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C_2-Ketol elongation by transketolase-catalyzed asymmetric synthesis

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ABSTRACT

The asymmetric synthesis of new carbon–carbon bonds represents a cornerstone of both organic chemistry and biochemistry. Among the variety of synthetic reaction methodologies the aldol and ketol reactions continue to be major technology platforms in the science of synthesis. The efficient utilization of resources and energy towards the synthesis of the product and the reduction of waste are important goals of sustainable chemistry and industrial biotechnology. The transition from stoichiometric to catalytic asymmetric versions of carbon–carbon bond forming reactions is a major topic in various catalysis research areas such as inorganic catalysis, organocatalysis and biocatalysis. α-Hydroxyketones are important structural elements in many compounds, but general chemical procedures for asymmetric chain elongation involve several reaction steps with the stoichiometric use of protecting groups. Catalytic methods utilizing transketolases (TKs) as biocatalysts are highly attractive because of their capability of creating new carbon–carbon bonds with high selectivity and broad substrate specificity. The use of hydroxypyruvate makes the chain elongation by two carbon atoms irreversible and provides the practical advantage of changing the reaction thermodynamics from equilibrium to complete conversion. The large-scale production of transketolase and the irreversible C_2-ketol donor β-hydroxypyruvate have provided the tools to make C_2-ketol elongation attractive for preparative work. The number of reaction steps required for two-carbon extension can thereby be reduced compared with classical chemical synthesis routes.

1. Introduction

The α-hydroxyketone or α-ketol functionality is an important structural motif present in many important compounds. Non-terminal α-ketols can be obtained from the corresponding non-terminal alkenes by oxidation with potassium permanganate under neutral conditions [1–3]. Heterogeneous oxidation of alkenes with a small amount of *t*-butanol and water has been shown to result in the formation of α-ketols in modest to good yields [4]. These oxidative methods lack however enantioselectivity and are more difficult to apply for the synthesis of terminal α-ketols and molecules carrying additional functional groups which could be oxidized as well. The construction of chiral α-hydroxyketones is of much interest and asymmetric dihydroxylation of enol ethers has led to α-hydroxyketones in high enantiomeric purity [5]. The two-carbon chain elongation of the corresponding aldehydes by the use of α-ketoacid decarboxylases has led to such well-known examples as (R)-phenylacetylcarbinol (PAC) [6].

The use of two-carbon increments for the elongation of a carbon backbone towards higher homologues is widespread in nature. Fatty acids in mammalian cells are synthesized in two-carbon fatty acyl elongation reactions, catalyzed by multifunctional fatty acid synthase in the cytosol or by four sequential enzymes starting with fatty acyl elongase in the microsomes [7]. Elongated fatty acids like the arachidonic acid homologue adrenic acid have important roles in coronary arteries [8]. The chain elongation function by a two-carbon unit can also be found in microbial polyketide synthases and the similarity of domain arrangement with the architecture of eukaryotic fatty acid synthases reveals their close evolutionary relationships [9].

2. Chemical two-carbon chain extension methodology

Functional group interconversions with simultaneous chain elongation by two carbon atoms have been developed in many synthetic areas of organic chemistry as shown in the overview of Fig. 1. Alcohols can be converted in one step into nitriles with simultaneous C_2-elongation by the phosphonium salt cyanomethyltrimethylphosphonium iodide [10]. The chemical C_2-elongation of polyunsaturated fatty acids is achieved in a four-step reaction sequence from the parent fatty acid methyl ester to the target polyunsaturated fatty acid [11]. Statin side-chain build-

Abbreviations: C_2, structural molecular building block of two connected carbon atoms with non-carbon containing functional groups; TK, transketolase.

