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Journal of Molecular Catalysis B: Enzymatic 5 (1998) 459–466

JOURNAL OF MOLECULAR CATALYSIS B: ENZYMATIC

Modified L-threose and D-erythrose as substrates of transketolase and fructose-1,6-bisphosphate aldolase. Application to the synthesis of new heptulose analogues

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Received 24 November 1997; accepted 12 February 1998

Abstract

Nine substituted butanals lacking α-hydroxyl group were tested as substrates for transketolase and fructose-1,6-bisphosphate aldolase in order to demonstrate the usefulness of these enzymes for the synthesis of 4-deoxy-D-fructose and 4-deoxy-L-sorbose derivatives as well as 5-deoxy-heptuloses of D and L configurations. All compounds lead to the corresponding ketoses by aldolase catalysis, but only a 4-phosphorylated one has a sufficient reactivity to ensure a transketolase catalysed synthesis. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Butanals; Transketolase; Aldolase; Ketose

1. Introduction

Fructose-1,6-bisphosphate aldolase (FB-aldolase) and transketolase appear today as major tools for the de novo synthesis of monosaccharides [1–5]. FB-aldolase condenses dihydroxyacetone phosphate onto aldehydes, leading to ketoses-1-phosphates, easily hydrolysed to give ketoses [6–11] when transketolase transfers a hydroxyacetyl group from hydroxypyruvic acid (or in vivo a ketose) onto α-hydroxyaldehydes to form ketoses [12–15]. Due to the enantioselectivity of transketolase towards α-hydroxyaldehydes, both enzymes provide ketoses of D-threo configuration on carbon 3 and 4 (Scheme 1). However, transketolase is also able to act on aldehydes lacking an α-hydroxyl group and lead to 4-deoxyketoses which cannot be obtained by FB-aldolase catalysed syntheses. Starting from the same substrate, transketolase and FB-aldolases will lead to homologous compounds. We have already used this strategy to prepare precursors in the biosynthesis and/or synthesis of natural polyhydroxylated piperidines and pyrrolidines [16,17].

In this paper we describe the reactivity of transketolase and FB-aldolase with modified L-threose and D-erythrose and the aldolase catalysed syntheses of the corresponding heptuloses. Our aim was to demonstrate the potential of these enzymes for the synthesis of close ana-

