine the high number of functional groups and the inherent information on chirality of carbohydrates that have a higher degree of diversity than normal hexoses. They are consequently very interesting synthons for a variety of chemical procedures [20–22], and some of them have been effectively used for the synthesis of antibiotics [23–26] and amino sugars [27]. Therefore, the composition in solution is of interest for both the chemistry and

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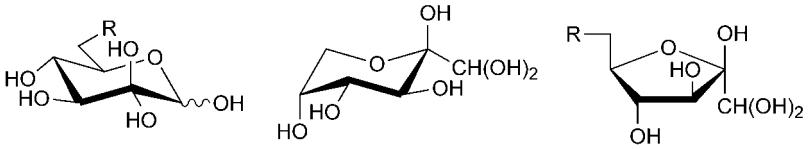
Scheme 1. *Composition of* D-*Glucosone* (**1**), *6-Deoxy*-D-*glucosone* (**2**), *and* D-*Gentiobiosone* (**3**) *in* H_2O



R = OH	**1a** α (36%)	**1c** α (21%)	**1d** (12%)
	1b β (31%)		
R = H	**2a** α (49%)		**2c** (8%)
	2b β (43%)		
R = Glc(β-1,6)O	**3a** α (60%)		**3c** (15%)
	3b β (25%)		

biology of keto aldoses. Especially the feasibility of chemical reactions suffers from the presence of manifold forms, and the knowledge about the different isomers could help to establish an attractive chemistry for keto aldoses [28].

We recently obtained a number of 2-keto and 3-keto aldoses by enzymatic oxidation [29], and we now report their solution structures as determined by NMR spectroscopy. Aqueous solutions of the investigated keto aldoses showed a profound complexity with up to ten or fifteen different forms present.

2. Results. – *Structural Assignments by NMR Spectroscopy.* The compositions of solutions of keto aldoses were determined by standard NMR methods. ^{1}H,^{1}H Connectivities were deduced from phase-sensitive DQF COSY spectra and ^{1}H,^{13}C connectivities from HMQC spectra. The analysis of 2D-correlated spectra of keto aldoses, however, is complicated because the coupling pattern of the ring is broken by the quaternary C-atom. When isomers are present in comparable amounts, the assignment of the quaternary-C-atom resonances and the ^{1}H resonances before and after the quaternary C-atom belonging to the individual isomer is often problematic. Also, the structural identification of α- and β-anomers in 2-keto aldoses is not straightforward due to the lack of J(1,2) coupling constants. We achieved both the isomeric assignments and the structural identification in most cases by evaluation of rare long-range J(H,H) coupling constants, the determination of J(C(1),H–C(1)) in coupled ^{13}C-NMR spectra, and by applying temperature changes (*e.g.*, heating to 50–70°) to enhance the intensity of the signals of minor forms.

We usually started the analysis by assigning the number of different isomers from the anomeric regions of the ^{13}C- and ^{1}H-NMR spectra as, for example, depicted in *Fig. 1* for D-allosone (**4**). The ^{13}C-NMR spectrum shows ten quaternary C-atoms, thus indicating ten different forms, but the initial ^{1}H-NMR spectrum only had nine different H–C(1) *singlets*, one of which easily separated into two upon increasing the temperature. In the HMQC spectrum (*Fig. 1*), finally ten different forms were unequivocally identified from the anomeric region of the spectrum, and analysis of the coupling pattern in H,H-COSY spectra (*Fig. 2*) was achieved for all – including the minor – forms of **4**.

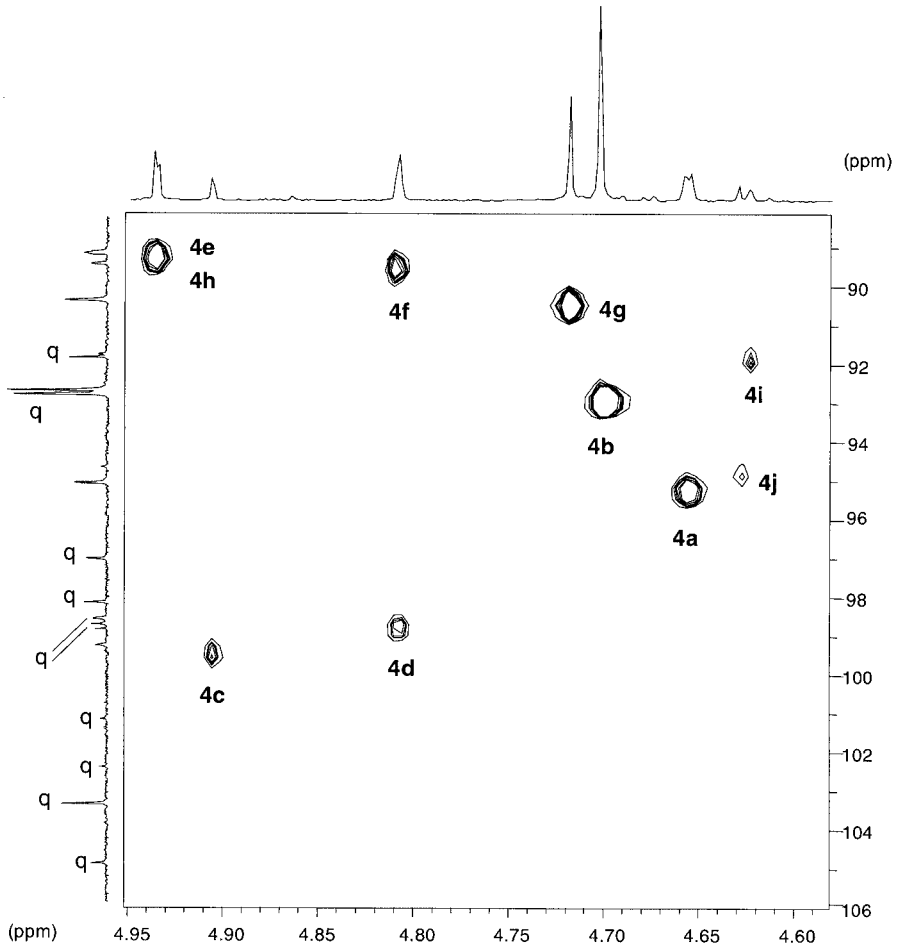


Fig. 1. *Anomeric region of the HMQC spectrum of* D-*allosone* (**4**) *showing the assignments for* C(1) *and* H–C(1) *of the ten different forms* **4a**–**4h**. At the left side, a ^{13}C-NMR spectrum with 'q' denoting the quaternary C-atoms is shown. Signals of **4e** and **4h** are separated at this temperature (300 K); signal of **4a** is a *doublet* due to a long-range $J(1,3)$ coupling.