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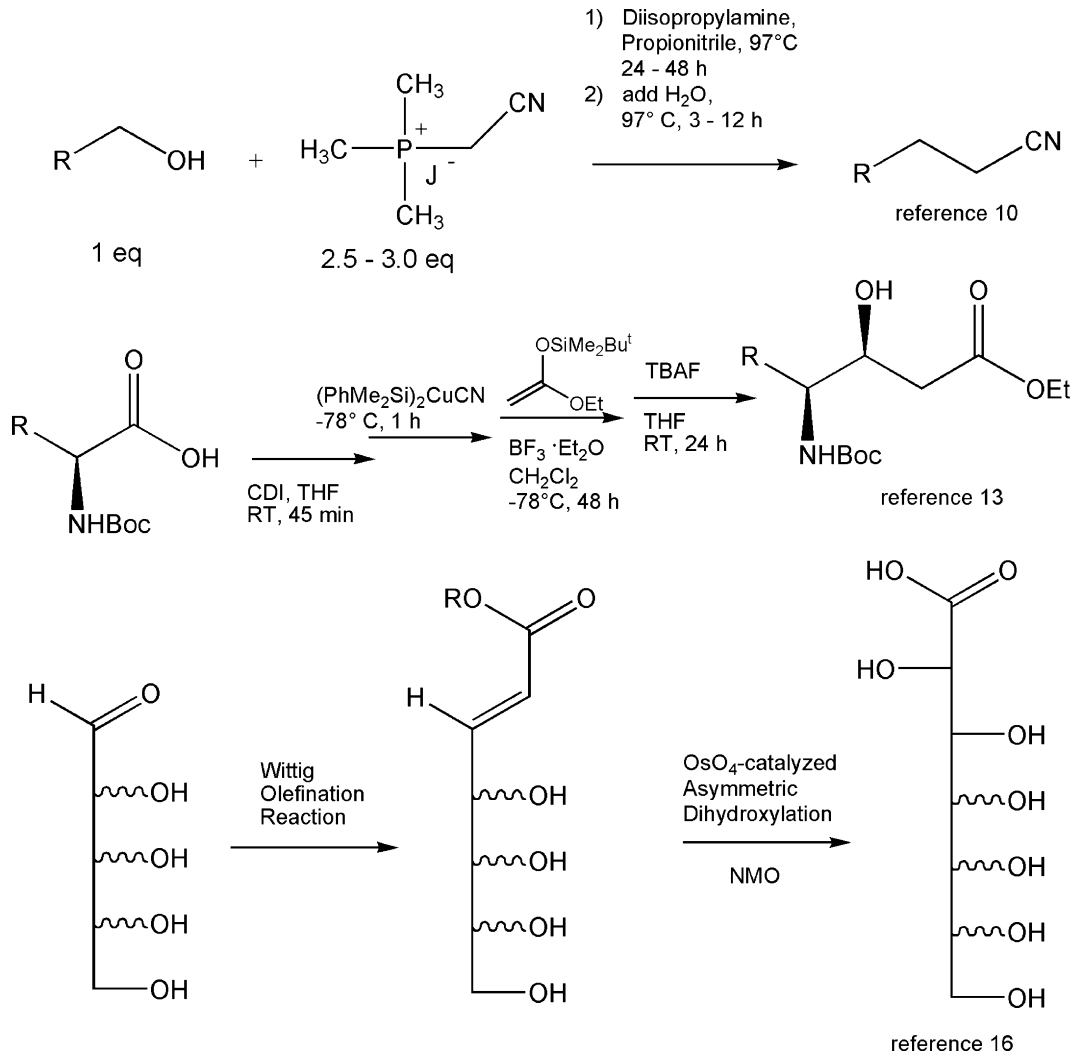

Fig. 1. Overview of selected chemical two-carbon elongation approaches: above the one-step conversion of alcohols into nitriles with simultaneous C_2-elongation by cyanomethyltrimethylphosphonium iodide, in the middle the stereoselective two-carbon elongation of the carbon chain in N-Boc-protected α-aminoacylsilanes and at the bottom the route to higher sugars by two-carbon chain elongation using the reaction sequence of the Wittig and dihydroxylation reactions.