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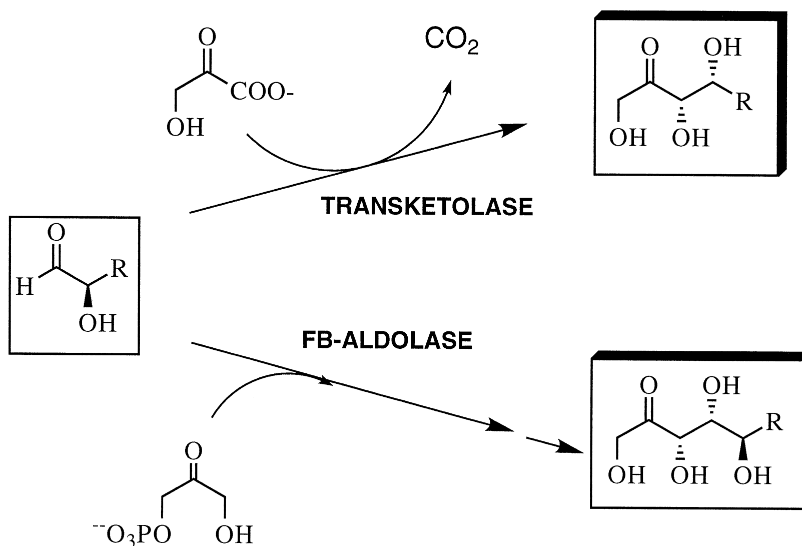
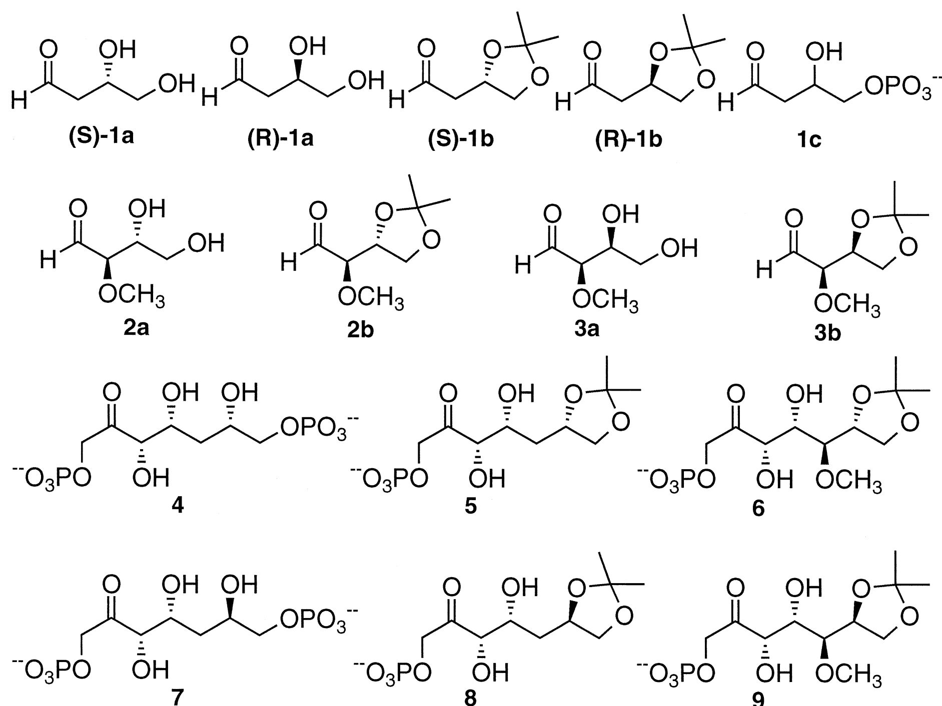
PII: S1381-1177(98)00070-8



Scheme 1. Reactions catalysed by transketolase and FB-aldolase.

logues of D-fructose and L-sorbose using transketolase, or heptuloses of the D or L configurations using FB-aldolase. We focused on 2-deoxy-D and L-erythrose **1**, 2-*O*-methyl-D-erythrose **2** and 2-*O*-methyl-L-threose **3** derivatives (Scheme 2), as substrates for these enzymes in



Scheme 2.

order to obtain deoxy or *O*-methyl ketoses, potential inhibitors of the sugar metabolism.

Other tetroses had already been studied as substrates of these enzymes. So, D-erythrose is not a substrate for FB-aldolase [18] whereas it is a good substrate for transketolase as is L-threose. No synthesis was undertaken with them because the expected products are the common D- and L-fructose [16,17]. Racemic 2,4-dihydroxybutyraldehyde is not a substrate for transketolase [12], but we have shown that 2,3-dihydroxybutyraldehyde is a good substrate leading to the syntheses of 6-deoxy-D-fructose and 6-deoxy-L-sorbose from racemic 2,3-dihydroxybutyraldehyde [19] and of 6-deoxy-L-sorbose from 4-deoxy-L-threose [20]. Racemic 3-hydroxybutyraldehyde [21] and 3,4-dihydroxybutyraldehyde [22] are substrates for FB-aldolase.