The structural identifications in the NMR spectra of keto aldoses were accomplished by analysis of coupling constants and chemical-shift values. The latter was facilitated by comparison with known resonances for keto aldoses [3–14], aldoses, and the different isomers of model compounds [30–33]. As model compounds for the hydrated forms of the individual 2-keto aldose, we used two homomorphous aldoses and one homomorphous ketose. Thus, for D-allosone (**4**), the aldoses D-allose and D-altrose, and the ketose D-psicose (**6**) served as model compounds for the identification of different isomers. In some cases, we additionally had to determine the NMR data of these compounds.

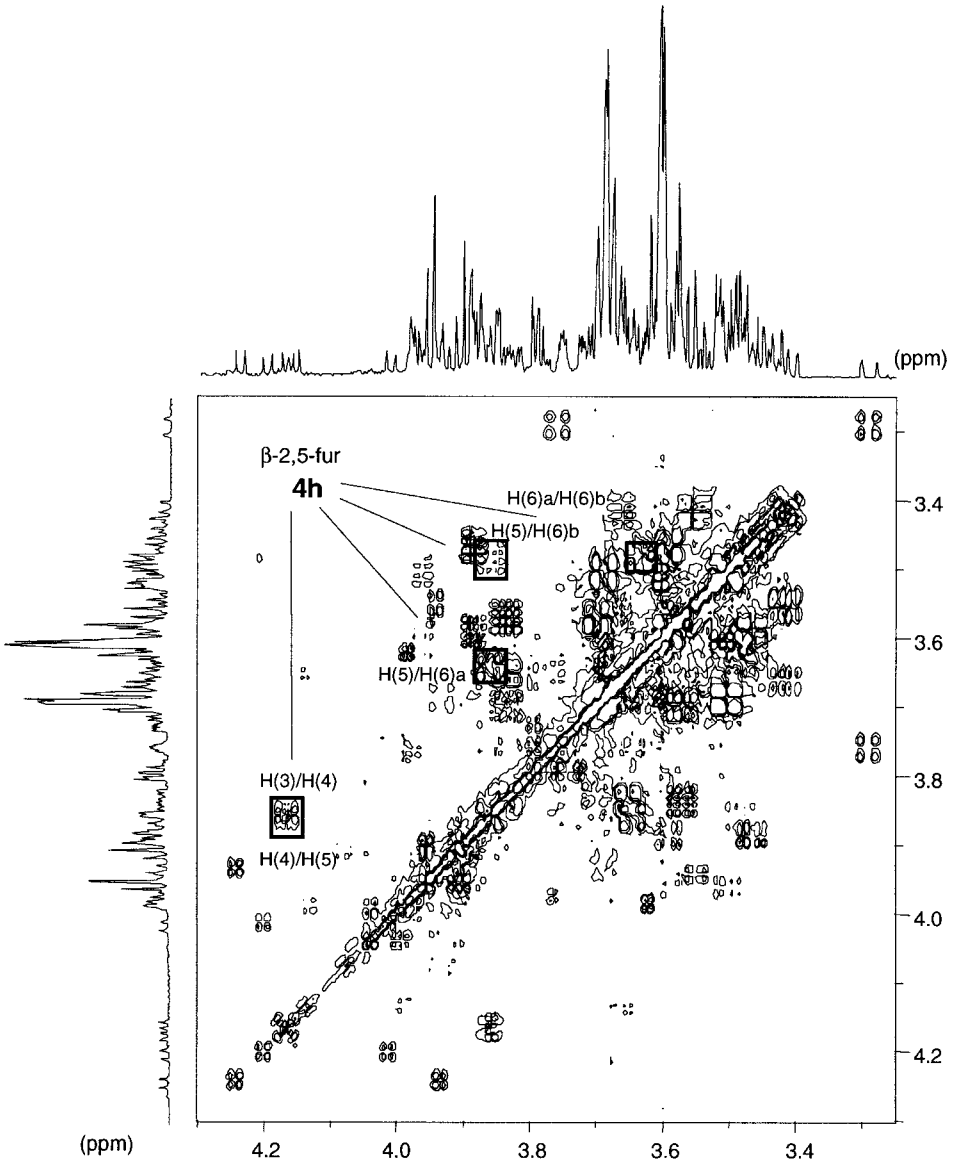


Fig. 2. *The nonanomeric region of a DQF-H,H-COSY spectrum of* D-*allosone* (**4**) *showing the assignment for the minor β-2,5-furanoid form* **4h** (6%)

Composition of Aqueous Solutions of Keto Aldoses. a) Arabino *Compounds. Shaked* and *Wolfe* [4], and later *Koths et al.* [24] found that a solution of D-*arabino*-hexos-2-ulose (D-glucosone, **1**) contained four hydrated isomers **1a**–**1d** with proportions of 48, 20, 26, and 6%, respectively, but neither paper reported the NMR data. We found an equilibrated aqueous solution of **1** to consist of the four hydrated forms

1a–**1d** in relative amounts of 36, 31, 21, and 12%, respectively (*Scheme 1*). No signals corresponding to nonhydrated forms could be detected. The slight variations in the proportions of the isomers found originally by *Shaked* and *Wolfe* might be due to different temperatures, pH, and concentrations, but most probably account for the observation that the equilibration of different forms of keto aldoses usually takes several hours in aqueous solution. In all cases, we carefully tested for the completeness of equilibration by NMR spectroscopy, sometimes accelerating this process by heating to 50°. The anomeric C(1) signals of the hydrated 1,5-pyranose forms of D-glucosone (**1**) were assigned by comparison with the data of D-glucose and D-mannose, whereas the anomeric signals of **1c** and **1d** in the range of 90 ppm correspond nicely to signals found for anomeric $CH(OH)_2$ groups and were compared to D-fructofuranose and D-fructopyranose. The complete NMR data of **1** have recently been published [34].

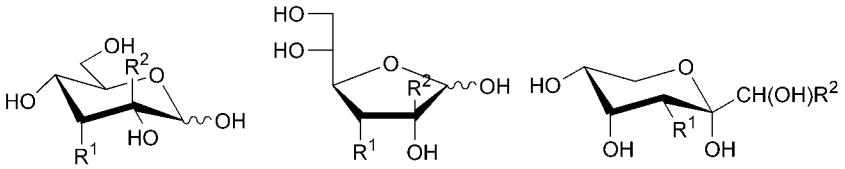
The NMR spectra of the other *arabino*-configured compounds 6-deoxy-D-*arabino*-hexos-2-ulose (6-deoxy-D-glucosone, **2**) and 6-*O*-(β-D-glucopyranosyl)-D-*arabino*-hexos-2-ulose (D-gentiobiosone, **3**) resembled those of D-glucosone (**1**). Both **2** and **3** showed comparable ratios of isomers with 1,5- and 2,5-cyclization (*Scheme 1*), *i.e.*, the most abundant forms were the α-1,5-pyranose (**2a** and **3a**) and β-1,5-pyranose structures (**2b** and **3b**), with minor amounts of β-2,5-furanose compounds (**2c** and **3c**). Due to the lack of a OH group at C(6), neither **2** nor **3** is able to form 2,6-pyranoidic compounds (as **1c**).

b) Ribo- *and 3-Deoxy Compounds.* Inversion of the *arabino*-compounds at C(3) to an axial 3-OH configuration (D-*ribo*-hexos-2-ulose, D-allosone, **4**) or deoxygenation (3-deoxy-D-*erythro*-hexos-2-ulose, 3-deoxy-D-glucosone, **5**) resulted in much more complicated equilibrium compositions (*Scheme 2*). Interestingly, both keto aldoses form the same species and ten isomers in aqueous solution (**4a**–**4j** and **5a**–**5j**).

