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Glucose isomerase catalysed isomerisation reactions of (2*R*,3*R*)-configured aldofuranoses into the corresponding open-chain 2-ketoses [1]

Michael Ebner, Arnold E. Stütz *

Institut für Organische Chemie der Technischen Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria

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Abstract

Immobilised glucose isomerase (EC 5.3.1.5) accepted various (2*R*,3*R*)-configured aldofuranoses such as D-erythrose, as well as homologous C-5-modified D-ribose derivatives, as substrates. In the case of D-erythrose, quantitative conversion into D-*glycero*-tetrulose took place. D-Ribofuranoses were converted into the corresponding open-chain 2-ketoses in isolated yields of 65%. Surprisingly, L-erythrose also turned out to be a substrate of this enzyme. © 1998 Elsevier Science Ltd.

Keywords: Glucose isomerase; Erythrose; Erythrulose, D-Ribofuranoses; Open-chain ketoses

1. Introduction

Glucose isomerases (EC 5.3.1.5) from various microorganisms have been found to catalyse the conversion of D-glucose (**1**) into D-fructose (**2**, Scheme 1) and are currently, in immobilised form, employed on a large scale to the industrial exploitation of this economically important transformation [1]. Most of these enzymes function in vivo as D-xylose isomerases, their K_M values with D-xylose being one to two orders of magnitude smaller than those with D-glucose as substrate [2]. In order to gain insight into the substrate tolerance of glucose isomerase, several investigators have probed the enzyme with a wide range of unnatural aldoses as well as 2-ketoses. The first successful transformation of an unnatural substrate reported was the conversion of 6-deoxy-6-thio-D-glucose into the corresponding D-fructopyranose [3], the stable hemiacetal bond between the sulfur and C-2 in the product being responsible for the driving force of the reaction. Subsequently, in a very important investigation, Bock and co-workers found that D-glucose derivatives bearing modifications at C-6 or C-3 were converted by the enzyme of a *Streptomyces* species in yields varying between 10 and ca. 40%, while epimers of D-glucose such as D-mannose, D-allose, D-galactose, as well as L-idose were not accepted as substrates [4]. An interesting finding was the quantitative conversion of 5-deoxy-D-*xylo*-hexofuranose ('5-deoxy-D-glucose') into the corresponding 2-ketohexopyranose. These results

* Corresponding author. Tel.: +43-316-8738247; fax: +43-316-8738740; e-mail: stuetz@orgc.tu-graz.ac.at.

[1] Dedicated to Professor Yoshito Kishi on the happy occasion of his 60th birthday.

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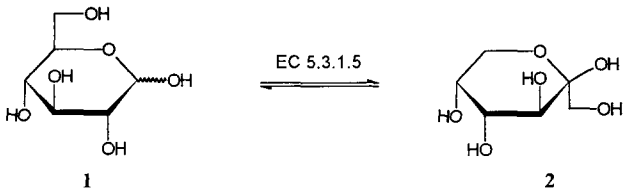


1 2

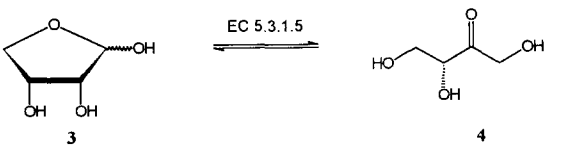
Scheme 1.

were reproduced and extended by Wong and his group who employed glucose isomerase for the conversion of enzymatically prepared non-natural D-fructoses into the corresponding D-glucopyranose derivatives [5–7]. By this means, mixtures of diastereomers obtained from an aldolase- or *trans*ketolase-catalysed carbon–carbon bond-forming step which contained L-sorboses could be conveniently separated as the latter were not isomerised to L-idose derivatives [6]. Recently, we have reported several preparatively useful extensions of the glucose isomerase-catalysed reaction. Following Bock's results, it could be demonstrated that immobilised glucose isomerase (Sweetzyme T) quantitatively converts 5-modified D-glucofuranoses into the corresponding D-fructopyranoses [8], the driving force of the reaction being attributed to the release of ring strain in the starting materials. Furthermore, it was found that L-idofuranoses also undergo the rearrangement to give the corresponding L-*sorbo* isomers in high yields. Based on the observation that the five-membered ring in these aldofuranoses is obviously highly unstable, we expected that 5-modified D-xylofuranoses, as well as 5,6-dimodified D-glucofuranose derivatives, might give access to rare open-chain 2-ketoses when exposed to the enzyme's action. Gratifyingly, this could be shown for either series of compounds [9] as well as, very recently, for 5,6-dimodified analogues of L-idose, the isomerisation products of which have proven very useful in the synthesis of a range of interesting glycosidase inhibitors [10]. In search for further extensions of the method, the behaviours of some selected (2*R*,3*R*)-configured aldofuranoses towards the enzyme were investigated.