2. Results and discussion

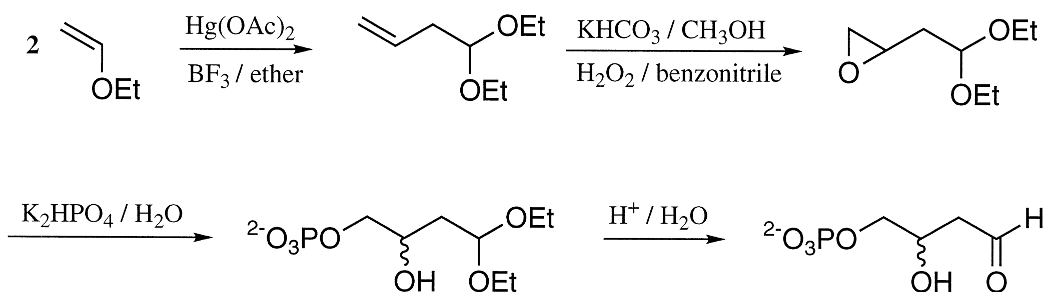
2.1. Preparation of the substrates

We prepared compounds **(*R*)-1a**, **(*R*)-1b**, **3a** and **3b** from D-isoascorbic acid and **(*S*)-1a**, **(*S*)-1b**, **2a** and **2b**, from L-ascorbic acid. Their synthesis will be published elsewhere. Racemic **1c** was synthesized according to Scheme 3: the epoxyde of 1,1-diethoxy-3-butene was opened by inorganic phosphate in water at pH 8. Although the phosphate ion is a poor nucleophile, the reaction proceeded regioselectively with a reasonable yield of 35%. Diethylacetal of **1c** was isolated by precipitation of its barium salt and lead to **1c** after acidic hydrolysis.

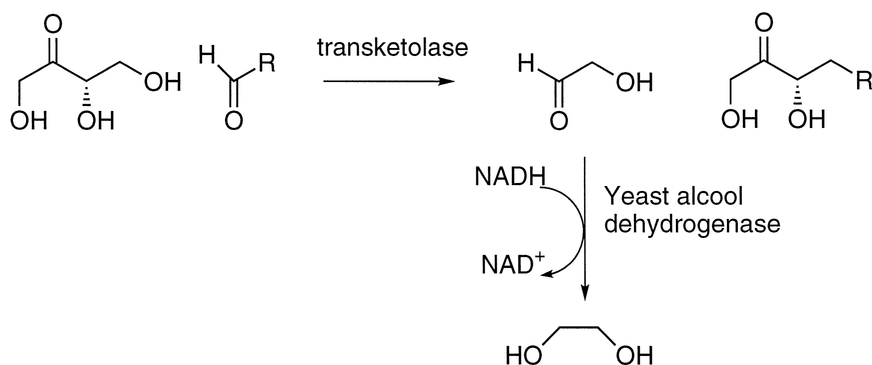
2.2. Transketolase activity

Compounds **1–3** were assayed as substrates for transketolase, using the assay developed in our laboratory which uses L-erythrulose as ketose donor instead of hydroxypyruvate or xylulose-5-phosphate (Scheme 4) [23]: the reaction releases glycolaldehyde which is reduced by NADH in the presence of yeast alcohol dehydrogenase, allowing UV spectroscopy monitoring. We measured kinetic constants, K_m and initial maximum rate V_{max} relative to one of the natural substrates ribose-5-phosphate. The results are reported in Table 1.

Initial rates observed for the unphosphorylated compounds are in the same range as for other analogues of the natural substrates (5–10% relative to ribose-5-phosphate), but the K_m values are higher so that the efficiency of transketolase in these cases appear very low. This confirms the previous observations that α-hydroxyaldehydes are the best substrates of transketolase. However, the presence of the α-hydroxyl group is not a requisite since reaction occurs. The best of our substrates is **2a**, which presents the configuration of D-erythrose. The steric hindrance of the dioxolane ring could explain the low reactivity of **1b**, **2b** and **3b**, but the deprotection of the diol in **1a**, **2a** and **3a** does not improve it significantly. This could be



Scheme 3. Synthesis of racemic 3,4-dihydroxybutanal-4-phosphate.



Scheme 4. Assay for transketolase.

explained by the nature of the species actually present in solution, free aldehyde or cyclic hemiacetal: if the aldehyde is the only substrate, the presence of the cyclic form will increase the apparent K_m.

A ^{13}C NMR study of the behavior of **1** in water has been published by Snyder and Serianni [24]: the α (25.3%) and β (59.2%) anomers, the free aldehyde (3.1%) and the hydrated open form (12.4%) are present. Careful examination of ^{13}C NMR spectra allowed us to calculate the percentage of the various forms for compounds **1a**, **2a** and **3a**. We found for **1** values very close to the literature data: 26% of the α anomer, 62% of the β anomer and 12% of the hydrated open form; free aldehyde is undetectable. For α-methoxy compounds **2a** and **3a**, it appears that no open form is present and the anomer α/anomer β ratio is 30:70. The K_m values of transketolase substrates like ribose-5-phosphate, for which the main form is the cyclic hemiacetal form, can be explained either by a very high affinity of the open form or, more probably, by a specific stabilisation of the open form in the enzymatic site. This specific stabilisation appears to be inefficient for aldehydes lacking an α hydroxyl group.