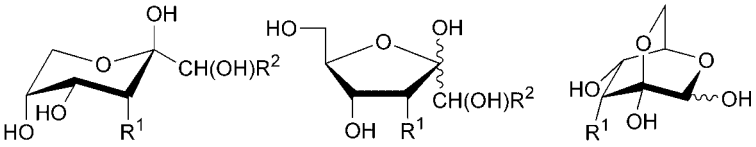
The 1,5-pyranose- and 1,4-furanose-ring forms show the characteristic ^{13}C-NMR resonances. The anomers of the 1,5-pyranose structures were assigned on the basis of their J(C(1),H–C(1)) (169.0 and 163.6 Hz for **4a** and **4b**, 167.5 and 162.1 Hz for **5a** and **5b,** resp.). Both forms **4a** and **5a** additionally exhibit a characteristic long-range W-coupling of $J(1,3(e)) = 1.3$ Hz, confirming the assignment. Four ^{13}C-signals were observed within a range of 1.5 at *ca.* 90 ppm. They were characteristically assigned to two 2,6-pyranose (**4e** and **4f**) and two 2,5-furanose forms (**4g** and **4h**). Evidence for the furanoid forms **4g** and **4h**, however, was given by the chemical shifts of the corresponding C(2)-atoms (103.42 and 105.00 ppm) and the C(5)-atoms (around 83 ppm). The data of the 1,4-furanose anomers **4c** and **4d** are very similar to the data of 1,4-furanose ring structures observed for D-ribosone [6], whereas the data for the isomers **4e**–**h** formed by ring closure at C(2) closely resemble those of the corresponding isomers of the ketose D-psicose (**6a**–**6d**, *Scheme 2*). The composition and the ^{13}C-NMR data of **6** have been described [31][32][35][36]; we additionally assigned the ^{1}H-NMR spectrum for comparison purposes.

The NMR spectra of the 3-deoxy compounds **5a**–**5h** are comparable to those of D-allosone (**4**) and were assigned accordingly. The NMR data of 1,4- and 1,5-cyclized forms of 3-deoxy-D-glucosone (**5a**–**5d**), moreover, are in agreement with the ^{1}H- [37] and ^{13}C-NMR data [38], and the composition [37] of 3-deoxy-D-*ribo*-hexose (3-deoxy-D-glucose (**7**); *Scheme 2*). The ^{1}H-NMR data were assigned by us, whereas, for the 2,5-

Scheme 2. *Composition of* D-*Allosone* (**4**) *and 3-Deoxy*-D-*glucosone* (**5**) *in* H_2O, *and Isomers of* D-*Psicose* (**6**) *and 3-Deoxy*-D-ribo-*hexose* (**7**)



$R^1 = R^2 = OH$	**4a** α (12%) **4b** β (36%)	**4c** α (4%) **4d** β (5%)	**4e** (6%)
$R^1 = H, R^2 = OH$	**5a** α (18%) **5b** β (11%)	**5c** α (4%) [a] **5d** β (2%) [a]	**5e** (3%)
$R^1 = OH, R^2 = H$			**6a**
$R^1 = R^2 = H$	**7a** α **7b** β	**7c** α **7d** β	



$R^1 = R^2 = OH$	**4f** (7%)	**4g** α (18%) **4h** β (6%)	**4i** α (3%) **4j** β (3%)
$R^1 = H, R^2 = OH$	**5f** (29%)	**5g** α (13%) **5h** β (10%)	**5i** α (4%) **5j** β (6%)
$R^1 = OH, R^2 = H$	**6b**	**6c** α **6d** β	

[a]) Assignments can be exchanged.

and 2,6-cyclized forms **5e**–**5h**, the data of 3-deoxy-D-*erythro*-hex-2-ulose (3-deoxy-D-fructose) [39][40] were helpful.

c) *Structural Assignment of Bicyclic Structures.* Besides the furanoid and pyranoid forms **a**–**h**, D-allosone (**4**) and 3-deoxy-D-glucosone (**5**) form bicyclic intramolecular hemiacetals (**4i** and **4j**, and **5i** and **5j**) in small amounts. The proportions of these structures may, however, increase significantly in other solvents (unpublished data). Similar bicyclic forms have been reported to occur in methyl glycosides of D-glucosone and D-gulosone [41], and in isopropylidene derivatives of D-galactosone and methyl α- and β-D-galactosone [42][43]. We also observed such structures in solutions of D-glucosone (**1**), D-allosone (**4**), and isopropylidene derivatives of D-allosone in organic solvents [29]. The composition of **5** has already been discussed by *Weenen* and *Tjan* [10]. Although the NMR data of their major component agree with our data, the

structural assignments differ considerably. Whereas *Weenen* and *Tjan* assumed bicyclic forms to prevail, we found the bicyclic forms **5i** and **5j** in amounts of only 10%.