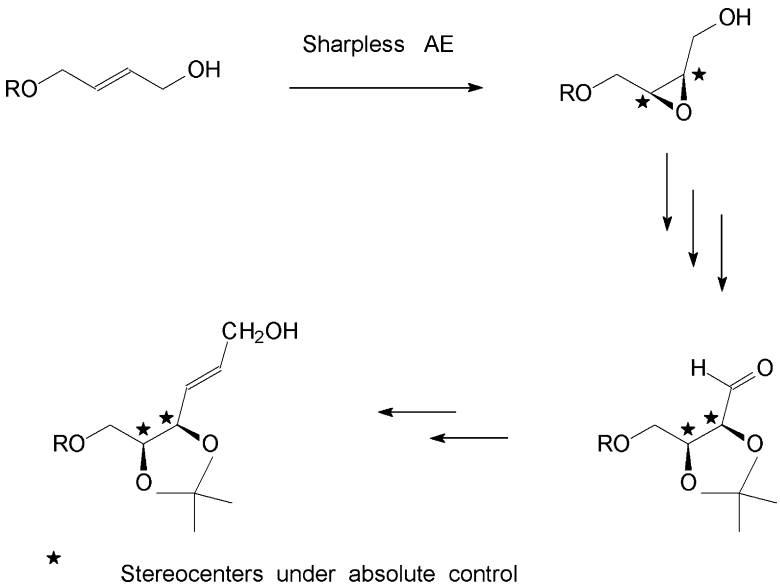

Fig. 2. Masamune–Sharpless synthesis of hexoses by stereocontrolled two-carbon chain extension: this formal extension of the carbonyl functional group in aldehydes by two carbon atoms has been developed as a general methodology and represents a milestone.

ing blocks, functionalized β-amino alcohols and statin analogues have been prepared by different stoichiometric reaction sequences leading to stereoselective C_2-elongation [12,13]. Claisen ester condensation has been used for the synthesis of a β-keto aminoacid ester by two-carbon elongation [14].

The synthesis of higher sugars by carbon chain extension has been of much interest for more than a century. A two-carbon extension of unprotected aldoses by a Wittig reaction followed by osmiumtetroxide-catalyzed dihydroxylation, shown in Fig. 1, yielded higher sugars with high diastereoselectivity when starting from sugars with the 2,3-threo configuration [15,16]. The synthesis of higher carbon amino sugars was also achieved by a sequence of a Wittig reaction and *cis*-dihydroxylation with osmiumtetroxide [17]. The 3-deoxy-D-arabino-2-heptulosonate (DAH) was obtained by a two-carbon chain elongation of 2,3,5-tri-O-benzyl-D-arabinose and a few subsequent steps [18]. The formal extension of the carbonyl functional group in aldehydes by two carbon atoms has been developed as a general methodology, shown in the reaction sequence overview of Fig. 2, and applied to the synthesis of all hexose isomers in a milestone work by Masamune and Sharpless [19].

The transition from stoichiometric to catalytic versions of carbon–carbon bond formation reactions is a highly active research topic [20]. New oxidative routes like catalytic α-hydroxylations of carbonyl compounds and catalytic ketohydroxylations of olefins have recently been developed for the synthesis of α-hydroxyketones [21].

3. Biocatalytic two-carbon chain extension methodology

Glycine-dependent aldolases catalyze the reversible aldol addition of glycine to an aldehyde acceptor. Deoxyribose-5-phosphate aldolase is unique among the aldolases, because the donor is acetaldehyde and the reaction leads to β-ketols. The biocatalytic transfer of the acetyl-group from acetyl-coenzyme A is widespread in biochemistry and acetyl-coenzyme A can be recycled in a two-phase system for the preparation of citrate catalyzed by citrate synthase [22]. R-α-Hydroxyketones of high optical purity have been obtained by pyruvate decarboxylase-catalyzed condensation between pyruvate and a wide range of substituted benzaldehydes [23]. The enzymatic acyloin condensation of phenylpyruvic acid and acetaldehyde by phenylpyruvate decarboxylase gave the 3R-