As expected, the phosphorylation of the 4-hydroxyl group makes **1c** a very good substrate for transketolase, because the open form is the only one present and the phosphate group allows an anchorage in the active site of the enzyme as with the natural substrate, D-erythrose-4-phosphate. At a concentration of 15 mM, the activity

Table 1
Kinetic data for the reactions of substituted butanals with transketolase and FB-aldolase

Substrates	Transketolase		FB-aldolase	
	V_{max} (%) relative to ribose-5-phosphate	K_m (mM)	V_{max} (%) relative to glyceraldehyde-3-phosphate	K_m (mM)
(*S*)-1a	4	34.5	0.25[a]	
(*S*)-1b	5	31.3	1.18[a]	
(*R*)-1a	8	22.4	0.25[a]	
(*R*)-1b	6	28.7	1.18[a]	
(*R*, *S*)-1c	61[b]	3.8	7.8	6.4
2a	27	12.2	0.62	10
2b	11	36.4	1.74	23
3a	6	31.7	0.42	58
3b	10	34.7	0.39	50

[a] V at 50 mM.
[b] V at 15 mM.

is 60% of that for ribose-5-phosphate. At higher concentrations, inhibition occurs. As the assays were done with racemic **1c**, it is not possible, at this stage, to know if the values refer to only one enantiomer or to both.

2.3. Aldolase activity

Compounds **1–3** were submitted to the action of FB-aldolase. We determined kinetic constants, K_m and initial maximum rate, V_{max}. For the 2-deoxy analogues **1**, we only measured the velocity at a concentration of 50 mM. (***S***)**-1a** and (***R***)**-1a** are poor substrates. Protection of the hydroxyl groups in (***S***)**-1b** and (***R***)**-1b** significantly increases the reactivity. As for transketolase catalysed reactions, the phosphorylated compound **1c** is a good substrate, with a low K_m value and initial rate 7.8% relative to glyceraldehyde phosphate (about 80% relative to glyceraldehyde). The favourable effect of the phosphorylation of aldoses has already been pointed out by Bednarski et al. [25]. Among the 2-methoxy analogues **2** and **3**, compound **2a** with the configuration of D-erythrose presents unexpected good values, the reaction rate being increased in **2b** by the protection of the hydroxyl groups. Compounds **3a** and **3b** with the configuration of L-threose appear as the poorest substrates, with very weak affinity for the enzymatic site, considering the high K_m values.

2.4. Enzymatic syntheses

According to our previous experiences, it is difficult to carry out a synthesis with poor substrates like the unphosphorylated **1–3**, even using a large amount of transketolase easily extracted from spinach leaves. However we attempted to effect a synthesis with the best of these substrates, **2a**. Unfortunately, we were unable to isolate the product.

Compound **1c** could be submitted to the transketolase catalysed reaction with success but, as both enantiomers are probably substrates, the synthesis would lead to a mixture of the 4-deoxy-D-fructose and 4-deoxy-D-sorbose which would be very difficult to purify, at least in the desired phosphorylated form. The synthesis of optically pure **1c** is in progress in our laboratory.

2.4.1. FB-aldolase catalysed synthesis of protected heptuloses

Among the compounds **1-3**, only racemic **1a** had already been used for an aldolase catalysed synthesis [22]. The reaction proceeds with thermodynamically controlled enantioselectivity, so that (***R***)**-1a** reacts first, leading to a heptulose of the L series, more stable in the pyranose form. In this work, we decided to perform only syntheses with the protected substrates (***R***) and (***S***)**-1b**, **2b** and **3b** in order to obtain acyclic protected heptuloses, easy to handle and characterise. Moreover, the activities for these protected compounds were in the same range or even better than for the unprotected one.