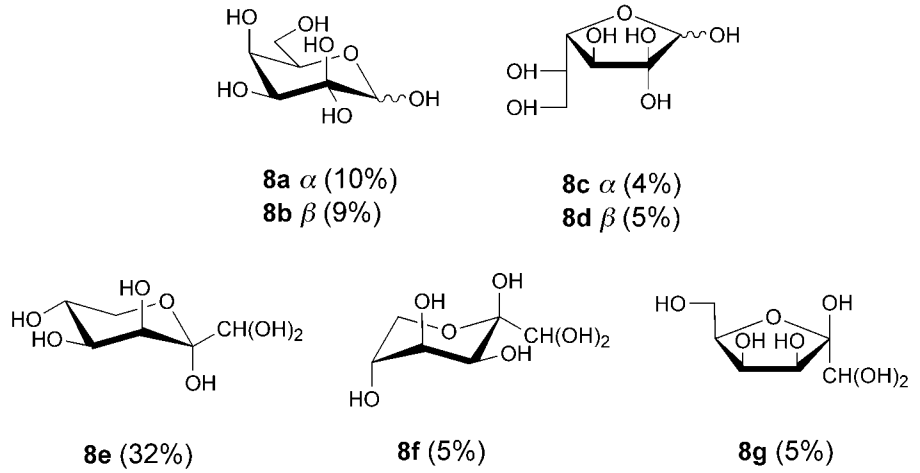
All hemiacetal bicyclic structures show characteristic chemical shifts and coupling constants, which we used for identification. The C(2)-atoms exhibit a downfield shift to 101 – 104 ppm. This is a typical shift for hemiacetal structures, which would also be expected to occur in 2,5-furanose forms; however, the C(3)-atoms of the hemiacetal structures resonate relatively upfield (at 67.63 and 69.98 ppm in the bicyclic derivatives **4i** and **4j** *vs.* 70.52 and 75.29 ppm in the furanose compounds **4g** and **4h**). The same is true for the 3-deoxy β-derivative **5j** (39.21 ppm), whereas the C(3)-atom of the α-anomer **5i** is strongly influenced by the α-anomeric configuration (42.59 ppm), a feature also observed in the data of 3-deoxy-D-glucose [37]. The bicyclic structures, moreover, show downfield shifts of the C(5)-atoms, and the C(6) positions prove to be extremely sensitive to the anomeric configuration, *i.e.*, the ^{13}C-NMR shifts of C(6) of both anomers show remarkable differences of *ca.* 6 ppm. A comparable influence on the chemical shifts and the very characteristic sensitivity for the anomeric configuration are detected also in the ^{1}H-NMR spectra. From the H,H coupling constants, it is evident that the bicyclic hemiacetal structures adopt slightly distorted boat conformations: J(4,5) is *ca.* 0 Hz, and the two small coupling constants J(5,6a) and J(5,6b) of 1 – 2 Hz point to a pure *gg* conformation at the C(5)/C(6) torsion. Our assignment for the anomers is based on the coupling constants J(C(1),H–C(1)) for **4i** (166.0 Hz) and **4j** (164.0 Hz), and for **5i** (167.9 Hz) and **5j** (164.3 Hz), although the differences between the anomers are rather small due to the boat conformation. Similar spectroscopic features were, however, observed for the bicyclic structure of D-glucosone (**1**) in organic solvents (unpublished data) and other bicyclic hemiacetals [7][29][41][43].

d) D-*Galactosone.* D-lyxo-*Hexos-2-ulose* (D-Galactosone, **8**) shows the most-complicated NMR spectra of all here examined keto aldoses. The spectra did not even allow determination of the exact number of isomeric forms. Presumably, 15 to 18 components exist in aqueous solution; seven major forms representing 70% of the solution could be assigned structurally (*Scheme 3*). The anomeric 1,5-pyranoses **8a** and **8b** were again identified through their coupling constants J(C(1),H–C(1)) (169.0 for α- and 162.3 Hz for the β-anomer). Due to the low proportions of the 1,4-furanoid forms **8c** and **8d**, it was not possible to completely determine their NMR data. The assignment of the isomers formed by ring closure at C(2), **8e** – **8g**, is complete and in accordance with the corresponding isomers of D-tagatose [21][31][32][44]. Approximately 30% of the solution was not identified and consists of up to ten different isomeric forms of **8** containing, surprisingly, also nonhydrated forms (^{13}C-NMR shifts of *ca.* 205 ppm). An increase in temperature leads to a simplification of the NMR spectra: at 70° *ca.* 85% of the solution is made by nine different isomers representing each more than 5% of the solution.

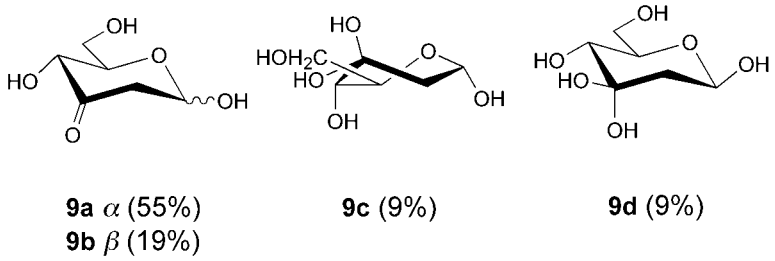
In addition to the 2-keto aldoses presented, we determined the composition of the 3-keto aldose 2-deoxy-D-*erythro*-hexos-3-ulose (**9**) and the pentoketose 1-deoxy-D-ribulose (**10**).

e) *2-Deoxy*-D-erythro-*hexos-3-ulose.* An aqueous solution of the 3-keto aldose **9** contains seven or eight isomers; four of these forms, **9a** – **9d** were identified and comprise 92% of the solution (*Scheme 4*). They consist of only pyranose structures with the nonhydrated anomers **9a** and **9b** prevailing (74%). It was already observed for

Scheme 3. *Composition of* D-*Galactosone* (**8**) *in* H_2O



Scheme 4. *Composition of 2-Deoxy-3-keto-*D-*glucose* (**9**) *in* H_2O



other 3-keto aldoses that forms with a free keto group prevail in H_2O [5][41]. This is also the case for the 'precursor' compound 3-keto-D-glucose, but unlike **9**, the latter favors furanose structures [5].

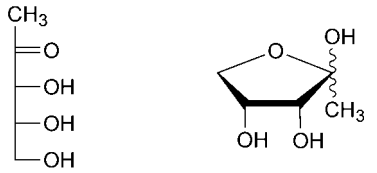
The analysis of the pyranose forms of **9** was straightforward, since both ^{1}H- and ^{13}C-NMR data are quite characteristic. Interestingly, the hydrated α-pyranose **9c** adopts a slightly distorted $^{O}T_4$-conformation as evidenced by the coupling constants $J(1,2qe) = 1.3$, $J(1,2qa) = 5.6$, and $J(4,5) = 3.0$ Hz. Obviously, **9c** avoids an unfavorable 1,3-diaxial interaction between the OH groups at C(1) and C(3) in a $^4C_1$-conformation.

We furthermore observed that the 2-deoxy-3-keto compound **9** easily exchanges its $CH_2(2)$ protons. After 24 h in D_2O, the ^{1}H-NMR signals of the deoxy protons of **9** had disappeared completely, and the proportions of the C(2)-deuterated isomers **9a**–**9d** were 46, 19, 12, and 14%, respectively. This kind of C,H acidity has already been reported, although in a much slower reaction, for 3-keto-D-glucose [5].

f) *1-Deoxy-*D-*ribulose.* Although 1-deoxy-D-ribulose (**10**) is a ketose, we wish to describe its equilibrium composition in H_2O, since we obtained this compound during the same investigations of enzymatic oxidation that led to the keto aldoses described here [29]. In 1977, *Horton* and co-workers already reported that 1-deoxyribulose (**10**)

consists of a 2:1:1 mixture of isomers in DMSO, however, without being able to identify the structures [45]. We also found a mixture of three components for **10** (*Scheme 5*). Surprisingly, the open-chain form **10a** was assigned to be the major isomer besides minor amounts of the anomeric furanose structures **10b** and **10c**. A predominant formation of the open-chain form was already observed for 1-deoxy-D-xylulose [46].

