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Aldose–ketose interconversion in pyridine in the presence of aluminium oxide

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Abstract—The reaction rate of the Lobry de Bruyn–Alberda van Ekenstein transformation of aldoses to ketoses in boiling pyridine was strongly increased by the addition of aluminium oxide. In addition to aldose–ketose transformation, 2-epimers of the starting aldoses and 3-epimers of the primarily produced ketoses were formed to some extent, as reported also when these reactions are carried out without aluminium oxide. The relative amounts of the primary ketose and the starting aldose in the reaction mixtures may be explained on the basis of their stability, predicted from reported free energy calculations. Isomerisation of ketoses to aldoses was much slower than the reverse reaction. The relative free energies are also in these cases important, the very stable *xylo*-2-hexulose gave only 7% and 6% of the aldoses gulose and idose, respectively, after boiling for 7 h in pyridine in the presence of aluminium oxide.

Keywords: Aldose; Ketose; Transformation; Pyridine; Aluminium oxide

1. Introduction

The Lobry de Bruyn–Alberda van Ekenstein aldose–ketose transformation[1] has found extensive application in preparation of ketoses, in particular after the introduction of pyridine both as a solvent and as a base in 1927.[2] Pyridine has much less tendency to induce side reactions than alkaline aqueous solutions, only aldose–ketose transformation and, to a certain degree, epimerisation occur. Despite relatively sluggish conversion, and often with low yields, the reaction has been attractive because of its simplicity and since the starting aldoses usually applied are inexpensive. In addition, unchanged aldose may in several cases be recovered by crystallisation,[3–5] and yields are often calculated from the amount of aldose consumed. The Lobry de Bruyn–Alberda van Ekenstein transformation has been reviewed in 1958 by Speck[6] and in 2001 by Angyal.[7]

Throughout the last fifty years, several enzymatic and microbial methods have been developed for aldose–ketose transformation.[6,8] Rare 2-hexuloses have also been prepared by enzymatic 3-epimerisation of more common 2-hexuloses.[9–11] Such enzymatic epimerisations have been included in a strategy for bioproduction of rare sugars, elaborated by Izumori.[12,13] Enzymatic reactions have the advantage of being stereospecific, but they are often laborious, and isomerases, epimerases or microorganisms from which they may be isolated are needed. In our opinion there is still need for simple, general chemical methods for aldose–ketose transformations.

One reason for the low yields when the isomerisation is carried out in pyridine is that the ketose–aldose equilibrium is rarely reached as a consequence of sluggish reaction. In a recent publication,[14] we reported that a remarkable increase in reaction rate was achieved by addition of aluminium oxide to the pyridine solution as an additional catalyst. It might seem of interest in this connection that several reports have appeared on the application of aluminate in aqueous base-catalysed

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aldose–ketose transformation. Isomerisation of glucose to fructose was reported in a patent in 1964.[15] Since then, this method has also been used in the isomerisation of reducing disaccharides, lactulose has been prepared from lactose[16] and maltose has been converted to maltulose in aluminate solution[17] and on aluminate resin.[18] A possible mechanism for the isomerisation of glucose to fructose has been suggested[19] on the basis of the known capability of aluminate to form complexes with monosaccharides.[20] Increased yield of fructose from glucose in alkaline solution on the addition of aluminate is explained by stronger ability of the ketose to form aluminate complex.[19] In a previous paper from our laboratory, the isomerisation of aldoses of the *arabino* and *lyxo* series in aluminate solution was reported.[21] The results supported the suggested[19] mechanism, based on stabilisation of a *trans*-1,2-enediol intermediate by 1,3-aluminate complexation.

In our recently reported work on isomerisation of aldoses in pyridine with aluminium oxide,[14] the aldoses investigated, especially glucose and xylose, belong to the most stable ones, and they are not expected to give the highest yields of ketoses. To get more information about the potential of this improved reaction for preparation of less common ketoses, we decided to examine the effect of aluminium oxide on the isomerisation of several other aldoses in pyridine.

Whereas production of aldohexoses by enzyme-catalysed isomerisation of 2-hexuloses has been reported,[22–24] ketoses are not suitable as starting materials for preparation of aldoses by isomerisation in pyridine, mainly because two 2-epimeric aldoses are formed, and in addition, 3-epimerisation of the ketose occurs. However, since the presence of aluminium oxide has been found to increase the reaction rate of aldose–ketose transformation, it seemed of interest to also investigate the effect of this catalyst on the reverse reaction. Therefore, two 2-hexuloses have been treated with aluminium oxide in pyridine under the same conditions as those used for the aldoses.