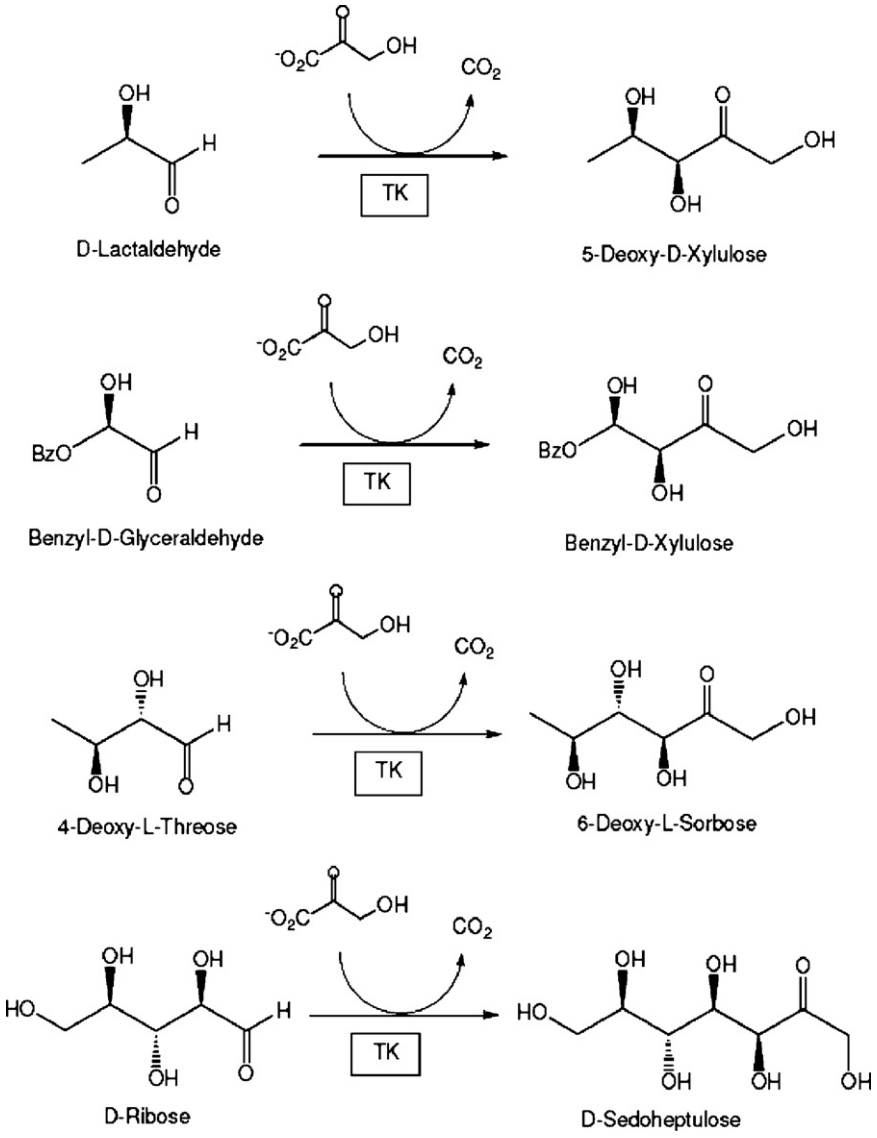

Fig. 3. Biocatalytic C_2-ketol elongation of 2-hydroxyaldehydes: the ketol group is transferred from the donor hydroxypyruvate to a 2-hydroxyaldehyde acceptor with the configuration 2R.

hydroxy-1-phenyl-2-butanone [24]. Chiral 2-hydroxyketones have been obtained with high stereoselectivity from the carboligation of aldehydes catalyzed by thiaminediphosphate-dependent enzymes [25,26].

Transketolase catalyzes central two-carbon chain extension in metabolic pathways and it is not surprising that this enzyme has also caught the attention of the science of synthesis. The biocatalytic transfer of the two-carbon ketol group is particularly attractive for the synthesis of a variety of carbohydrates, chiral intermediates, stable-isotope-labelled compounds and metabolites in organic synthesis [27–35]. A selection of transketolase-catalyzed asymmetric C_2-elongations of non-phosphorylated 2-hydroxyaldehydes and ω-phosphorylated aldehydes is presented in Figs. 3 and 4, respectively. The use of transketolases has been facilitated by recombinant protein expression and the large-scale synthesis of ketol donors [36].