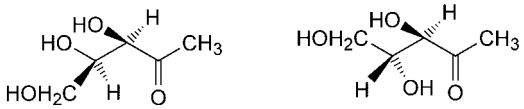
Scheme 5. *Composition of 1-Deoxy-*D*-ribulose* (**10**) *in* H_2O



10a (72%) **10b** α (14%)
10c β (14%)

The coupling constant $J(3,4) = 4.9$ Hz in the open-chain form **10a** is very small for a pure conformation with a favorable antiperiplanar orientation of C(2) and C(5) ($^2G_+$ in *Scheme 6*), and thus an *anti* orientation of H–C(3) and H–C(4) [33]. Indeed, *Vuorinen* and *Serianni* already found in solutions of D-ribulose that the other stable conformer ($^2G_+$ and $^3G_+$) with a *gauche* relationship and a small coupling constant for $J(3,4)$ prevailed [47]. On the basis of the same data, we estimate the relative populations of $^2G_+$ and $^3G_+$, and the $^3G_+$ conformer in the open-chain form **10a** to be 77 and 23%, respectively.

Scheme 6. *Conformations of The Open-Chain Keto Forms* **10a** *of 1-Deoxy-*D*-ribulose*



$^2G_+$, $^3G_+$ $^2G_+$

(77%) (23%)

3. Discussion. – Although the first 2-keto aldose was already synthesized in 1889 by *Emil Fischer* [48], the exact structure in solution could, for a long time, only be assumed. About 50 years ago, several researchers attempted to describe possible equilibrium isomers [49–51], but the analytical methods at that time were not sufficient to confirm these considerations. Only after the establishment of powerful NMR methods have more and more keto aldoses been structurally elucidated [3–14].

A common interpretation of the observed isomeric equilibria, however, has not yet been given. In this work, we enhance the knowledge of some so far structurally undescribed 2-keto aldoses. By combining our new data and those known from the literature, it is now possible to present a general explanation for the equilibrium compositions in aqueous solutions of 2-keto aldoses.

It is well-established that, in hexoses, pyranose forms are more stable than furanose forms, and that pyranose forms of ketoses are less stable than those of aldoses. Consequently, we find pyranose forms to be the main isomers in all investigated compounds. Increased proportions of furanose forms compared to the *arabino*-derivatives D-glucosone (**1**), 6-deoxy-D-glucosone (**2**), and D-gentiobiosone (**3**) are found, however, for D-allosone (**4**), 3-deoxy-D-glucosone (**5**), and D-galactosone (**8**) (*Table 1*). The latter account for the fact that furanose stabilities are mainly governed by interactions between vicinal *cis*-substituents [1]. The higher proportions of 1,4-furanose compounds in **4**, **5**, and **8** compared to the D-glucose-derived compounds **1**, **2**, and **3** are formed because of the lack of unfavorable *cis* interactions between the 3-OH group and the bulky C(5)–C(6) side chain. This effect is even much more pronounced in the furanose forms with C(2) cyclization, which show proportions of 24 (**4g** and **4h**) and 23% (**5g** and **5h**) due to the absence of *cis*-interactions between the 4-OH group and the C(6) side chain. Generally, the C(2)-cyclized forms are more expressed in the hexosuloses **4**, **5**, and **8** than in the *arabino* derivatives **1**, **2**, and **3**. Due to the stability of their 2,6-pyranoses, these compounds are even the main forms for **5** and **8** (*Table 1*).

Table 1. *Isomers of Keto Aldose in Water at 300 K*

	Proportion [%] of										
	1,5-pyr		1,4-fur		2,6-pyr		2,5-fur		Bicyclic		Other
	α	β	α	β	α	β	α	β	α	β	forms[a])
D-Glucosone (**1**)	36	31				21		12			
6-Deoxy-D-glucosone (**2**)	49	43						8			
D-Gentiobiosone (**3**)	60	25						15			
D-Allosone (**4**)	12	36	4	5	6	7	18	6	3	3	
3-Deoxy-D-glucosone (**5**)	18	11	4[b])	2[b])	3	29	13	10	4	6	
D-Galactosone (**8**)	10	9	4	5	32	5		5			30
2-Deoxy-D-*erythro*-hexos-3-ulose (**9**)	64	28									8

[a]) Unidentified forms. [b]) Assignments may be exchanged.

In all cases where the aldehyde group is used for cyclization, the keto group at C(2) was observed to be hydrated in H_2O as solvent. This is due to the inductive effect of the anomeric center, which increases the electrophilicity of the C(2) group. Only in the case of the 3-keto aldose **9** do forms with the nonhydrated keto group prevail in H_2O, which is in agreement with similar observations for other 3-keto derivatives [5][41].

We already mentioned that we used the similarity of model compounds, namely two homomorphous aldoses and one homomorphous ketose, for the verification of NMR structural assignments. For example, hydrated D-glucosone with both an axial and an equatorial OH group at C(2) (**1a**, and **1b**, resp.) may be compared to the aldoses D-glucose and D-mannose, and the 2,6-cyclized form **1c** to the ketose D-fructose

(*Scheme 7*). This comparison reveals not only similar NMR data, but, additionally, similar forms with comparable proportions in aqueous solution, which is easily demonstrated by comparing the relative proportions of C(1)-cyclized forms to the model aldoses and of C(2)-cyclized forms to the model ketose (*Table*s *2* and *3*).

