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Conversion of L-rhamnose into ten of the sixteen 1- and 6-deoxyketohexoses in water with three reagents: D-tagatose-3-epimerase equilibrates C3 epimers of deoxyketoses

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ABSTRACT

The efficient isomerization of L-rhamnose [the only cheaply available deoxy hexose] to 1-deoxy-L-psicose, 1-deoxy-D-psicose, 1-deoxy-L-fructose, 1-deoxy-D-fructose, 1-deoxy-L-tagatose, 6-deoxy-L-psicose, 6-deoxy-D-psicose, 6-deoxy-L-fructose, 6-deoxy-D-fructose, and 6-deoxy-L-tagatose is described. The conversion of rhamnose to ten of the sixteen 1- and 6-deoxyketohexoses is accomplished in water in three steps. The range of substrates for D-tagatose-3-epimerase (DTE) is extended to 1- and 6-deoxyketoses. An authentic sample of 6-deoxy-D-psicose is prepared from D-psicose.

Izumoring has provided the biotechnology for the isomerization of any of the sixteen aldohexoses or eight ketohexoses into any other hexose[1] and allows practical access to significant amounts of hitherto unstudied hexoses.[2] The technique depends on the ability of D-tagatose-3-epimerase (DTE) to equilibrate the C-3 epimeric ketoses in each of the four pairs of ketoses (**3D**/**4D**, **3L**/**4L**, **6D**/**7D**, and **6L**/**7L**).[3] DTE is a promiscuous enzyme which epimerizes a wide range of substrates, including 5-deoxyketoses[4] and *C*-branched sugars;[5,6] this Letter reports that the C3 epimers of 1- and 6-deoxyketoses are also equilibrated. There have been very few examples of the isomerization of deoxy sugars.[7] This Letter describes the synthesis of ten 1- and 6-deoxyketohexoses from L-rhamnose **1L** [the only cheaply available deoxy hexose] by the use of just three reagents in water—(i) hydrogenation in the presence of Raney nickel, (ii) specific oxidation of *S,S*-diols adjacent to the terminal carbon by *Enterobacter aerogenes* IK7, and (iii) DTE equilibration of epimeric pairs at C3 of 1- and 6-deoxyketohexoses; this sequence can be performed iteratively to give the deoxyketoses shown in Scheme 1. For the sake of clarity, alditols are shown in dark green, 6-deoxyketoses in blue and 1-deoxyketoses in red.

L-Rhamnose (50 g) **1L** was reduced to L-rhamnitol **2L**[8] by Raney nickel in 96% yield; oxidation of **2L** by *E. aerogenes* IK7 (IK7) gave the readily crystallized[9] 1-deoxy-L-fructose (37 g) **3L** [Scheme 3].[10] Microbial oxidations of polyols to 2-ketoses are highly stereoselective in regard to the configuration of the two secondary alcohols adjacent to the terminal carbon atom [Scheme 2]. The advantages of microbial oxidation of alditols are (i) the reactions are performed on whole cells without the extraction of biocatalysts and without the addition of co-factors, and (ii) the oxidation reactions proceed to completion so there is no need for separation from other carbohydrates. Additionally, although the microbes may possess many different polyol dehydrogenases, the oxidations are completely stereoselective for the diol [*RR*, *RS*, *SR* or *SS*] adjacent to the terminal carbon atom. This may be illustrated by oxidation of the three readily available hexitols D-mannitol, D-glucitol and galactitol. *Gluconobacter* strains oxidize polyols with *R* configurations at both sterogenic centers of the diol t-*RR*.[11] Thus D-mannitol [with t-*RR* motifs at C5 and C4 as well as C2 and C3] is oxidized at either C2 or C5 to give D-fructose; in contrast, oxidation of D-glucitol [with one t-*RR* motif at C5 and C4] results in only oxidation at C5 to give L-sorbose,[12] long used in the manufacture of ascorbic acid.[13] *Enterobacter agglomerans* 221e selectively recognizes a t-*SR* fragment[14] and thus oxidizes D-glucitol to D-fructose; oxidation of *meso*-galactitol with *E. agglomerans* 221e with a t-*SR* motif at C2 and C3 gives D-tagatose[15] whereas oxidation by *Klebsiella pneumoniaie* 40b recognizes a t-*RS* diol fragment at C5 and C4 to give the enantiomer L-tagatose.[2,16]