4. Transketolases

In vivo, transketolase acts like a transferase which catalyzes the transfer of an α-ketol group from a ketose phosphate to an aldose phosphate by thiaminediphosphate catalysis [37]. Transketolase (EC 2.2.1.1) was already isolated and crystallized more than 50 years ago from yeast [38]. It has since then been prepared from spinach, many other biological sources and by recombinant gene expression in *Escherichia coli* [39–41] and *Saccharomyces cerevisiae* [42]. Transketolase from *S. cerevisiae* was the first thiaminediphosphate-dependent enzyme for which a three-dimensional structure has been determined [43–45] followed by the structure for the enzyme from *E. coli* [46]. Catalytically important residues in yeast transketolase [47] and a key reaction intermediate in enzymatic thiamine catalysis has been identified [48]. The availability of sufficient transketolase facilitated its applications as catalysts for the stereocontrolled formation of carbon–carbon bonds in chemoenzymatic synthesis [49]. The fermentation of the recombinant *E. coli* [50], downstream processing and purification of the transketolase to a stable lyophilized powder, as summarized in the process scheme of Fig. 5, has been developed at large-scale at Sigma–Aldrich and has been a prerequisite for the rapid growth of industrial applications [36]. In order to analyze the enzyme activities during transketolase productions, it was necessary to synthesize the substrate D-xylulose-5-phosphate. The basic steps of the industrial production shown in Fig. 5 take care of the structural stability of transketolase [51,52] and include protection against proteolytic degradation, denaturation and oxidative deactivation of the transketolase. Mutant transketolases with improved activities towards non-natural substrates like propionaldehyde [53], non-phosphorylated aldehydes [54] have been obtained by directed evolution.