Scheme 7. D-*Glucosone* (**1**) *and the Model Compounds*

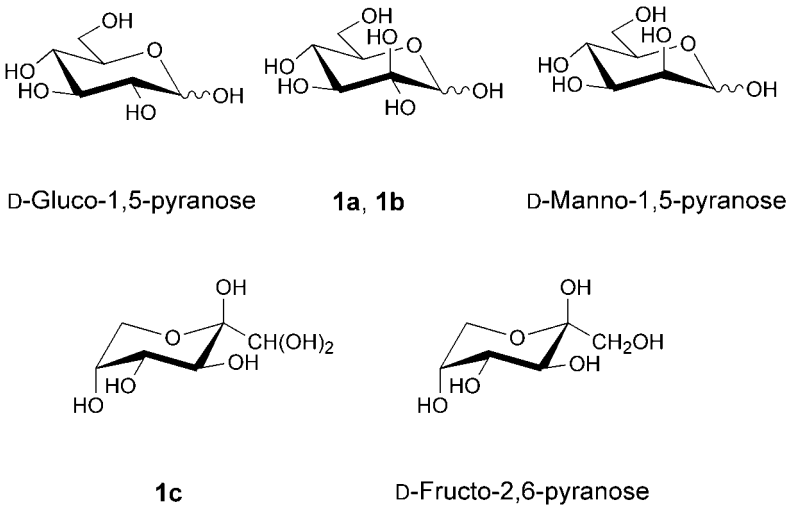


Table 2. *Relative Ratios of* C(1)-*Cyclized Forms*

	Relative ratio [%]			
	1,5-pyr		1,4-fur	
	α	β	α	β
D-Glucose [52]	37	63	–	
D-Glucosone (**1**)	54	46	–	
D-Mannose [52]	67	33	–	
6-Deoxy-D-glucose [37]	36	64	–	
6-Deoxy-D-glucosone (**2**)	53	47	–	
6-Deoxy-D-mannose [52]	60	40	–	
D-Allose [52]	15	85	41	59
D-Allosone (**4**)	25	75	44	56
D-Altrose [52]	39	61	57	43
3-Deoxy-D-glucose [37]	31	69	24	76
3-Deoxy-D-glucosone (**5**)	62	38	67	33
3-Deoxy-D-mannose [53]	64	36	100	–
D-Galactose [52]	32	68	32	68
D-Galactosone (**8**)	53	47	44	56
D-Talose [52]	58	42	61	39
D-Ribose [52]	31	69	36	64
D-Ribosone [6]	35	65	43	57
D-Arabinose [52]	68	32	59	41
D-Xylose [52]	37	63	–	
D-Xylosone [6]	67	33	–	
D-Lyxose [52]	71	29	–	

Table 3. *Relative Ratios of* C(2)*-Cyclized Forms*

	Relative ratio [%]			
	2,6-pyr		2,5-fur	
	α	β	α	β
D-Glucosone (**1**)	0	64	0	36
D-Fructose [1]	3	72	5	20
D-Allosone (**4**)	16	19	49	16
D-Psicose (**6**) [32]	22	24	39	15
3-Deoxy-D-glucosone (**5**)	5	53	24	18
3-Deoxy-D-fructose [40]	5	57	22	16
D-Galactosone (**8**)	76	12	0	12
D-Tagatose [21]	79	14	2	5
D-Ribosone [6]	–		83	17
D-Ribulose [54]	–		75	25
D-Xylosone [6]	–		16	84
D-Xylulose [54]	–		23	77

As depicted in *Table 2*, we found in all investigated 2-keto aldoses, and in published data for the pentos-2-uloses D-ribosone and D-xylosone [6] that the relative ratios of anomers of 1,5-pyranose and 1,4-furanose forms are intermediate between those of the two model aldoses. This seems to be logical, since the only difference in each of the model aldoses is an additional OH group at C(2). An unfavorable *gauche* interaction between an additional axial OH group at C(2) and the anomeric OH group decreases the proportion of the β-anomer in favor of the α-anomer compared to the model aldose with an equatorial OH group at C(2). On the other hand, the proportion of the α-1,5-pyranose anomer should be smaller than that of the homomorphous aldose with an axial OH group at C(2) due to the *gauche* interaction between the additional equatorial OH group and the anomeric OH group. Similar considerations hold true for the anomeric ratios of 1,4-furanose forms.

Likewise, the relative ratios of anomeric 2,6-pyranose and 2,5-furanose forms of 2-keto aldoses resemble the values for the model ketose (*Table 3*). It is, therefore, evident that the steric and electronic influence of the additional OH group is negligible due to its exocyclic position.

The relationship between the composition of a 2-keto aldoses, and that of its model aldoses and ketoses in all cases shown here might eventually be used to roughly predict the composition of aqueous solutions of other keto aldoses. We are aware that this does not include 'unusual' forms such as bicyclic structures found especially in D-allosone (**4i** and **4j**) and 3-deoxy-D-glucosone (**5i** and **5j**), as well as open-chain or dimeric forms [55].

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Experimental Part

The keto aldoses were obtained by enzymatic oxidation of the corresponding aldoses [29][56]. Elemental analysis established the purity of the compounds [29]. 3-Deoxy-D-*ribo*-hexose (**7**) was synthesized from 1,2 : 5,6-

di-*O*-isopropylidene-D-glucofuranose [57]. Aq. solns. of sugars were equilibrated for 1 d at ambient temp. NMR Spectra were recorded on a *Bruker AMX-500* spectrometer at 500.14 MHz for ^{1}H and 125.76 MHz for ^{13}C at 300 K, applying standard 1D and 2D spectroscopy (gated decoupling, phase-sensitive, and DQF-COSY, TOCSY, HMQC). Chemical shifts δ are given in ppm and are referenced to internal acetone ($\delta = 2.030$ and 30.50 ppm) for D_2O as solvent. Coupling constants J are given in Hz. CH_2 H-Atoms are designated as 'a' and 'b' with 'a' being the downfield shifted H-atom. For NMR data, see *Tables 4–11*.

Table 4. *^{1}H-NMR Data of 6-Deoxy*-D-arabino-*hexos-2-ulose* (**2**) *and 6*-O-*(β*-D-*Glucopyranosyl)*-D-arabino-*hexos-2-ulose* (**3**) *in D_2O* (n.d.: not determined)

	H–C(1) *J*(3,4) H–C(1′) *J*(1′,2′)	H–C(3) *J*(4,5) H–C(2′) *J*(2′,3′)	H–C(4) *J*(5,6a) H–C(3′) *J*(3′,4′)	H–C(5) *J*(5,6b) H–C(4′) *J*(4′,5′)	H_a–C(6) *J*(6a,6b) H–C(5′) *J*(5′,6′a)	H_b–C(6) H_a–C(6′) *J*(5′,6′b)	 H_b–C(6′) *J*(6′a,6′b)
2a	4.684	3.502	3.089	3.736	1.067		
	9.7	9.6	6.3				
2b	4.468	3.278	3.044	3.298	1.093		
	9.5	9.5	6.2				
2c	4.711	3.946	3.632	3.605	1.120		
	7.8	7.8	6.0				
3a	4.745	3.556	3.393	3.842	3.958	3.698	
	9.3	10.1	1.9	5.5	11.6		
	4.309	3.123	3.310	3.193	3.270	3.723	3.527
	7.9	9.4	9.4	9.4	2.0	5.7	12.4
3b	4.510	3.343	3.330	3.437	4.004	3.648	
	9.5	AB	1.5	5.8	12.3		
	4.319	3.123	n.d.	n.d.	n.d.	n.d.	n.d.
	8.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3c	4.740	3.995	3.899	3.753	n.d.	n.d.	
	7.8	8.3	n.d.	n.d.	n.d.		
	4.336	3.123	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 5. *^{13}C-NMR Data of 6-Deoxy*-D-arabino-*hexos-2-ulose* (**2**) *and 6*-O-*(β*-D-*Glucopyranosyl)*-D-arabino -*hexos-2-ulose* (**3**) *in D_2O*