E. agglomerans 221e also oxidizes t-*SR* polyols with a terminal CH_3 rather than a CH_2OH group; thus, 1-deoxy-D-galactitol **13D**[17] [obtained by hydrogenation of L-fucose **12L**] is oxidized to 1-deoxy-D-tagatose **8D** from the t-*SR* diol at C2 and C3 [Scheme 4]. The enantiomer **13L** [derived from D-fucose **12D**] with the t-*SR* diol between C5 and C4 forms 6-deoxy-D-tagatose **5D**.[18]

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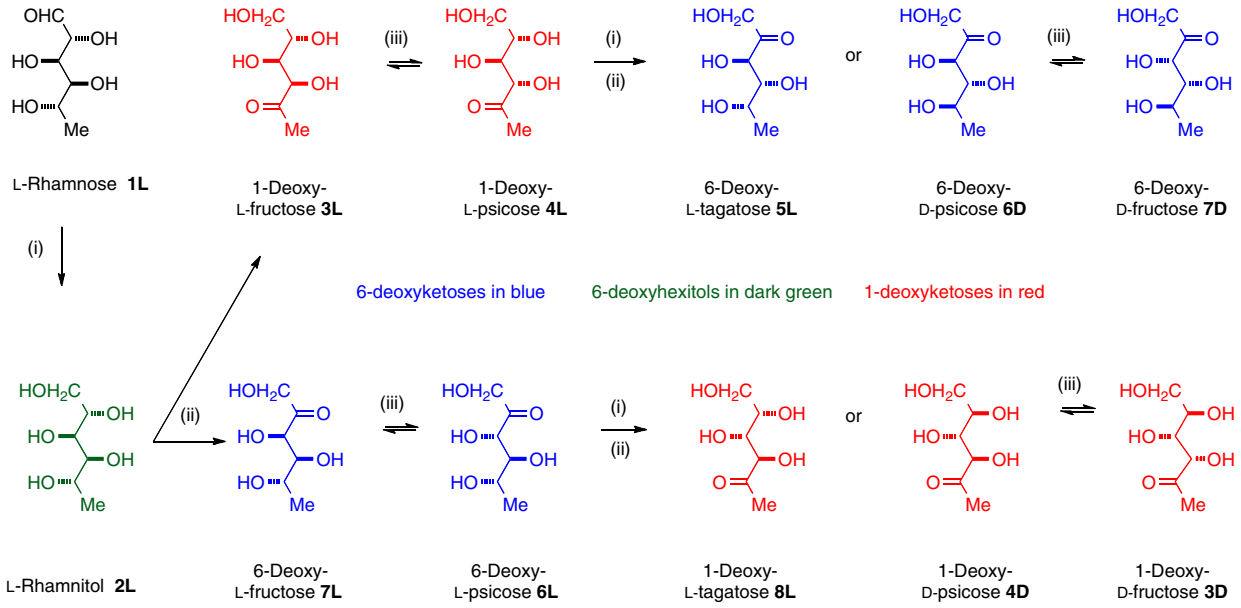
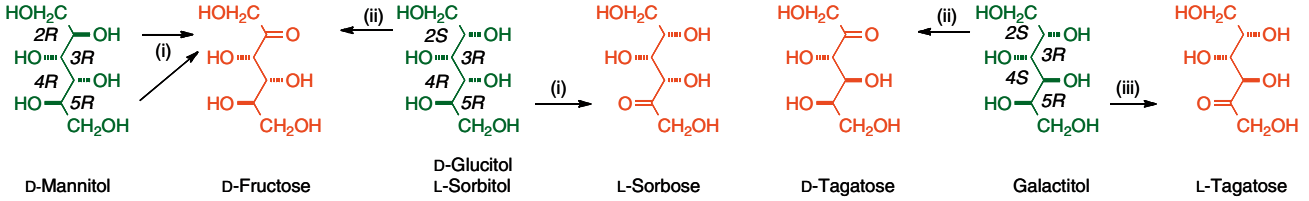
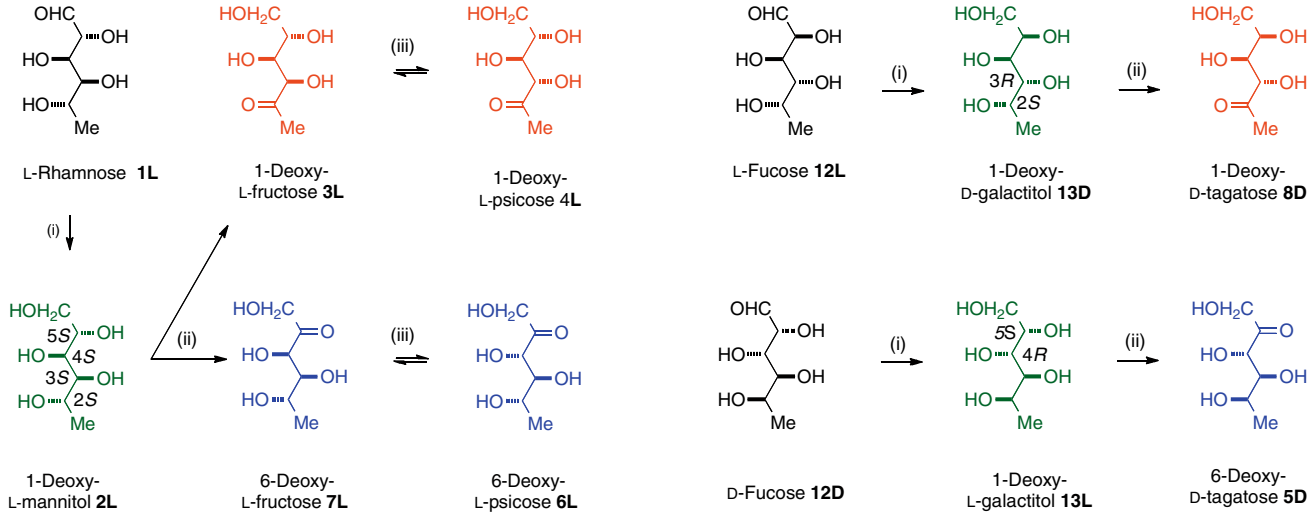