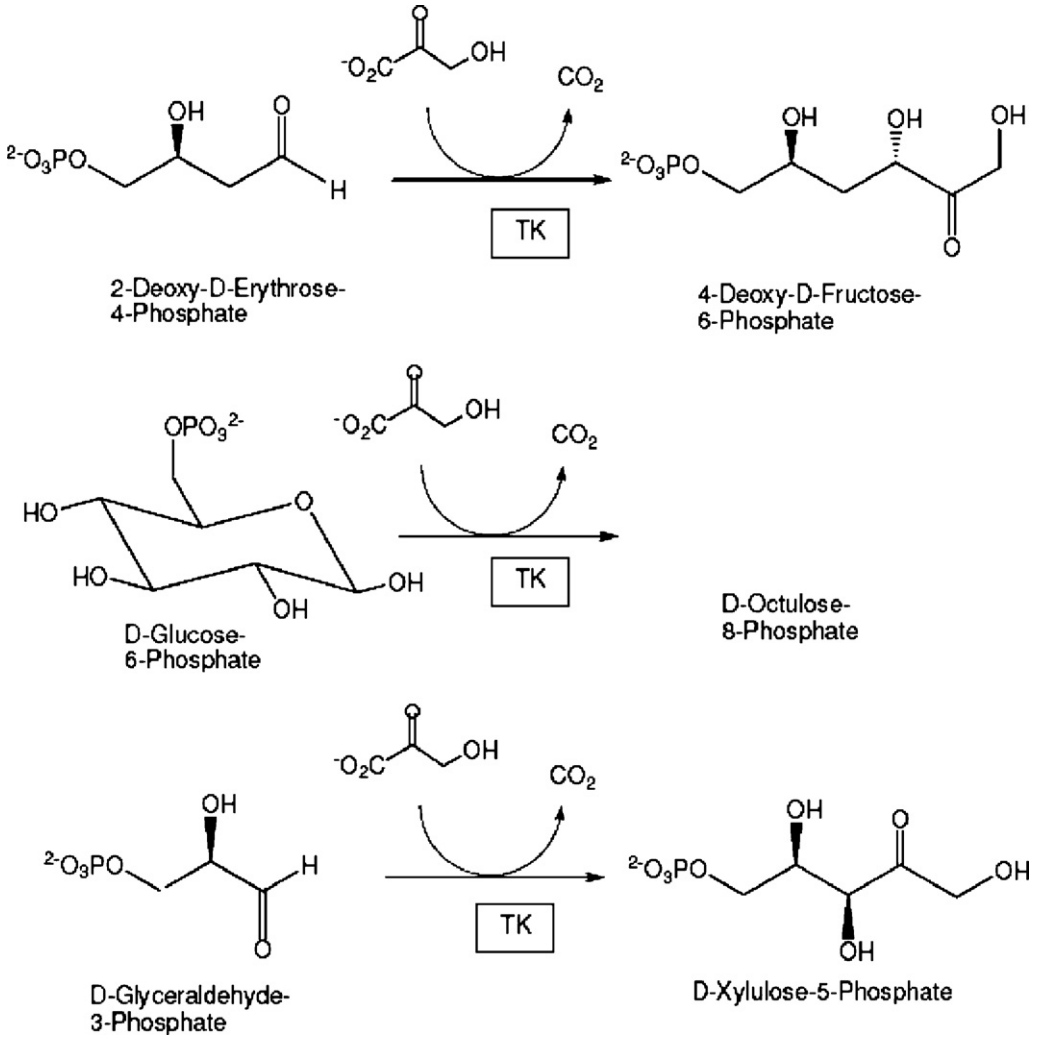

Fig. 4. Biocatalytic C_2-ketol elongation of ω-phosphorylated 2-hydroxyaldehydes: the transfer reactions of the ketol group to phosphorylated acceptors, common in sugar metabolism, are physiological reactions and useful for the synthesis of metabolites.

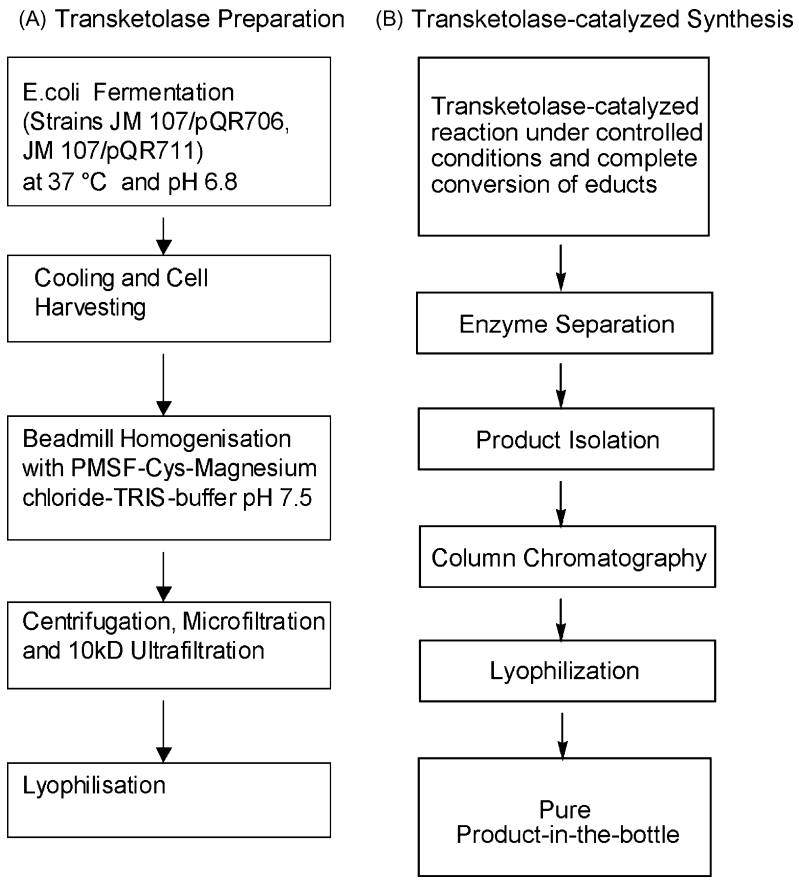

Fig. 5. Process scheme for the transketolase preparation (A) and for the transketolase-catalyzed synthesis of products (B): it has been useful to separate the step of the enzyme production from the enzyme application.