2. Results and discussion

As a method for qualitative and quantitative analysis of the monosaccharides in the reaction mixtures, GC–MS of their *O*-isopropylidene derivatives was chosen. Under certain conditions, most monosaccharides dealt with in this work, with the exception of altrose, idose and talose, give exclusively or mainly one derivative.[25] As a result, less complex gas chromatograms are obtained than those of, for example, trimethylsilyl derivatives or acetates. In addition, the mass spectra of *O*-isopropylidene derivatives are more characteristic and, unlike those from trimethylsilyl derivatives and acetates, often discriminate between configurational isomeric sugars.[26] EI mass spectra of the derivatives of most of the common monosaccharides have been reported,[26–28] and mass spectral data of the derivatives of the less common aldoses altrose, gulose, idose and talose are shown in Table 1. From altrose, 1,2:5,6- and 1,2:3,4-di-*O*-isopropylidene derivatives are formed in a ratio of about 2:1 under the derivatisation conditions applied in this work, whereas 1,2:5,6 and 2,3:5,6 derivatives are obtained from talose.[29] Contrary to what is the situation with glucose, a 1,2:3,5-di-*O*-isopropylidene derivative is formed in substantial amounts from its 5-epimeric aldose, idose, in addition to the main 1,2:5,6-di-*O*-isopropylidene derivative. This difference may at least in part be explained by the fact that the 2,2-dimethyl-1,3-dioxane ring, involving C-3, C-4, C-5 in the idose derivative, may adopt a chair conformation without unfavourable 1,3-diaxial C–C interactions, as seen by inspection of a molecule model. In the 1,2:3,5-di-*O*-isopropylidene derivative of glucose on the other hand, this is impossible, and this glucose derivative is formed in

Table 1. Mass spectral data for the acetals of altrose, gulose, idose and talose

1,2:4,5-Di-*O*-isopropylidene-β-D-altrofuranose *m/z* (% rel. int.): 245 (63), 187 (16), 159 (24), 143 (16), 131 (13), 127 (29), 101 (68), 85 (32), 73 (52), 59 (62), 55 (48) 43 (100)

1,2:3,4-Di-*O*-isopropylidene-β-D-altropyranose: 245 (24), 229 (4), 187 (27), 185 (7), 171 (16), 144 (5), 127 (23), 113 (43), 100 (55), 85 (53), 71 (38), 59 (73), 43 (100)

2,3:5,6-Di-*O*-isopropylidene-L-gulofuranose: 245 (88), 187 (36), 141 (13), 129 (11), 127 (24), 115 (12), 109 (14), 101 (100), 99 (19), 85 (30), 81 (27), 72 (25), 59 (88), 43 (100)

1,2:5,6-Di-*O*-isopropylidene-β-D-idofuranose: 245 (74), 187 (46), 159 (9), 131 (13), 129 (26), 127 (38), 113 (12), 101 (100), 85 (27), 59 (74), 55 (25), 43 (100)

1,2:3,5-Di-*O*-isopropylidene-β-D-idofuranose: 245 (59), 229 (12), 187 (22), 171 (11), 129 (52), 127 (33), 113 (100), 109 (15), 100 (67), 85 (62), 72 (19) 69 (20), 59 (96), 57 (19), 55 (17), 43 (100)

2,3:5,6-Di-*O*-isopropylidene-D-talofuranose: 245 (40), 187 (34), 159 (5), 141 (7), 129 (29), 127 (13), 115 (7), 101 (100), 95 (15), 85 (20), 81 (16), 73 (32), 59 (81), 55 (17), 43 (100)

1,2:5,6-Di-*O*-isopropylidene-β-D-talofuranose: 245 (97), 187 (5), 185 (11), 167 (9), 159 (35), 129 (10), 115 (8), 113 (13), 101 (92), 99 (21), 85 (23), 73 (36), 72 (31), 59 (100), 55 (77), 43 (100)

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose: 245 (79), 187 (73), 159 (46), 145 (21), 131 (44), 129 (41), 127 (75), 113 (32), 101 (100), 85 (72), 72 (49), 69 (51), 59 (88), 55 (40), 43 (73)

1,2:3,5-Di-*O*-isopropylidene-α-D-glucofuranose: 245 (29) 229 (5), 187 (5), 171 (13), 142 (24), 129 (42), 127 (18), 113 (100), 109 (8), 101 (16), 100 (24), 85 (44), 69 (17), 59 (91), 57 (18), 55 (18), 43 (100)

negligible amounts under the conditions applied in this work. The mass spectral data of this minor, as well as those of the major derivative of glucose, are shown in Table 1 for comparison with the data of the corresponding derivatives of D-idose.