Scheme 1. L-Rhamnose **1** to ten deoxyketoses. Reagents: (i) H_2, Ni, H_2O; (ii) *Enterobacter aerogenes* IK7, H_2O; (iii) DTE, H_2O.



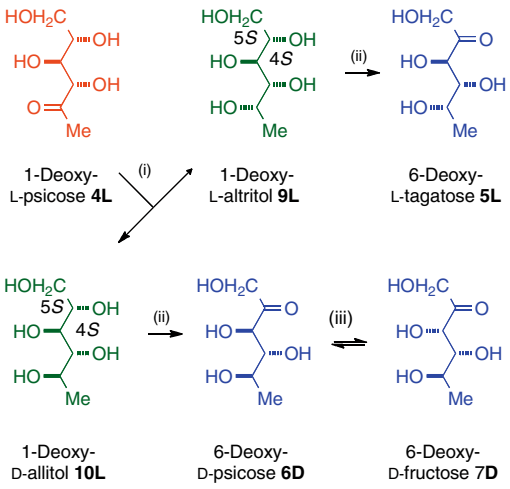
Scheme 2. Oxidation at C2 or C5. Reagents: (i) *(R,R)* by *Gluconobacter*; (ii) *(S,R)* by *Enterobacter agglomerans* 221e; (iii) *(R,S)* by *Klebsiella pneumoniaie* 40b.



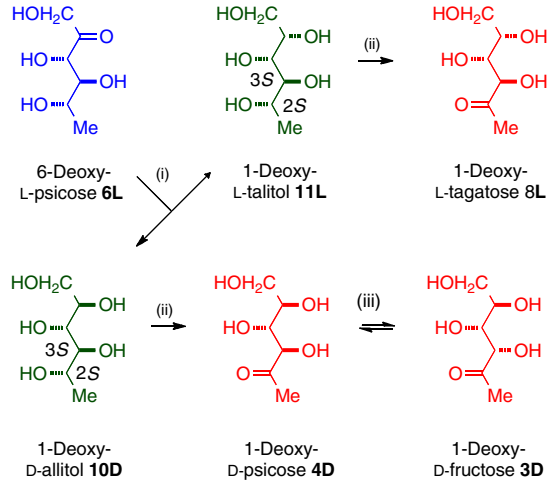
Scheme 3. Reagents: (i) H_2, Ni, H_2O; (ii) *Enterobacter aerogenes* IK7, H_2O; (iii) DTE, H_2O.