2. Results and discussion

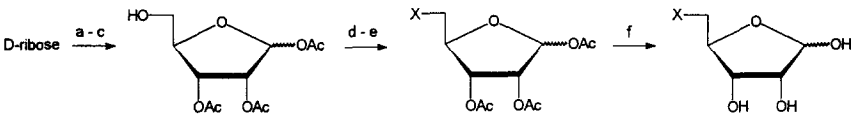
There are reports in the literature that some xylose isomerases can exhibit side activities towards (2*R*,3*R*)-configured aldoses such as D-ribose [2,11,12] and, in rare cases as with the enzyme from *Streptomyces albus*, also D-allose [13]. Based on previous findings [8,9] that ring enlargement or other means of strain release in the course of the enzyme-catalysed aldose-to-ketose isomerisation enhance the conversion rate, we felt that aldofuranoses with the (2*R*,3*R*)-configuration and not bearing bulky substituents at C-4 might be accepted as substrates by Sweetzyme T, which also stems from a *Streptomyces* species. Initial experiments with D-erythrose (**3**), as the most simple and stereochemically least demanding representative of the class of sugars under consideration, immediately gave encouraging results as this tetrose was quantitatively converted into the corresponding open-chain 2-ketose, D-erythrulose (D-*glycero*-tetrulose, **4**, Scheme 2). No reaction could be detected in the opposite direction employing compound **4** as the substrate. The low isolated yield of the product is likely to be due to the fact that commercially available D-erythrose is less than 80% pure as it contains considerable amounts of moisture.

Formal extension of the carbon chain at C-4 by a fluoromethyl group leads to 5-deoxy-5-fluoro-D-ribofuranose (**5**). This compound is easily accessible from D-ribose by the following sequence of reactions (Scheme 3): 5-*O*-tritylation with chlorotriphenylmethane in pyridine, per-*O*-acetylation employing acetic anhydride in the same reaction vessel, conventional removal of the trityl group [14] to give partially protected intermediate **9**, activation of C-5 by formation of the 5-triflate with the aid of trifluoromethanesulfonic anhydride in the presence of pyridine, and the displacement of the leaving group by fluoride with pre-dried tetrabutylammonium fluoride in dry acetonitrile, followed by deprotection of compound **10** (sodium methoxide in MeOH). Substrate **5** was found to be accepted by the enzyme giving a 3:1 mixture in favour of the corresponding open-chain D-ribulose **7**, providing an isolated yield of 65% (Scheme 4). No sign of isomerisation could be detected in absence of the enzyme under otherwise identical reaction conditions as well as in the presence of sodium bicarbonate as a base. 5-Azido-5-deoxy-D-ribose **6**, prepared via intermediate **11** by following the procedure for the synthesis of aldose **5** but employing sodium azide in acetone in the displace-



3 4

Scheme 2.



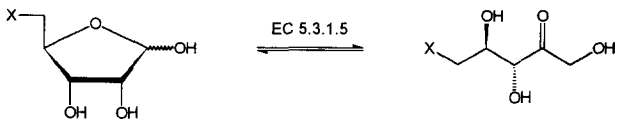
9 X = F 10, X = N_3 11 X = F 5, X = N_3 6

Scheme 3. (a) Ph_3CCl, Pyr; (b) Ac_2O; (c) $BF_3 \cdot Et_2O$, MeOH, $CHCl_3$; (d) Tf_2O, Pyr; (e) Bu_4NF, CH_3CN (for comp. **10**) or NaN_3/Acetone (for comp. **11**); (f) NaOMe, MeOH.

ment step (Scheme 3), was another substrate that could be successfully converted into the corresponding open-chain ketose **8** (Scheme 4). From NMR spectra of the reaction mixture, the ratio of the desired product and starting material was estimated to be 3:1. As with compound **7**, the isolated yield of ketose **8** was 65%, which demonstrates the applicability of this approach in the D-ribofuranose series.