5. Irreversible ketol donors

A series of ketoses, like e.g. erythrulose [55], can be used as reversible ketol donors for the transketolase-catalyzed two-carbon chain extension. For synthetic purposes, however, the irreversible ketol donor hydroxypyruvate is favoured over a ketose donor, because the reaction leads to a coupled transfer and decarboxylation reaction going to completion. Transketolase also accepts hydroxypyruvate as a donor substrate, which leads to a coupled transfer and decarboxylation reaction. This is of synthetic interest, because the reaction becomes irreversible. The synthesis of the irreversible ketol donors hydroxypyruvic acid and hydroxypyruvate salts is based on a nucleophilic substitution reaction of bromopyruvic acid with the hydroxide anion. This reaction has not been investigated much in the last 50 years since the first preparations of pure crystalline salts of hydroxypyruvate, both for enzymatic experiments and as metabolize and analytical standard [56]. Both the lithium salt and the sodium salt have been described [56,57], but side-reactions like decarboxylations and condensation reactions narrowed down the windows of operation. In addition challenging purification problems appeared and prevented scale-up. The reproducibility of this procedure was poor, because the influence of reaction parameters like pH, temperature and educt concentration, the reaction control and purification procedure on product and side-product formation has not been investigated. Therefore a robust and scalable synthetic procedure at 0.2 M educt concentration, 20 °C and pH 8.5 for the highly pure lithium, sodium and potassium hydroxypyruvate as well as for the hydroxypyruvic acid has been developed [58].

6. Transketolase-catalyzed C_2-elongation bioprocesses

The stereospecific C_2-elongation catalyzed by transketolase has been used for the synthesis of various chiral products [59–62]. Racemic 2-hydroxyaldehydes have been C_2-elongated in good yields to 5-substituted 5-deoxy-D-xyluloses by yeast transketolase, giving as well the L-2-hydroxyadehydes in excellent optical purity [63]. Practical protocols for the yeast transketolase-catalyzed condensation of hydroxypyruvate with a wide variety of 2-hydroxyadehydes have been developed for the mg-scale. This reaction was also used in the synthesis of the four carbohydrates L-idose, L-gulose, 2-deoxy-L-xylohexose and L-xylose [64]. The class of dideoxyiminoalditols, in which the ring oxygen of a sugar is replaced by NH, has proven to contain potent inhibitors of a wide range of glycosidases. The transketolase-catalyzed C_2-elongation of enantiomerically pure glyceraldehydes, 3-O-benzylglyceraldehyde, lactaldehyde or lactaldehyde analogues, hydroxybutyraldehyde and dihydroxybutyraldehyde allow the construction of C_5- or C_6-fragments as advanced intermediates. Key steps in the synthesis of the potent glycosidase-inhibitors 1,4-dideoxy-1,4-imino-D-arabinitol [65] and 1,2,5-trideoxy-1,5-imino-D-arabinohexitol [66] consist of yeast transketolase-catalyzed C_2-elongations in excellent yields. The bottlenecks in the transketolase-catalyzed condensation of glycolaldehyde and hydroxypyruvate to L-erythrulose have been identified. Efficient engineering solutions to overcome these bottlenecks have been developed, leading to space–time yields of 45 $g\,l^{-1}\,d^{-1}$ [67,68]. The same product erythrulose has been found also in a one-substrate reaction with yeast transketolase, using only glycolaldehyde as substrate [69]. Novel ketotriols have been