Scheme 4. Reagents: (i) H_2, Ni, H_2O; (ii) *Enterobacter agglomerans* 221e, H_2O

The fourth t-*SS* diol stereochemical motif is recognized by *E. aerogenes* IK7 (IK7) as shown in the oxidation of *meso*-allitol to D-psicose.[19] Oxidation of L-rhamnitol (1-deoxy-L-mannitol) **2L** by IK7 over 6 h gave 65% of 1-deoxy-L-fructose **3L**[9] $[\alpha]_D^{20}$ +85.0 (*c* 1.0, H_2O), [with t-*SS* at C5 and C4] and 25% of 6-deoxy-L-fructose **7L** $[\alpha]_D^{20}$ +12.5 (*c* 1.0, H_2O) {lit.[20] for enantiomer **7D** $[\alpha]_D^{20}$ −14} [with t-*SS* at C2 and C3] [Scheme 3]. Prolonged oxidation (12 h) reduced the yield of 6-deoxy-L-fructose **7L** (to 10%) but increased the yield of 1-deoxy-L-fructose **3L** to 75%. The microbial cells of IK7 were washed and could be re-used several times. The two deoxyketoses **3L** and **7L** were separated from the reaction mixture by a one-pass separation system.[21] 1-Deoxy-L-fructose **3L** was epimerized at C3 to 1-deoxy-L-psicose **4L** $[\alpha]_D^{20}$ −1.0 (*c* 1.0, H_2O) by immobilized DTE and reached an equilibrium state after 12 h containing 75% of substrate **3L** and 25% of product **4L** (3:1). Similarly, 6-deoxy-L-fructose **7L** was epimerized by immobilized DTE to 6-deoxy-L-psi-



Scheme 5. Reagents: (i) H_2, Ni, H_2O; (ii) *Enterobacter aerogenes* IK7, H_2O; (iii) DTE, H_2O.



Scheme 6. Reagents: (i) H_2, Ni, H_2O; (ii) *Enterobacter aerogenes* IK7, H_2O; (iii) DTE, H_2O.

cose **6L** $[\alpha]_D^{20}$ −17.1 (*c* 1.0, H_2O) and reached an equilibrium state which contained equal amounts of **6L** and **7L** (1:1) after 12 h.

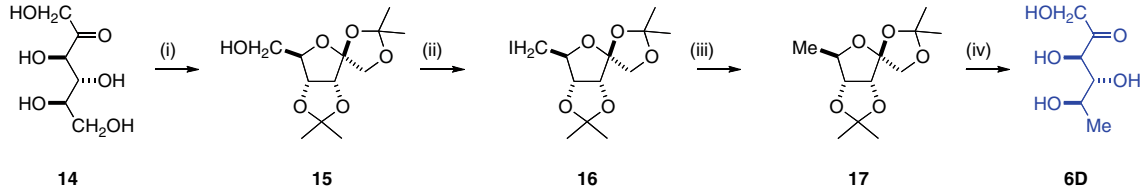
1-Deoxy-L-psicose **4L** was further elaborated to three 6-deoxyketoses [Scheme 5]. Hydrogenation of **4L** in the presence of Raney nickel gave a 96% yield of a 1:1 mixture of the two polyols 1-deoxy-L-altritol **9L** $[\alpha]_D^{20}$ −5.0 (*c* 1.0, H_2O) and 1-deoxy-L-allitol **10L** $[\alpha]_D^{20}$ −12.9 (*c* 1.0, H_2O) which was separated by preparative HPLC. 1-Deoxy-L-altritol **9L** [with t-*SS* at C5 and C4] was oxidized quantitatively by IK7 to 6-deoxy-L-tagatose **5L** $[\alpha]_D^{20}$ +1.6 (*c* 1.0, H_2O) {for enantiomer **5D**[18] $[\alpha]_D^{20}$ −2.2 (*c* 1.0, H_2O)} in 8–10 h. Similarly the IK7 oxidation of 1-deoxy-L-allitol **10L** by IK7 [with t-*SS* at C5 and C4] to 6-deoxy-D-psicose **6D** $[\alpha]_D^{20}$ +17.0 (*c* 1.0, H_2O) proceeded in quantitative yield. As the microbial oxidations proceeded to completion, no separation of carbohydrate products was necessary. Alternatively, the mixture of the polyols **9L** and **10L** was treated with IK7 and the product 6-deoxyketoses **5L** and **6D** separated after the completion of the oxidation. Reaction of 6-deoxy-D-psicose **6D** with immobilized DTE afforded a 1:1 mixture of **6D** with 6-deoxy-D-fructose **7D** $[\alpha]_D^{20}$ −13.0 (*c* 1.0, H_2O), the enantiomer of **7L** formed in the oxidation of rhamnitol **2L**. As a strategy there is an option to separate either two deoxyhexitols **9L** from **10L** or two deoxyketoses **5L** from **6D**, whichever is easier.