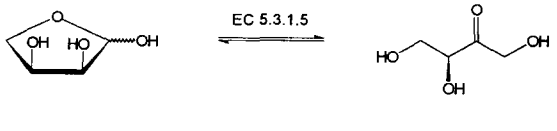
In conclusion, immobilised glucose isomerase (Sweetzyme T) is able to convert (2*R*,3*R*)-configured aldotetrose as well as D-ribofuranoses modified at C-5 into the corresponding open-chain 2-ketoses, the latter being the predominant products of the isomerisation reactions. Ongoing experiments are probing the reactivities of selected (2*R*,3*R*)-configured hexofuranoses towards the enzyme.

It is interesting to note that L-erythrose (**12**), the enantiomer of substrate **3**, was also quantitatively isomerised by the enzyme into L-erythrulose (L-*glycero*-tetrulose, **13**) (Scheme 5). A possible explanation is that L-erythrose might be able to adopt a productive conformation in the roughly funnel-like shaped active site [15] with the hydroxyl group at C-2 in a similar position as the 2-OH of D-xylose or D-glucose. This could be feasible due to its relatively small size and the freely rotating hydroxymethyl group at C-3. Clearly, this hypothesis needs further experimental support.



X = F 5, X = N_3 6 X = F 7, X = N_3 8

Scheme 4.



12 13

Scheme 5.

As in the case of compound **4**, low isolated yields of ketose **13** might be due to impurities in the commercially available starting material. In control experiments, in absence of enzyme at neutral as well as slightly basic pH values, the substrate failed to react under the conditions employed. As with enantiomer **4**, no sign of isomerisation could be detected with compound **13** as the substrate.

3. Experimental

General methods.—Melting points were recorded on a Tottoli apparatus and are uncorrected. Optical rotations were measured on a JASCO Digital Polarimeter or with a Perkin–Elmer model 341 spectropolarimeter with a path length of 10 cm. NMR spectra were recorded at 200 as well as 300 MHz (^1H), and at 50.29 and 75.47 MHz (^{13}C). $CDCl_3$ was employed for protected compounds and D_2O or CD_3OD for free sugars. Chemical shifts are listed in δ employing residual, not deuterated, solvent as the internal standard. The signals of the protecting groups were found in the expected regions and are not listed explicitly. TLC was performed on precoated aluminum sheets (E. Merck 5554). TLC plates were stained with concd H_2SO_4 containing 5% vanillin. For column chromatography Silica Gel 60 (E. Merck) was used. Mixtures of ethyl acetate–petroleum ether (1:10 to 3:1) were used for both TLC and column chromatography of protected compounds, and ethyl acetate as well as ethyl acetate–MeOH mixtures (10:1 to 4:1) were employed for TLC and chromatography of unprotected sugars. Saturated aqueous bicarbonate for washing was freshly prepared. D- and L-Erythrose, L-erythrulose as well as D-ribose were purchased from Fluka and Sigma.

General method for isomerisation reactions with immobilised glucose isomerase.—To a 5% solution of the respective free sugar in distilled water, a few

drops of a 1% aqueous solution of $MgSO_4$ and 4 equiv (w/w) of immobilised glucose isomerase (Sweetzyme T, Novo) were added, and the mixture was spun on a rotary evaporator or shaken at 60 °C for 3–8 h. After the appropriate reaction time, the solids were filtered off, the solution was concentrated under reduced pressure, and the residue was chromatographed on silica gel. Alternatively, in case of similar polarities of product and starting material, the aqueous solution was treated with bromine in the presence of calcium carbonate to oxidize remaining aldose to the corresponding lactone to allow for easier separation. Nitrogen was bubbled through the brown solution, the solids were removed by filtration, the solution was concentrated under reduced pressure, and the residue subjected to chromatography. The aldonolactone can be recycled by conventional reduction to the free aldose [16].