The syntheses were carried out on a 2 or 3 mmol scale, using an excess of aldehyde in order to consume the dihydroxy-acetonephosphate completely so that the products were isolated by precipitation of their barium salt. Although (***S***) and (***R***)**-1b** present the same initial velocity at 50 mM in the aldolisation reaction, the S isomer (D configuration) gave the 6,7-*O*-isopropylidene-5-deoxy-D-*arabino*-hept-2-ulose-1-phosphate **6** in a 65% yield, while the R isomer (L configuration) led to the corresponding L-*xylo*-3-hept-2-ulose-1-phosphate **8** with a modest 21% yield. The yields obtained with the 2-methoxy compounds **2b** and **3b** are also higher for the D-isomer (83%) than for the L (10%), which appears to be a very poor substrate on the basis of the kinetic constants.

The expected heptuloses-1-phosphate were easily characterized by ^{13}C NMR spectroscopy since all signals were attributed: *J* mod experiment allowed to attribute the C1 and C7 signals, which were differentiated since C1 appears as a doublet due to the coupling with phosphorous ($J = 3.8$ Hz). Carbons of the two methyl and the quaternary carbon of the dioxolane rings, as

well as the carbon of the carbonyl group appear at a very characteristic shift, respectively near to 28, 112 and 214 ppm. The other signals were attributed by comparison with the spectra of the aldehyde precursors. FAB + mass spectroscopy results are also coherent with the proposed structures, with a signal at 337 (diprotonated monosodium salt) for the 5-deoxy compounds and 389 (protonated disodium salt) and 367 (diprotonated monosodium salt) for the 5-deoxy-5-methoxy compounds.

2.4.2. Aldolase catalysed syntheses from 3,4-dihydroxybutanal-4-phosphate **1c**

Although possessing a racemic substrate leading to a mixture of heptuloses-1,7-bisphosphate, we were interested in carrying out the reaction on a preparative scale in order to control the feasibility of the synthesis and the possible enantioselectivity of the FB-aldolase. In a first run, the aldehyde was reacted with an equimolecular amount of dihydroxyacetone phosphate. After 12 h, the products were isolated as their barium salt with a 65% yield. ^{13}C NMR of the product shows that the two diastereoisomers expected are present in a 1:2.5 ratio. This result suggests that although both enantiomers are substrates, the enzyme is able to discriminate between them. The synthesis was repeated with a half equimolecular amount of dihydroxyacetone phosphate. In this case, indeed, only one compound was obtained. This compound was submitted to the action of acid phosphatase and the hydrolysed heptulose was analysed by ^{13}C NMR spectroscopy. The spectrum was identical to the one published by Liu et al. [22] for the 5-deoxy-L-*xylo*-hept-2-ulose obtained by FB-aldolase catalysed synthesis from racemic **1a**. This result shows that FB aldolase presents the same enantioselectivity towards **1a** and **1c**. However, the separation of this compound from the residual aldehyde appears to be a difficult task without phosphate group hydrolysis and therefore was not undertaken.

3. Experimental

3.1. Materials

Chemicals were purchased from Aldrich, yeast transketolase, FB-aldolase, alcohol dehydrogenase and other biochemicals from Sigma. Dihydroxyacetone phosphate was prepared according to our published procedure [26]. 3-butanol diethylacetal was prepared according to Ref. [27] from ethyl–vinyl ether. 3,4-epoxybutanoldiethylacetal was prepared according to Ref. [22].

3.2. Instrumentation

NMR spectra were recorded on a ^{1}H (400 Mhz) and ^{13}C (100 Mhz) Bruker AC400.

3.3. Enzymatic assays

3.3.1. Determination of transketolase activity

To 1 ml of glycylglycine buffer (0.1 M, pH 7.5) containing thiamine pyrophosphate (1.2 mg), $MgCl_2$ (0.2 mg), NADH (0.2 mg), erythrulose (12 mg), yeast alcohol dehydrogenase (3 U) and transketolase (1 U), was added to the tested aldehyde (20 to 200 μl of a solution of variable concentration, for a concentration in the assay of 1 to 100 mM). The optical density at 340 nm is recorded. The rate of reaction is $V_{ald.} = \Delta DO/min/6.22$, in μmole/min/ml of solution. The activity was measured in the same conditions for ribose-5-phosphate at 50 mM. The V_{rel} is $V_{ald.}/V_{ribose\text{-}5\text{-}P}$.