As previously observed,[14] the reaction rate of aldose–ketose transformation in boiling pyridine increases remarkably on the addition of aluminium oxide. The difference in the content of *xylo*-2-hexulose with time in a solution of gulose in boiling pyridine in the presence and absence of aluminium oxide is shown in Figure 1, and the change in composition of monosaccharides with time in the reaction mixtures after similar treatment of six aldoses is seen in Table 2. The relatively unstable aldohexose gulose is rapidly isomerised to the very stable ketose *xylo*-2-hexulose (sorbose), 54% after 30 min and 70% after 2 h. The stability of the sugars can be predicted from their free energies, which have been calculated for aldohexoses, aldopentoses and ketohexoses in their pyranose forms.[30,31] From talose about 50% of *lyxo*-2-hexulose (tagatose) is formed after 30 min. However, further treatment leads to a decrease in the amount of product. This may, at least in part, be explained by 3-epimerisation to the very stable ketose *xylo*-2-hexulose. As much as 19% of this hexulose is present in the reaction mixture after 1 h. It is seen that allose is isomerised less rapidly than gulose and talose, the rate is about the same as that observed for mannose and glucose.[14] This is in accordance with an earlier reported relatively slow isomerisation of allose in alkaline water solution.[32]

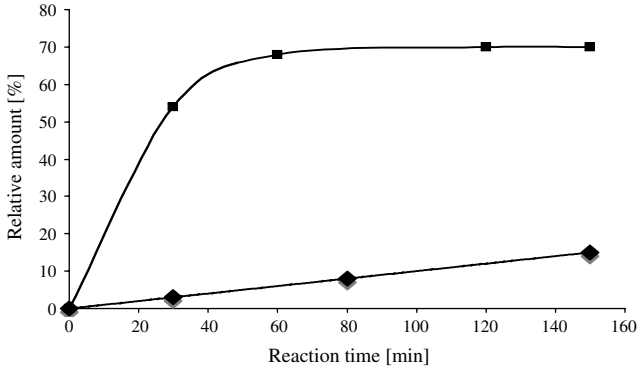


Figure 1. Change in content of *xylo*-2-hexulose (sorbose) with time in a solution of gulose in boiling pyridine with –■–■–■– and without –◆–◆–◆–aluminium oxide.

The aldopentoses, xylose and arabinose, were found in our previous work[14] to give less than 30% of the corresponding 2-pentuloses within 2 h with aluminium oxide in boiling pyridine. The low yield of the pentuloses is a result of the low free energy of these aldopentoses, in addition to the high free energy of the 2-pentuloses, which are unable to exist in pyranose forms.[7] Lyxose, on the other hand, which has a higher free energy than xylose and slightly higher than that of arabinose, is seen from Table 2 to give 45% *threo*-2-pentulose (xylulose) after 2 h. Prolonged reaction time does not increase the amount of the pentulose, 2-epimerisation of lyxose to the very stable xylose (19% is present after 2 h) is a competing reaction. L-Rhamnose (6-deoxy-L-mannose) gave only 28% of 6-deoxy-L-*arabino*-2-hexulose (6-deoxy-L-fructose) after 2 h. This is in accordance with the yield reported by Ennifar and El Khadem,[3] 27% (63% based on the L-rhamnose consumed) after 5 h in boiling pyridine without aluminium oxide.