	C(1) C(1′)	C(2) C(2′)	C(3) C(3′)	C(4) C(4′)	C(5) C(5′)	C(6) C(6′)
2a	94.79	93.93	73.51	74.29	68.10	17.01
2b	95.14	93.38	76.29	74.00	72.18	17.01
2c	90.41	100.69	75.73	79.84	76.41	18.86
3a	94.80	93.70	73.67	68.77	71.14	69.08
	102.88	73.30	75.80	69.85	76.09	60.95
3b	95.24	93.13	76.42	68.63	75.04	69.05
	102.88	73.30	75.80	69.85	76.09	60.95
3d	90.18	101.24	75.80	75.04	81.17	n.d.
	102.88	73.30	75.80	69.85	76.09	60.95

Table 6. *^{1}H-NMR Data of* D-ribo-*Hexos-2-ulose* (**4**), D-*Psicose* (**6**)[a]), *and* D-lyxo-*Hexos-2-ulose* (**8**) *in D_2O*

	H_a–C(1) H_b–C(1)	H–C(3) *J*(1a,1b)	*J*(3,4)	H–C(4)	*J*(4,5)	H–C(5)	*J*(5,6a)	*J*(5,6b)	H_a–C(6)	*J*(6a,6b)	H_b–C(6)
4a	4.658[b])	3.691	3.5	3.651	10.1	3.833	2.5	6.0	3.689	12.2	3.570
4b	4.705	3.687	3.2	3.605	*AB*	3.603	1.3	5.9	3.687	12.1	3.506
4c	4.910	3.797	*AB*	3.790	n.d.	3.657	3.5	6.9	3.547	12.0	3.416
4d	4.811	3.941	7.4	3.550	n.d.	3.657	3.5	6.9	3.560	12.0	3.416
4e	4.939	3.650[c])	n.d.	3.981	5.5	3.618	5.7	1.3	3.603[d])	n.d.	3.473[e])
4f	4.811	3.722[f])	3.2	3.789	3.5	3.752	1.4	3.7	3.861	12.6	3.641
4g	4.721	3.951	5.6	3.898	5.6	3.881	2.6	4.8	3.590	12.7	3.466
4h	4.939	3.857	4.6	4.162	8.0	3.858	3.1	6.0	3.636	12.5	3.484
4i	4.626	3.929	6.5	4.238	0.0	3.982	2.1	1.0	3.762	12.0	3.289
4j	4.632	4.011	6.5	4.179	0.0	3.943	2.3	2.3	3.576	*AB*	3.576
6a	3.482	3.501	2.5	4.000	2.5	3.629	4.5	*AB*	3.615	11.9	3.468
	3.246	11.7									
6b	3.593	3.609	3.3	3.808	3.3	3.753	1.5	3.5	3.868	12.7	3.607
	3.384	12.0									
6c	3.394	3.896	*AB*	3.896	*AB*	3.895	2.8	5.0	3.562	12.5	3.441
	3.366	12.4									
6d	3.456	3.841	4.6	4.143	7.6	3.802	3.2	6.0	3.621	12.3	3.413
	3.385	11.5									
8a	4.800	3.687	3.5	3.765	1.1	3.954	n.d.	n.d.	3.570	n.d.	*ca.* 3.55
8b	4.472	3.527	3.7	3.701	1.1	3.531	n.d.	2.8	3.590	9.5	3.554
8c	4.801[g])	3.877	9.1	3.536	3.2	3.568	n.d.	6.2	n.d.	11.6	3.504
8d	4.940[g])	3.776	8.0	3.759	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8e	4.852	3.798	3.1	3.632	9.5	3.671	11.3	5.0	3.578[d])	10.4	3.412[e])
8f	4.833	3.864	3.9	3.821	4.8	3.715	1.7	1.5	3.976	12.8	3.453
8g	4.741	4.089	5.0	4.135	4.0	3.878	4.6	7.1	3.674	12.0	3.590

[a]) ^{13}C-NMR data see ref. [31][32][35][36]. [b]) *J*(1,3) = 1.3 Hz. [c]) Uncertain. [d]) Axial. [e]) Equatorial. [f]) *J*(3,5) = 1.4 Hz. [g]) Signal assignments may be exchanged.

Table 7. *^{1}H-NMR Data of 3-Deoxy-*D-erythro-*hexos-2-ulose* (**5**) *and 3-Deoxy-*D-ribo-*hexose* (**7**)[a]) *in D_2O*

	H–C(1) *J*(1,2)	H–C(2) *J*(2,3a)	H_a–C(3) *J*(2,3b)	H_b–C(3) *J*(3a,3b)	H–(4) *J*(3a,4)	H–C(5) *J*(3b,4)	H_a–C(6) *J*(4,5)	H_b–C(6) *J*(5,6a)	*J*(6a,6b) *J*(5,6b)
5a	4.618[b])		1.998[c])	1.728[d])	3.514	3.587	3.671	3.513	13.7
				12.7	5.0	11.4	n.d.	2.2	6.5
5b	4.522		2.162[c])	1.555[d])	3.498	3.295	3.693	3.500	12.1
				13.0	5.0	11.4	9.8	2.5	6.7
5c	4.741		2.015	1.936	3.952	3.573	3.501[e])	3.327[e])	n.d.
				12.9	5.3	9.6	n.d.	n.d.	n.d.
5d	4.866		2.088	1.986	4.092	3.589	3.531	3.369	12.0
				13.3	7.8	6.3	10.8	n.d.	6.5
5e	4.588		1.824	1.742	4.000	3.614	3.725[d])	3.477[c])	11.3
				14.7	4.1	3.3	3.0	10.5	5.0
5f [10]	4.602		1.651[d])	1.642[c])	3.911	3.673	3.815	3.590	12.8
				AB	9.6	5.2	3.1	1.2	2.1
5g	4.706		2.299	1.722	4.084	3.991	3.535	3.441	12.3
				14.2	7.5	3.9	4.9	3.8	5.2
5h	4.749		2.076	2.026	4.210	3.761	3.574	3.474	12.1
				13.7	7.4	7.1	5.7	3.8	6.2

Table 7 (cont.)