3.3.2. Determination of FB-aldolase activity

To 1 ml of triethanol amine buffer (0.1 M, pH 7.5) containing dihydroxyacetone phosphate (20 mM) and FB-aldolase (1 U) was added to a solution containing the tested aldehyde (20 to 200 μl at variable concentration). Immediately after 5 or 10 min of reaction, 0.1 ml of the solution was withdrawn, quenched with 30 μl of 7% perchloric acid solution, neutralized with

20 μl of 1 N NaOH and diluted with 0.5 ml of TEA buffer. This solution was assayed for DHAP [26]. DHAP concentration variation gave the activity of the FB-aldolase. Comparison of this value with the activity of the aldolase solution used for the natural substrate makes it possible to calculate the velocity relative to glyceraldehyde-3-phosphate (V_{rel}).

3.4. 3,4-Dihydroxybutanal-4-phosphate diethylacetal

To a solution of dipotassium hydrogen phosphate (7.4 g, 42.5 mmol) in 60 ml of water was added to **1** (2.6 g, 16.2 mmol) and the mixture was heated under reflux for 24 h. During this time the mixture turned dark yellow. The solution was extracted with 3×30 ml of ether. A solution of barium acetate (15 g, 55 mmol) in 20 ml of water was added to the aqueous layer. Then the mixture was adjusted at pH 8. The precipitate was removed by centrifugation. Four volumes of ethanol were added and the resulting solution was kept at 4°C overnight. The precipitate thus formed was obtained by centrifugation and dried in vacuo to obtain **2** (2.2 g, 35% from **1**).

^{1}H NMR (D_2O, HOD = 4.9 ppm) 1.25 (m, 6H, $CH(OCH_2CH_3)_2$), 1.85 (m, 2H, CH_2CH-$(OEt)_2$); 3.75 (m, 7H, $CH(OCH_2CH_3)_2$, CH-$(OEt)_2$, CH_2OPO_3Ba); 3.95 (m, 1H, $CHOH$). ^{13}C NMR (D_2O): δ17.10 (C_6), 39.52 (C_3), 65.77 (C_5), 70.32 (C_2, $J = 7.04$ H_2) 70.95 (C_1, $J = 4.83$ H_2), 103.67 (C_4).

3.5. 6,7-O-Isopropylidene-5-deoxy-D-arabino-hept-2-ulose-1-phosphate ***5***

To 50 ml of a solution of DHAP (2.78 mmol) was added the aldehyde (*S*)-**1b** (800 mg, 5.56 mmol); the solution is completed to 100 ml, adjusted to pH 7.5 and FB-aldolase (200 U) was added. After 24 h, the mixture is concentrated to 30 ml, the pH adjusted to 8.2 and 9 ml of a solution containing 1.39 g (5.5 mmol) of barium chloride is added. After 1 h at 4°C, the precipitate formed is eliminated by centrifugation. To the surnageant, 160 ml of ethanol were added and the mixture is left overnight at 4°C and centrifuged. The solid is washed with alcohol and acetone. Water (20 ml) is added and the mixture is treated by ion exchange resin Dowex Na^+ form. The mixture is filtered out and the solution lyophilized giving 0.81 g (65% yield) of **5** as its sodium salt.

^{1}H NMR (D_2O): δ1.38 (s, 3H); 1.39 (s, 3H); 3.51–4.85 (unresolved broad signal, 8H). ^{13}C NMR (D_2O): δ27.35 and 28.55 (methyl groups); 39.02 (C_5); 68.10 (C_7); 70.10 (C_1); 71.36 (C_6); 76.05 (C_4); 80.76 (C_3); 113.18 (C_8); 218.93 (C_2).

3.6. 6,7-O-Isopropylidene-5-deoxy-L-xylo-hept-2-ulose-1-phosphate ***8***

The synthesis was realized as before, from 1.13 g (7.88 mmol) of aldehyde (*R*)-**1b**. A total of 0.37 mg of **7** was isolated as a sodium salt (21% yield).