Isomerisation of 2-hexuloses with aluminium oxide in boiling pyridine is much slower than the formation of ketoses from aldoses (Tables 3 and 4), and equilibrium is hardly reached after 9 h. It is, however, seen that more than 70% of *xylo*-2-hexulose remains after 7 h of reaction. This is in good agreement with the result after 2 h of the much more rapid reverse reaction, starting with gulose (Table 2). The amount of remaining *arabino*-2-hexulose after 9 h reaction time is 55%, whereas 22% and 13%, respectively, are present of glucose and mannose. This is more fructose and less glucose than usually observed for the glucose–mannose–fructose ratio, which is approximately 4:1:4,[7] depending on the base applied, the starting material and the solvent. This ratio is, however, very close to our previous observation[14] after 3 h reaction starting with glucose, giving 41%, 9% and 43%, respectively, of the three sugars. Ketoses are, as mentioned earlier, rarely used as starting material for base-catalysed transformation to aldoses,[7] and the application of aluminium oxide in pyridine seems from our results to make no improvement.

The relative amount of components in the product mixtures when isomerisation is carried out in aluminate solution is a result of the ability of the sugars to form

Table 2. Composition in percent in the reaction mixtures of unreacted aldose (A); 2-ketose (K); 2-epimeric aldose (EA); and 3-epimeric 2-ketose (EK) after different reaction times in pyridine in the presence of: [n]neutral Al_2O_3, [b]basic Al_2O_3

	30 min				60 min				120 min			
	A	K	EA	EK	A	K	EA	EK	A	K	EA	EK
D-Allose[n]	73	25	1	1	58	39	2	1	46	50	2	2
L-Gulose[b]	33	54	7	6	19	68	7	6	13	70	10	7
D-Galactose[n]	83	17	—	—	74	23	1	2	58	29	5	8
D-Talose[b]	23	51	13	13	18	48	15	19				
D-Lyxose[n]	43	39	10	8	40	42	10	8	23	45	19	13
L-Rhamnose[b]	71	24	3	2	66	27	5	2	57	28	10	5

Table 3. Composition in percent in the reaction mixtures of; unreacted *xylo*-2-hexulose (sorbose, S); gulose (G); idose (I) and *lyxo*-2-hexulose (tagatose, T) with neutral Al_2O_3 in pyridine

1 h				3 h				5 h[a]				7 h[a]			
S	G	I	T	S	G	I	T	S	G	I	T	S	G	I	T
85	7	5	3	78	7	7	8	76	8	6	6	72	7	6	6

[a] Less than 100% due to the formation of other products.

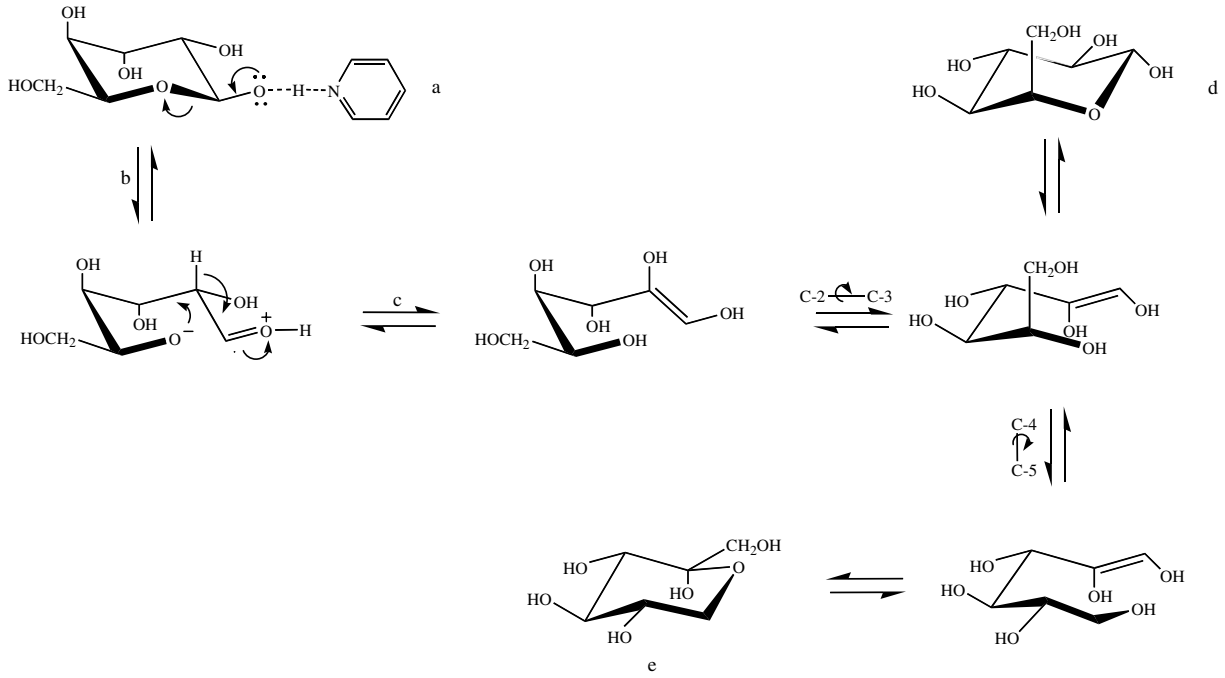
Table 4. Composition in percent in the reaction mixture of; unreacted *arabino*-2-hexulose (fructose, F); glucose (G); mannose (M) and *ribo*-2-hexulose (psicose, P) with neutral Al_2O_3 in pyridine