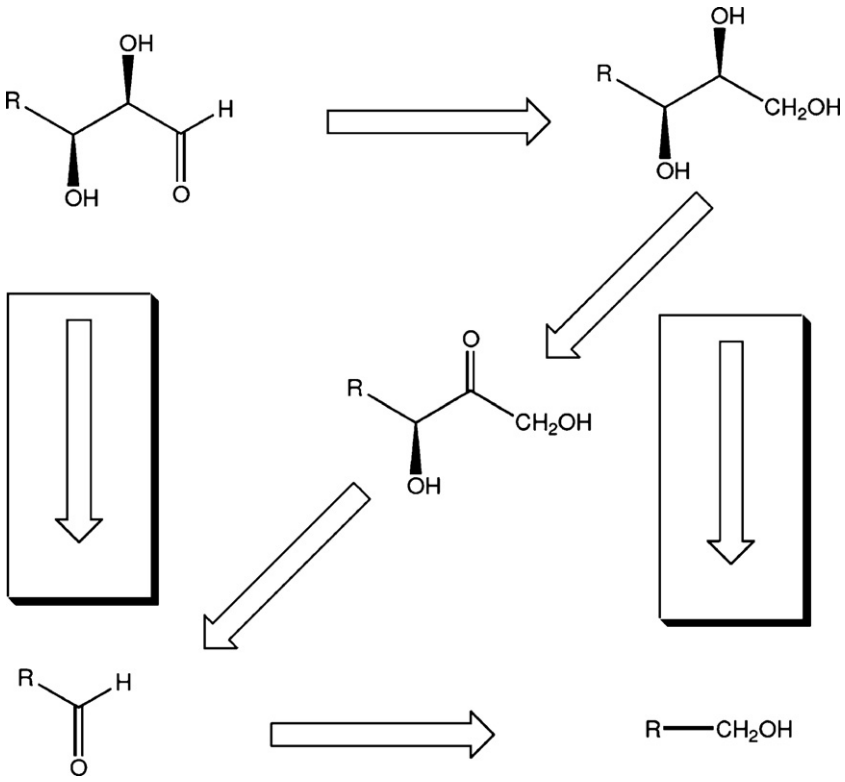

Fig. 6. Retrosynthetic scheme of a biocatalytic C_2-elongation with two new chiral centers: shows the importance of the oxidation of primary alcohol functions to aldehydes.

synthesized by *E. coli* transketolase-catalyzed coupling of hydroxypyruvate with enantiomerically pure (R)-α-hydroxyaldehydes, which were prepared from the corresponding α-hydroxyesters [70].

The synthesis of chiral metabolites by transketolase-catalyzed C_2-elongation allows a straightforward construction of the carbon backbone without the use of protecting groups. One central metabolite linking glycolysis with the pentose pathway is D-xylulose-5-phosphate, which was no longer available despite extensive investigations over many decades [71]. The key reaction step in all synthetic approaches is a transketolase-catalyzed condensation of hydroxypyruvate with D-glyceraldehyde-3-phosphate [72–75]. Final product purity and yield depend very much on the bioprocess selection [72], enzyme purity and the eluent in chromatography [71–74]. The transketolase-catalyzed bioprocess and the subsequent downstream processing/purification to the pure final product-in-the bottle require meaningful in-process analyses throughout the sequence of process steps. A typical scheme of a transketolase-catalyzed bioprocess including work-up and purification is shown in Fig. 5. The window of operation for this transketolase-catalyzed reaction is limited on one side by the lower transketolase activity at pH <7 and on the higher pH side by the concentration-dependent stability and toxicity of the acceptor to the transketolase [73].

The one-step synthesis of D-sedoheptulose from D-ribose and hydroxypyruvate catalyzed by transketolase shows the advantages of the biocatalytic method versus the chemical methods which require many steps and give racemates with poor yields [76,77].

7. Outlook

Many chemical methods for two-carbon chain extension involve safety, health- and environment-relevant reactions and reagents like the combinations of ethynylation/mercury-catalyzed hydration [78], ethynylation/ozonolysis [79] or Wittig olefination/benzyloxymercuration/demercuration [80]. It is nearly 50 years since the finding that in the course of transketolase action, an active glycolaldehyde-enzyme intermediate is formed which transfers the ketol group to a suitable aldehyde acceptor [81]. The need towards more sustainable chemistry and better step economy make the pyruvate/transketolase-tools the method of choice for catalytic asymmetric C_2-elongations of aldehydes, if the proper transketolase can be selected or engineered. The asymmetric transketolase-catalyzed reaction represents a promising modular reaction for carbon–carbon bond formation with improved safety, health and environment aspects [82] and tremendous opportunities for new synthetic routes can be envisaged.

The retrosynthetic scheme in Fig. 6 illustrates a short route to an asymmetric two-carbon chain extension introducing two new chiral centers from a simple primary alcohol to an aldehyde, which can be of further synthetic value. Whether the oxidation of the primary alcohol to the aldehyde is done by a chemical or a biocatalytic method, the whole sequence requires a proper interfacing of the chemical and biocatalytic steps [83]. The combination of two and more biocatalytic steps either as isolated enzymes in one reactor or expressed within a recombinant microorganism will provide further opportunities to move smaller or larger synthetic sequences from chemical methods to biocatalytic procedures [84,85].

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