^{1}H NMR (D_2O): δ1.26 (s, 3H); 1.21 (s, 3H); 3.46–4.90 (unresolved broad signal 8H). ^{13}C NMR (D_2O): δ26.97 and 28.11 (methyl group); 38.86 (C_5); 68.15 (C_7); 70.52 (C_1); 72.01 (C_6); 76.55 (C_4); 81.09 (C_3); 113.77 (C_8); 218.39 (C_2).

3.7. 6,7-O-Isopropylene-5-O-methyl-D-arabino-hept-2-ulose-1-phosphate ***6***

From 0.8 g (4.60 mmol) of aldehyde **2b**, 0.915 g (83% yield) of the sodium salt of **6** were isolated.

^{1}H NMR (D_2O): δ1.25 (s, 3H); 1.32 (s, 3H); 3.83 (m, 1H, H4); 4.05 (dd, 1H, $J = 9.1$ Hz and 1.5 Hz); 4.11–4.33 (unresolved, 2H, H7); 4.63–4.76 (unresolved, 2H, H5 and H6); 4.78 (m, 2H, H1). ^{13}C NMR (D_2O): δ26.73 and 27.63 (methyl groups); 63.22 (OCH_3); 66.10 (C_7); 70.68 (C_1); 73.60 (C_5); 77.77 (C_6); 78.84 (C_4); 81.48 (C_3); 112.14 (C_8); 214.45 (C_2).

3.8. 6,7-O-Isopropylidene-5-O-methyl-L-xylo-hept-2-ulose-1-phosphate **9**

An amount of 0.15 g of **9** (10% yield) was isolated from 1.10 g (6.3 mmol) of the aldehyde **3b**.

^{1}H NMR (D_2O): δ1.21 (s, 3H); 1.29 (s, 3H); 3.78 (m, 1H, H4); 4.02 (dd, $J = 9.1$ and 1.5 Hz); 4.10–4.40 (unresolved, 2H, H7); 4.65–4.78 (unresolved, 2H, H5 and H6); 4.79 (m, 2H, H1). ^{13}C NMR (D_2O): δ27.11 and 27.99 (methyl groups); 63.26 (OCH_3); 68.44 (C_7); 70.75 (C_1); 73.64 (C_5); 78.31 (C_6); 78.93 (C_4); 82.20 (C_3); 112.13 (C_8); 214.73 (C_2).

3.9. 5-Deoxy-D-arabino-heptulose-1,7-bisphosphate, **4**, and 5-deoxy-L-xylo-hept-2-ulose-1,6-bisphosphate, **7**

3,4-Dihydroxybutyraldehyde-4-phosphate diethylacetal barium salt was stirred with a suspension of Dowex resin H^+ form. After 30 min the resin was filtered off and the mixture was adjusted to pH 7.5 with 1 N NaOH. The water was removed under reduced pressure to give 1.1 g of residue which was used for the next step without more purification. To 20 ml of a solution of DHAP (150 mM) was added 0.67 g (2.9 mmol) of the aldehyde and the solution was adjusted to pH 7.5. FB-aldolase (200 U) was added and the mixture stirred at 30°C. The reaction progress was followed by titration of DHAP. After 12 hours, 80 ml of methanol were added and the precipitate was filtered off to give 0.85 g (65.4% yield) of **4** and **7** in a 1:2.5 ratio.

Compound **7**: ^{1}H NMR (D_2O): δ1.6 (1H HC_5), 2.15 (1H HC_5), 3.4–4.5 (7H). ^{13}C NMR: 37.02 (C_5), 69.05, 69.33 ($2 \times CH_2$), $J = 4.47$ H_2), 70.38 (CHOH), 71.09 (C_6, $J = 7.63$ Hz), 74.75 (CH), 100.55 (C_2).