1 h				3 h				5 h				7 h				9 h			
F	G	M	P	F	G	M	P	F	G	M	P	F	G	M	P	F	G	M	P
78	10	8	4	68	13	12	7	62	17	13	8	56	21	13	10	55	22	13	10

complexes.[19] In pyridine with aluminium oxide, however, it is obvious from the present, as well as from our previous work,[14] that the relative free energies are of major importance, as is also evident using pyridine alone.[7] When the relative free energies are calculated from the pyranose forms only,[30] however, conclusions for some of the aldoses will be misleading. For altrose, talose and idose, furanose anomers contribute significantly, more than 30%, to the composition in aqueous solution at equilibrium.[31] Since, in addition, the amount of furanose forms of aldoses is reported to increase in pyridine and with elevated temperatures,[31] the real relative free energy of idose, for example, under conditions in the present work is considerably lower than that calculated from the pyranose forms due to the entropy of mixing. This fact is possibly the explanation of the perhaps somewhat unexpected formation of as much as 6% of idose from the very stable *xylo*-2-hexulose with aluminium oxide in refluxing pyridine. In this context, it is of interest to note that D-idose has been reported to be present in the equilibrium mixture when D-*xylo*-2-hexulose was treated with D-xylose ketol isomerase,[33] presumably formed as an epimerisation product from the primarily produced gulose, and as much as 10% of D-gulose has been found in the equilibrium mixture from the same 2-hexulose after treatment with an L-rhamnose isomerase.[24] In addition to GC–MS-identification, the formation of gulose and idose from *xylo*-2-hexulose in the present work was further confirmed by thin layer chromatography.

As to the mechanism of the reaction, it is obvious from the product composition that it cannot be similar to that operating in the isomerisation in aqueous aluminate solution, with a 1,3 aluminate stabilised *trans*-1,2-enediol intermediate. Such intermediates would not lead to C-2 epimerisation for aldoses with threo configuration at C-2–C-3,[19,21] the lack of such epimerisation of galactose, 6-deoxygalactose and arabinose has been shown,[21] and no mannose or glucosylmannoses were observed from glucose[19] or reducing glucosylglucoses[34] in aqueous aluminate solution. There has been much discussion about the mechanism of the Lobry de Bruyn–Alberda van Ekenstein transformation for more than 60 years.[6,7] A detailed study of the enolisation process in alkaline, aqueous solution was reported by de Wit et al.,[35] concluding with a suggested mechanism with initial proton-removal from O-1 of the aldopyranoses, cleavage of the C-1–O-5 bond followed by a rate-determining, intramolecular proton shift from C-2 to O-5 in open chain, pseudo-cyclic intermediates to give *cis*-1,2-enediol anions.[35] To our knowledge, no suggestions of the mechanism in pyridine have been reported. However, a mechanism similar, but with some modifications, to that proposed by de Wit et al. might also be operating in pyridine. Despite being a too weak base to remove the proton from O-1, pyridine is a good proton acceptor and can cause polarisation of the O–H bond. The result is increased negative charge on O-1, as shown for β-L-gulopyranose in Scheme 1 (a), facilitating ring opening (b). A proton shift from C-2 to O-5 (c) will lead to, in this case, a neutral, open chain, pseudo-cyclic 1,2-enediol intermediate. It is likely that this process is rate-determining, as in aqueous alkaline solution. Then the catalytic effect of aluminium oxide is presumably through adsorption on the surface and stabilisation of the enediol intermediate produced by this rate-determining step, and thereby lowering the energy of the transition state. Based on the suggested mechanism, possible ways to L-idose (d) and L-*xylo*-2-hexulose (e) are shown in Scheme 1. It is seen that the same catalyst-stabilised enediol intermediate formed from gulose may also be formed from idose and, by proton shift from C-1 to the original ring-oxygen, from *xylo*-2-hexulose. By reversal of the three intermediate-forming processes, interconversion of the two aldoses and the 2-hexulose will occur.