Analogously, 6-deoxy-L-psicose **6L** was converted into three 1-deoxyketoses [Scheme 6]. Hydrogenation of **6L** by Raney nickel in water gave two polyols, 1-deoxy-L-talitol **11L** $[\alpha]_D^{20}$+11.6 (*c* 1.0, H_2O) and 1-deoxy-D-allitol **10D** $[\alpha]_D^{20}$ +13.3 (*c* 1.0, H_2O) {for the enantiomer **10L** $[\alpha]_D^{20}$ −12.9 (*c* 1.0, H_2O)}. 1-Deoxy-L-talitol **11L** [with t-*SS* at C2 and C3] was completely oxidized to 1-deoxy-L-tagatose **8L**[22] $[\alpha]_D^{20}$ +14.0 (*c* 1.0, H_2O) {for enantiomer **8D**[18] $[\alpha]_D^{20}$ −14.7 (*c* 1.0, H_2O)} by IK7 in 8–10 h. Also 1-deoxy-D-allitol **10D** [with t-*SS* at C2 and C3] was transformed into 1-deoxy-D-psicose **4D** $[\alpha]_D^{20}$+1.0 (*c* 1.0, H_2O) under similar conditions. Finally, 1-deoxy-D-psicose **4D** was epimerized to an equilibrium mixture of 25% **4D** and 75% 1-deoxy-D-fructose **3D** $[\alpha]_D^{20}$ −81.4 (*c* 1.0, H_2O) by immobilized DTE.

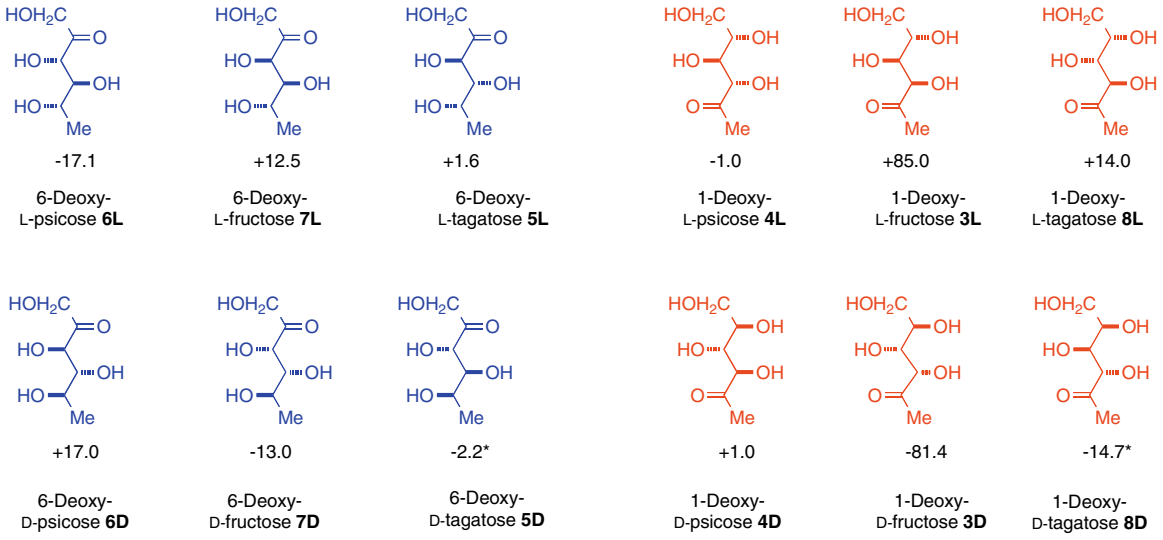
An unambiguous synthesis of 6-deoxy-D-psicose **6D** provided an authentic sample to compare with both 6-deoxy-psicose enantiomers **6D** and **6L** for proof of structure [Scheme 7]. A suspension of psicose **14** in acetone was treated at room temperature with concentrated aqueous hydrochloric acid and anhydrous copper sulfate to give the diacetonide **15**,[23] mp 51–53 °C, $[\alpha]_D^{22}$ −74.2 (*c* 1.06, $CHCl_3$), in 73% yield. Reaction of **15** with triflic anhydride in dichloromethane in the presence of pyridine, followed by treatment of the crude triflate with tetrabutylammonium iodide in THF afforded the iodide **16**, as an oil, $[\alpha]_D^{22}$ −44.2 (*c* 0.79, $CHCl_3$), in 64% yield. Hydrogenolysis of the iodide **16** in ethanol in the presence of triethylamine and palladium on carbon gave **17**, also as an oil, $[\alpha]_D^{22}$ −94.2 (*c* 1.07, $CHCl_3$) in 95% yield. Removal of the acetonides in **17** by Dowex in water gave 6-deoxy-D-psicose **6D**,[24] as a 3:1 mixture of anomers in 91% yield [overall yield of **6D** from D-psicose **14** was 40%]. The acid hydrolysis of the diacetonide **17** to afford **6D** was not convenient to accomplish on a large scale.