D-glycero-*tetrulose* (D-*erythrulose*, **4**).—Following the general procedure, D-erythrose (**3**, 200 mg, 1.71 mmol, Fluka 45681) was exposed to glucose isomerase for 8 h, after which period of time no starting material was detectable in the reaction mixture. Compound **4** was obtained as an off-white wax (132 mg, 66%): $[\alpha]_D^{20}$ −10.5° (*c* 2.1, H_2O) lit.: $[\alpha]_D^{20}$ −11.3° (*c* 1, H_2O) [17]; a commercially available sample of the enantiomer (Fluka 45698) exhibited $[\alpha]_D^{20}$ +10.2° (*c* 2, H_2O); ^1H NMR (MeOH-d_4): δ 4.54 (d, 1 H, $J_{1,1'}$ 19.5 Hz, H-1), 4.44 (d, 1 H, H-1'), 4.27 (dd, 1 H, H-3), 3.81 (dd, 1 H, $J_{3,4}$ 4.2 Hz, $J_{4,4'}$ 11.5 Hz, H-4), 3.74 (dd, 1 H, $J_{3,4'}$ 3.8 Hz, H-4'); ^{13}C NMR (MeOH-d_4): δ 213.1 (C-2), 77.8 (C-3), 67.7 (C-1), 64.9 (C-4).

1,2,3-Tri-O-*acetyl*-D-*ribofuranose* (**9**).—To a 5% solution of D-ribose (3.20 g, 21.3 mmol) in dry pyridine, chlorotriphenylmethane (7.20 g, 25.8 mmol, 1.21 eq.) was added, and the mixture was stirred at 40 °C until the starting material was no longer detectable by TLC. Acetic anhydride (9.1 g, 1.4 equiv per free OH) was added, and the mixture was kept at ambient temp until TLC showed practically quantitative conversion of the intermediate into a single, faster moving product. MeOH was added, and the mixture was concentrated under reduced pressure. The syrupy residue was partitioned between CH_2Cl_2 and 5% aqueous HCl, and the organic layer was washed with saturated aqueous sodium bicarbonate. The yellow solution was dried (sodium sulfate), and the solids were removed by filtration. Boron trifluoride–diethyl ether complex in Et_2O (4 mL) and MeOH (20 mL) were added, and the dark mixture was kept at ambient temp until TLC indicated completion of the reaction. Dichloromethane (100 mL) was added, and the solution was extracted with saturated aqueous sodium bicarbonate. The organic layer was dried (Na_2SO_4) and solids were removed by filtration. Chromatography of the oily residue gave syrupy compound **9** (2.84 g, 48% overall) as a mixture of anomers: ^{13}C NMR ($CDCl_3$): δ 98.1, 94.3 (C-1 α/β), 84.8, 82.4, 74.5, 70.4, 69.9 (C-2, C-3, C-4), 66.8, 61.8 (C-5). Anal. Calcd for $C_{11}H_{16}O_8$: C, 47.83; H, 5.84. Found: C, 47.62; H, 5.95.