The improvement of the Lobry de Bruyn–Alberda van Ekenstein transformation of aldoses to ketoses in pyridine, obtained by the addition of aluminium oxide as an additional catalyst, resulting in increased reaction



Scheme 1.

rate and thus the possibility to achieve higher yields, should still make this classical reaction interesting for synthesis of ketoses. Based on some of the presented results, work is in progress to develop procedures for preparation of rare ketoses.

3. Experimental

3.1. General methods

GC was performed with a Shimadzu GC-14B gas chromatograph, equipped with an open tubular fused silica column, wall coated with CP-SIL 43 CB. For GC–MS a HP 6890 gas chromatograph with a CP-WAX 52 CB capillary column was used. The gas chromatograph was used in combination with an AutoSpec Ultima 2000 (Micromass Ltd, Manchester England) mass spectrometer, operated in EI mode at 70 eV and an ion source temperature at 200 °C. TLC was performed on Silica Gel G plates with ethylacetate–acetic acid–formic acid–water 11:3:1:4 (v/v) as eluent. Spots were detected by spraying with diphenylamine–aniline–phosphoric acid[36] and heating at 110 °C for 5 min.

3.2. Materials

D-*threo*-2-Pentulose,[14] L-*erythro*-2-pentulose,[21] D-*lyxo*-2-hexulose (tagatose),[21] 6-deoxy-L-*arabino*-2-hexulose,[21] 6-deoxy-L-glucose,[21] D-allose,[37] D-idose,[38] and D-altrose[39] were prepared according to reported methods. D-Lyxose was prepared by a method based on the reported[40] isomerisation of D-xylose by treatment with triethylamine and $CaCl_2$. L-Gulose was obtained as described for the D-enantiomer[41] from L-gulono-1,4-lactone by the standard[42] reduction with sodium borohydride at pH 3–3.5, the pH was obtained by addition of Dowex 50 W (H^+) ion exchange resin. The other sugars were obtained commercially. The aluminium oxide samples used were activated neutral or activated basic Brockmann grade 1 (Merck). Pyridine was distilled from BaO or anhydrous Al_2O_3 and kept over KOH pellets.

3.3. Isomerisation of aldoses and ketoses, analysis of product mixtures

Aldose or ketose (100 mg) in pyridine (15 mL) was stirred with aluminium oxide (0.2 g) at reflux temperature. Aliquots (1 mL) were withdrawn at intervals, and after filtration, the solvent was evaporated under reduced pressure. The residues were stirred with 3% H_2SO_4 in acetone (3 mL) for 2 h. The solutions were neutralised with solid $NaHCO_3$ and subjected to GC or GC–MS for identification and quantification of aldoses,[43] ketoses[27] and deoxy sugars.[21] The isopropylidene derivatives were indistinguishable on both GC columns from the derivatives of the authentic monosaccharides, and so were their mass spectra.

3.4. Isomerisation of L-xylo-2-hexulose

L-*xylo*-2-Hexulose (0.5 g) was stirred with neutral Al_2O_3 (1 g) in pyridine (50 mL) for 4 h as described above. The

residue after removal of the solvent was thoroughly extracted with acetone (3×25 mL) at 55 °C. After concentration of the decanted solution to about 25 mL, much of the remaining *xylo*-2-hexulose crystallised on standing. After filtration, a small volume of the solution was treated with H_2SO_4 in acetone as described above, and GC on the two columns and MS showed the presence of the derivatives of *lyxo*-2-hexulose, *xylo*-2-hexulose, gulose and both derivatives from idose. A sample from the remaining, major part of the acetone solution was subjected to TLC, revealing the presence of gulose (bluish grey spot, R_f 0.36), *xylo*-2-hexulose (brownish red, R_f 0.41) and idose (bluish grey, R_f 0.44), inseparable from samples of the authentic sugars. *lyxo*-2-Hexulose was not detected, its chromatographic mobility is too close to that of *xylo*-2-hexulose.

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