	H–C(1) *J*(1,2)	H–C(2) *J*(2,3a)	H_a–C(3) *J*(2,3b)	H_b–C(3) *J*(3a,3b)	H–(4) *J*(3a,4)	H–C(5) *J*(3b,4)	H_a–C(6) *J*(4,5)	H_b–C(6) *J*(5,6a)	*J*(6a,6b) *J*(5,6b)
5i	4.560		2.482[f])	1.503[g])	4.305	4.005[h])	3.757	3.313	12.0
				14.0	7.5	2.5	0.0	1.5	< 3
5j	4.518		2.542[f])	1.350[g])	4.272	3.948[i])	3.590[e])	3.575	12.3
				14.0	7.4	2.5	0.0	< 3	n.d.
7a	4.927	3.575	1.950[d])	1.542[c])	3.415	3.488	3.617	3.506	11.5
	3.2	11.6	4.5	11.6	11.6	4.8	n.d.	1.9	4.0
7b	4.364	3.230	2.175[c])	1.332[d])	3.415	3.230	3.661	3.474	12.2
	7.9	4.6	11.5	11.5	5.0	11.5	9.5	1.9	6.3
7c	5.114	4.078	1.960	1.750	4.093	4.079	3.437	3.316	11.7
	3.7	n.d.	8.4[j])	13.3	n.d.	6.5[j])	n.d.	n.d.	7.1
7d	5.043	4.032	1.938	1.820	4.078	3.532	3.543	3.377	12.3
	0.5	4.6	< 0.5	14.0	9.6	6.5	n.d.	5.2	5.1

[a]) ^{13}C- and few ^{1}H-NMR data, see [37] and [38]. [b]) *J*(1,3a) = 1.3 Hz. [c]) Equatorial. [d]) Axial. [e]) Uncertain. [f]) Quasi-axial. [g]) Quasi-equatorial. [h]) *J*(3b,5) = 1.3 Hz. [i]) *J*(3b,5) = 1.2 Hz. [j]) Signal assignment may be exchanged.

Table 8. *^{13}C-NMR Data of* D-ribo-*Hexos-2-ulose* (**4**), *3-Deoxy*-D-erythro-*hexos-2-ulose* (**5**), *and* D-lyxo-*Hexos-2-ulose* (**8**) *in D_2O*

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	*J*(C(1),H–C(1))
4a	95.02	91.80	73.61	65.55	67.61	61.26	169.0
4b	92.74	92.65	73.51	66.17	73.84	61.58	163.6
4c	99.28	98.88	74.31	82.99	72.55	62.50	172.0
4d	98.58	98.76	73.65	80.89	71.86	62.48	172.5
4e	89.09[a])	97.01	65.94	71.86	66.32	58.00	n.d.
4f	89.36	98.17	70.46	65.40	69.01	64.56	164.8
4g	90.30	103.42	70.52	70.56	82.67	61.55	163.6
4h	89.04[a])	105.00	75.29	70.99	83.30	62.80	166.7
4i	91.68	101.22	69.98	71.97	82.01	61.00	166.0
4j	94.64	102.48	67.63	72.99	81.10	67.35	164.0
5a	93.47	93.24[a])	38.82	63.84	72.74	61.12	167.5
5b	96.04	92.02[a])	42.58	63.92	80.04	61.24	162.1
5c	98.81	97.73	36.82	77.79	73.84	62.70	172.0
5d	99.49	101.11	37.31	76.98	72.74	62.66	170.3
5e	91.13	96.59	32.78	66.85	66.27	59.11	163.5
5f [10]	91.77	97.76	30.75	65.19	67.42	64.26	163.6
5g	90.93	106.20	40.59	71.29	86.08	61.72	163.2
5h	91.02	105.67	40.26	70.73	86.55	62.43	162.9
5i	92.48	102.76	42.59	72.33	83.91	61.24	167.9
5j	94.60	104.47	39.21	72.94	82.77	67.50	164.3
8a	95.41	93.22[a])	68.47	69.75	71.01	61.18[a])	169.0
8b	95.64	93.20[a])	71.73	69.33	75.50	61.33[a])	162.3
8c	98.69[a])	97.75[a])	73.09	80.52	71.83	62.72	169.2
8d	99.65[a])	98.57[a])	74.33	81.82	n.d.	62.94	171.7
8e	89.02	98.04	70.31	71.33	66.48	62.53	166.4
8f	89.50	98.19	64.14	71.05	69.44	60.27	165.3
8g	90.35	102.29	71.09	71.19	80.30	61.07	165.9

[a]) Signal assignments may be exchanged.

Table 9. *^{1}H-NMR Data of 2-Deoxy*-D-erythro-*hexos-3-ulose* (**9**) *in D_2O*

	H–C(1) *J*(1,2a)	H_a–C(2) *J*(1,2b)	H_b–C(2) *J*(2a,2b)	H–C(4) *J*(4,5)	H–C(5) *J*(5,6a)	H_a–C(6) *J*(5,6b)	H_b–C(6) *J*(6a,6b)
9a	5.530	2.812[a])	2.401[b])	4.175[c])	3.862	3.717	3.683
	4.4	1.2	14.4	10.1	2.9	3.8	12.4
9b	4.933	2.643[b])	2.560[a])	4.066[d])	3.380	3.780	3.647
	2.6	9.3	14.3	10.1	2.2	5.2	12.4
9c	5.734	2.725[e])	2.292[f])	4.122	3.815	3.519	n.d.
	5.6[g])	1.3[h])	18.7	3.0[i])	6.5	3.0	12.2
9d	4.802	2.034[b])	1.538[a])	3.276	3.352	3.717	3.531
	2.2	9.7	13.3	9.8	2.8	5.9	12.2

[a]) Axial. [b]) Equatorial. [c]) *J*(2a,4) = 1.1 Hz. [d]) *J*(2b,4) = 1.2 Hz. [e]) Quasi-axial. [f]) Quasi-equatorial. [g]) Corresponding to a torsion angle of 43° [58]. [h]) Corresponding to a torsion angle of 71° [58]. [i]) Corresponding to a torsion angle of 65° [58].

Table 10. *^{1}H-NMR Data of 1-Deoxy*-D-erythro-*pent-2-ulose* (**10**) *in D_2O*

	Me	H–C(3)	*J*(3,4)	H–C(4)	*J*(4,5a)	*J*(4,5b)	H_a–C(5)	*J*(5a,5b)	H_b–C(5)
10a	2.094	4.135	4.9	3.850	5.4	6.4	3.456	11.7	3.421
10b	1.266	3.696	5.0	4.117	5.2	2.5	3.889	10.3	3.686
10c	1.246	3.734	5.0	4.378	6.1	4.9	3.943	9.6	3.520

Table 11. *^{13}C-NMR Data of 2-Deoxy*-D-erythro-*hexos-3-ulose* (**9**) *and 1-Deoxy*-D-erythro-*pent-2-ulose* (**10**) *in D_2O*

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
9a	93.22	46.43	209.56	72.87	74.84	60.98
9b	94.40	48.12	208.38	72.65	75.87	61.22
9c	95.48	44.83	91.02	78.93	71.75	61.92
9d	93.05	43.97	93.36	70.78	75.41	61.38
10a	26.94	213.48	78.04	72.38	61.44	
10b	23.48	102.50	74.65	70.09	71.39	
10c	21.65	106.34	76.57	70.81	70.35	

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