Compound **4**: ^{1}H NMR (D_2O): δ1.3 (1H HC_5), 1.95 (1H HC_5), 3.4–4.5 (7H). ^{13}C NMR (D_2O): δ23.23 (C_5), 65.35 (C_6, $J = 7.63$ H_2), 67.85 (CHOH), 69.30, 69.79 ($2 \times CH_2$, $J =$ 4.47 H_2), 70.08 (CHOH), 100.77 (C_2).

References

[1] C.H. Wong, G.M. Whitesides, Enzymes in Synthetic Organic Chemistry, Pergamon, Oxford, 1994, p. 195.
[2] K. Drauz, H. Waldmann, Enzyme Catalysis in Organic Synthesis, Chap. B4.1, VCH, New York, 1995.
[3] S. David, C. Augé, C.M. Gautheron, Adv. Carbohydr. Chem. Biochem. 49 (1992) 175.
[4] D.G. Drueckhammer, W.J. Hennen, R.L. Pederson, C.F. Barbas, C.M. Gautheron, T. Krach, C.H. Wong, Synthesis (1991) 499–525.
[5] E.J. Toone, E.S. Simon, M.D. Bednarski, G.M. Whitesides, Tetrahedron 45 (1989) 5365–5422.
[6] W.C. Chow, L. Chen, J.M. Fauy, C.H. Wong, J. Am. Chem. Soc. 116 (1994) 6191–6194.
[7] F. Effenberger, A. Straub, V. Null, Liebigs Ann. Chem. (1992) 1297–1301.
[8] K.K.C. Liu, T. Kajimoto, L. Chen, Z. Zhong, Y. Ichikawa, C.H. Wong, J. Org. Chem. 56 (1991) 6280–6289.
[9] W. Schmid, G.M. Whitesides, J. Am. Chem. Soc. 112 (1990) 9670–9671.
[10] A. Straub, F. Effenberger, P. Fischer, J. Org. Chem. 55 (1990) 3926–3932.
[11] C.H. Wong, G.M. Whitesides, J. Org. Chem. 48 (1983) 3199–3205.
[12] Y. Kobori, D.C. Myles, G.M. Whitesides, J. Org. Chem. 57 (1992) 5899–5907.
[13] F. Effenberger, V. Null, Liebigs Ann. Chem. (1992) 1211–1212.
[14] T. Ziegler, A. Straub, F. Effenberger, Angew. Chem. Int. Ed. Engl. 27 (1988) 716–717.
[15] J. Bolte, C. Demuynck, H. Samaki, Tetrahedron Lett. 28 (1987) 5525–5528.
[16] L. Hecquet, M. Lemaire, J. Bolte, C. Demuynck, Tetrahedron Lett. 35 (1994) 8791–8794.
[17] M. Lemaire, M.L. Valentin, L. Hecquet, C. Demuynck, J. Bolte, Tetrahedron: Asymmetry 6 (1995) 67–70.
[18] N. Bischofberger, H. Waldmann, T. Saito, E.S. Simon, W. Lees, M.D. Bednarski, G.M. Whitesides, J. Org. Chem. 53 (1988) 3457–3465.
[19] L. Hecquet, J. Bolte, C. Demuynck, Tetrahedron 50 (1994) 8677–8684.
[20] L. Hecquet, J. Bolte, C. Demuynck, Tetrahedron 52 (1996) 8223–8232.
[21] J.R. Durrwachter, C.H. Wong, J. Org. Chem. 53 (1988) 4175–4181.
[22] K.K.C. Liu, R.L. Pederson, C.H. Wong, J. Chem. Soc. Perkin Trans. 1 (1991) 2669–2673.
[23] L. Hecquet, J. Bolte, C. Demuynck, Biosci. Biotech. Biochem. 57 (1993) 2174–2176.
[24] J.R. Snyder, A.S. Serianni, Carbohydr. Res. 210 (1991) 21–38.
[25] M.D. Bednarski, H.J. Waldmann, G.M. Whitesides, Tetrahedron Lett. 27 (1986) 5807–5810.
[26] M.L. Valentin, J. Bolte, Bull. Soc. Chim. Fr. 132 (1995) 1167–1171.
[27] R.I. Hoaglin, D.G. Kubler, A.E. Montagna, J. Am. Chem. Soc. 80 (1958) 5460–5463.