All the ketoses in this Letter have the same molecular formula and exist in water as mixtures [pyranose and/or furanose forms]. Each of the products has been compared with samples either prepared by chemical methods[25] or biological techniques, which have provided material for X-ray crystallographic analysis.[18] The specific rotations of all the enantiomeric pairs are highly consistent [Scheme 8]; the ^{13}C and ^{1}H NMR spectra of each pair of enantiomers were essentially identical.[26]

In summary, L-rhamnitol **2L** has two different t-*SS* diols [between C2 and C3, and C4 and C5] both of which are oxidized by IK7. However, all the other alditols produced in this Letter have only one *SS* diol adjacent to a terminal carbon, allowing the



Scheme 7. Reagents: (i) Me_2CO, $CuSO_4$, concd HCl, 73%; (ii) $(CF_3SO_2)_2O$, CH_2Cl_2, pyridine; then $Bu_4N^+I^-$, THF, 64%; (iii) H_2, 10% Pd/C, Et_3N, EtOH, 95%; (iv) Dowex (50 W X8, H^+), H_2O, 91%.



Scheme 8. Specific rotations $[\alpha]_D^{20}$ (c 1.0, H_2O), of enantiomeric deoxyketoses. *From Ref. 18.

exquisite stereoselectivity of IK7 to be exploited in the synthesis of ten hitherto inaccessible deoxyketoses by only three reagents. This Letter describes the synthesis from rhamnose **1L** of the enantiomers of 1- and 6-deoxy psicose and fructose [**3D**, **3L**, **4D**, **4L**, **6D**, **6L**, and **7D**, **7L**] as well as 1-deoxy-L-tagatose **8L** and 6-deoxy-L-tagatose **5L**—whose enantiomers **8D** and **5L** may be synthesized from *E. agglomerans* 221e oxidation [recognizing a t-*SR* motif] of 1-deoxy-D-galactitol **13D** and 1-deoxy-L-galactitol **13L**, respectively. This Letter shows that the concept of Izumoring may be extended to produce deoxyhexoses.

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Supplementary data

Supplementary data associated with this paper can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.024.

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11. Whereas D-erythrose has *R* configuration at C3 and *S* at C2, any higher alditol related to D-erythritol will have *R* configuration at both carbons adjacent to the terminal C; this stereochemical motif is referred to in the Letter as t-*RR* [t for terminal C]. Alditols similarly related to D-threitol are described as t-*RS*, whereas L-erythritol is t-*SS* and L-threitol is t-*SR*.
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24. Selected data for 6-deoxy-D-psicose **6D**: ν_{max} (thin film): 3361 (br s, OH), δ_H (D_2O, 400 MHz) (A—major anomer): 1.23 (3H, d, Me^A, J 6.4), 1.33 (3H, d, Me^B, J 6.3), 3.49 (1H, d, $H1^A$, J 12.1), 3.47–3.56 (1H, m, $H1^B$), 3.55 (1H, d, $H1'^A$, J 12.1), 3.77–3.82 (2H, m, $H1'^B$, H^A), 3.98–4.03 (2H, m, $2 \times H^B$), 4.05–4.14 (3H, m, $2 \times H^A$, H^B); δ_C (D_2O, 100): 18.3 (Me^A), 19.9 (Me^B), 62.9 ($C1^B$), 64.1 ($C1^A$), 70.9 (CH^A), 75.7 (CH^B), 75.8 (CH^A), 76.7 (CH^B), 78.5 (CH^A), 79.1 (CH^B), 103.6 ($C2^A$), 105.9 ($C2^B$).
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26. See Supplementary data for ^{13}C NMR spectra of all the deoxyketoses prepared in this Letter.