1,2,3-Tri-O-*acetyl*-5-*azido*-5-*deoxy*-D-*ribofuranose* (**11**).—To a 2% solution of compound **9** (2.84 g, 10.3 mmol) in CH_2Cl_2 containing 5% of pyridine, trifluoromethanesulfonic anhydride (2.1 mL, 1.2 equiv) was added at 0 °C. When TLC indicated completed reaction to a single faster moving compound, CH_2Cl_2 (100 mL) was added, and the mixture was consecutively washed with 5% aqueous HCl and saturated aqueous sodium bicarbonate. The organic layer was dried (Na_2SO_4), solids were removed by filtration, and the filtrate was concentrated under reduced pressure to give a brown syrup that was dissolved in acetone (100 mL). Sodium azide (10 g, 15 equiv) was added, and the mixture was stirred at ambient temperature until TLC showed completed conversion into a slightly more polar compound. After addition of CH_2Cl_2 (150 mL), solids were filtered off. The filtrate was concentrated under reduced pressure. Chromatography of the oily residue furnished azidodeoxy sugar **11** as a colourless syrup (2.45 g, 79%). Anomers could not be obtained in analytically pure states. **11**α: ^1H NMR ($CDCl_3$) δ 6.42 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.23–5.10 (m, 2 H, H-2, H-3), 4.33 (ddd, 1 H, H-4), 3.62 (dd, 1 H, $J_{4,5}$ 3.2 Hz, $J_{5,5'}$ 13.2 Hz, H-5), 3.51 (dd, 1 H, $J_{4,5'}$ 3.7 Hz, H-5'); ^{13}C NMR ($CDCl_3$): δ 94.2 (C-1), 83.0 (C-4), 70.2, 70.1 (C-2, C-3), 52.0 (C-5); **11**β: ^1H NMR ($CDCl_3$) δ 6.17 (s, 1 H, H-1), 5.48–5.30 (m, 2 H, H-2, H-3), 4.31 (m, 1 H, H-4), 3.64 (dd, 1 H, $J_{4,5}$ 3.3 Hz, $J_{5,5'}$ 13.6 Hz, H-5), 3.27 (dd, 1 H, $J_{4,5'}$ 4.0 Hz, H-5'); ^{13}C NMR ($CDCl_3$): δ 98.0 (C-1), 80.4 (C-4), 74.3, 70.2 (C-2, C-3), 51.5 (C-5). Anal. Calcd for $C_{11}H_{15}N_3O_7$: C, 43.86; H, 5.02. Found: C, 43.72; H, 4.95.

5-Deoxy-5-*fluoro*-D-*ribofuranose* (**5**).—To a 2% solution of compound **9** (3.24 g, 11.7 mmol) in CH_2Cl_2 containing 5% of pyridine, trifluoromethanesulfonic anhydride (2.3 mL, 1.2 equiv) was added at 0 °C. When TLC indicated completed reaction to a single, faster moving compound, CH_2Cl_2 (100 mL) was added, and the mixture was consecutively washed with 5% aqueous HCl and saturated aqueous sodium

bicarbonate. The organic layer was dried (Na_2SO_4), solids were removed by filtration, and the filtrate was concentrated under reduced pressure to give a brown syrup that was dissolved in acetonitrile (100 mL). A solution of pre-dried [18] tetra butylammonium fluoride trihydrate (22 g, 6 equiv) in acetonitrile (35 mL) was added, and the mixture was kept at ambient temperature for 18 h. Removal of the solvent under reduced pressure and chromatography of the dark oily residue gave 1,2,3-tri-*O*-acetyl-5-deoxy-5-fluoro-D-ribofuranose (**10**) as a mixture of anomers (2.38 g, 73%). To a solution of compound **10** in dry MeOH (130 mL) a solution of NaOMe in MeOH (1 M, 5 mL) was added at 0 °C. When TLC indicated completed removal of the acetyl groups, the clear colourless solution was neutralised with an acidic ion exchange resin, Amberlite IR-120 [H^+], which was subsequently removed by filtration. The filtrate was concentrated under reduced pressure to give compound **5** (1.20 g, 92%) as a slightly yellow syrup: Due to the anomeric mixture (α/β 1:1) as well as the H,F-couplings in the ^{1}H NMR spectra, these were too poorly resolved to allow conclusive interpretation. ^{13}C NMR (MeOH-d_4): δ 103.2, 97.5 (C-1 α/β), 85.4, 84.1 ($J_{5,F}$ 170 Hz, C-5 α/β), 83.1, 82.0 ($J_{4,F}$ 18 Hz, C-4 α/β), 76.6, 72.1 (C-2 α/β), 71.3, 70.9 ($J_{3,F}$ 6 Hz, C-3 α/β). Anal. Calcd for $C_5H_9FO_4$: C, 39.48; H, 5.96. Found: C, 39.60; H, 6.15.

*5-Azido-5-deoxy-*D*-ribofuranose* (**6**).—To a 5% solution of compound **11** (2.45 g, 8.13 mmol) in dry MeOH, a methanolic solution of NaOMe (1 M, 5 mL) was added. After complete deprotection, the clear colourless solution was neutralised with an acidic ion-exchange resin, Amberlite IR-120 [H^+], which subsequently was removed by filtration. The filtrate was concentrated under reduced pressure to give compound **6** (1.37 g, 96%, mixture of anomers) as a colourless syrup: $[\alpha]_D^{20}$ +76.7° (*c* 2.7, MeOH); ^{1}H NMR (MeOH-d_4): δ 5.33 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1/α), 5.18 (s, 1 H, H-1/β), ratio α/β 1:3; ^{13}C NMR (MeOH-d_4): δ 103.4 (C-1/β), 98.2 (C-1/α), 82.6 (C-4/α), 82.4 (C-4/β), 77.0, 73.1 (C-2/β, C-3/β), 72.7, 72.4 (C-2/α, C-3/α), 54.8 (C-5/β), 53.5 (C-5/α). Anal. Calcd for $C_5H_9N_3O_4$: C, 34.29; H, 5.18. Found: C, 34.14; H, 5.26.

*5-Deoxy-5-fluoro-*D-erythro-*pent-2-ulose* (*5-Deoxy-5-fluoro-*D-*ribulose*, **7**).—Enzymatic isomerisation of aldofuranose **5** (932 mg, 6.13 mmol) according to the general procedure furnished ketose **7** (610 mg, 65%) as a colourless syrup: $[\alpha]_D^{20}$ +10.8° (*c* 0.4, MeOH); ^{1}H NMR (MeOH-d_4): δ 4.49 (m, 2 H, $J_{5,F}$ 40 Hz, H-5,5′), 4.51 (d, 2 H, $J_{1,1'}$ 6.7 Hz, H-1,1′), 4.21 (d, 1 H, $J_{3,4}$ 6.0 Hz, H-3), 4.16–3.85 (m, 1 H, $J_{4,F}$ 20 Hz, H-4); ^{13}C NMR (MeOH-d_4): δ 213.0 (C-2), 84.6 ($J_{5,F}$ 168 Hz, C-5), 75.8 ($J_{3,F}$ 5.5 Hz, C-3), 72.9 ($J_{4,F}$ 18.9 Hz, C-4), 68.1 (C-1). Anal. Calcd for $C_5H_9FO_4$: C, 39.48; H, 5.96. Found: C, 39.37; H, 5.89.

*5-Azido-5-deoxy-*D-erythro-*pent-2-ulose* (*5-azido-5-deoxy-*D-*ribulose*, **8**).—Enzymatic isomerisation of aldofuranose **6** (1.15 g, 6.57 mmol) following the general procedure yielded ketose **8** (0.75 g, 65%) as a colourless syrup: $[\alpha]_D^{20}$ +12.3° (*c* 0.3, MeOH); ^{1}H NMR (MeOH-d_4): δ 4.56 (d, 1 H, $J_{1,1'}$ 19.4 Hz, H-1), 4.43 (d, 1 H, H-1′), 4.16 (d, 1 H, $J_{3,4}$ 6.0 Hz, H-3), 3.91 (m, 1 H, H-4), 3.39 (m, 2 H, H-5,5′); ^{13}C NMR (MeOH-d_4): δ 212.7 (C-2), 77.0, 73,3 (C-3, C-4), 68.1 (C-1), 54.2 (C-5). Anal. Calcd for $C_5H_9N_3O_4$: C, 34.29; H, 5.18. Found: C, 34.20; H, 5.39.

L-glycero-*Tetrulose* (L-*erythrulose*, **13**).—Following the general procedure, L-erythrose (**12**, 220 mg, 1.88 mmol, Sigma E 0758) was exposed to glucose isomerase for 8 h, after which period of time no starting material was detectible in the reaction mixture. Compound **13** was obtained as a yellow wax (86 mg, 39%): $[\alpha]_D^{20}$ +10.0° (*c* 2.2, H_2O); lit.: $[\alpha]_D^{20}$ +11.5° (*c* 1, H_2O) [17]; a commercially available sample (Fluka 45698) exhibited $[\alpha]_D^{20}$ +10.2° (*c* 2, H_2O); ^{1}H as well as ^{13}C NMR data are identical with the values obtained from enantiomer **4**.

Acknowledgements

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