EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Cascade Reactions of Unprotected Ketoses with Ketones - a Stereoselective Access to C-Glycosides

Authors: Rainer Mahrwald; Celin Richter; Michael Krumrey; Kristin Klaue

To be cited as: Eur. J. Org. Chem. 10.1002/ejoc.201601058

Link to VoR: http://dx.doi.org/10.1002/ejoc.201601058

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

FULL PAPER WILEY-VCH

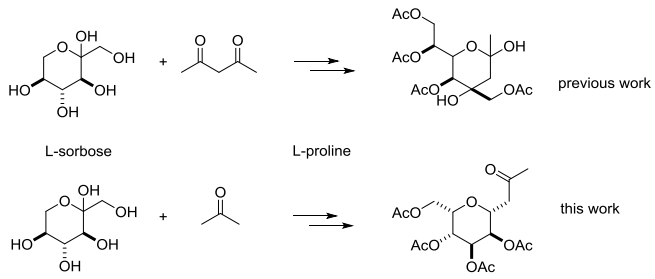
Cascade Reactions of Unprotected Ketoses with Ketones – a Stereoselective Access to C-Glycosides

Celin Richter,[a] Michael Krumrey,[a] Kristin Klaue,[a] and Rainer Mahrwald*[a]

Abstract: A highly stereoselective de-Bruyn-Ekenstein rearrangement / aldol condensation / intramolecular oxa-Michael cascade reaction of unprotected ketoses with ketones was elaborated. By the utilization of this new and operationally simple methodology an access to β-C-glycosides is given. Extremely matched and mismatched cases were observed by using with natural or unnatural proline in these cascade reactions.

Introduction

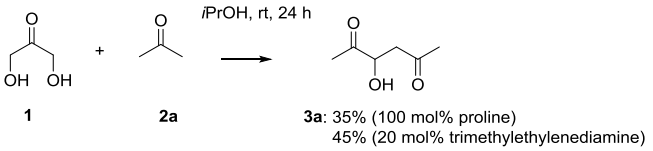
Recently we described organocatalyzed reactions of hydroxy ketones with 1,3-dicarbonyl compounds. During an amine-catalyzed Knoevenagel-addition / ketalization / retro-aldol cascade high chemo- and stereoselectivities were detected. By extending this transformation to reactions of ketohexoses with acetylacetone, the corresponding chain-elongated 3-deoxyketoses were isolated as predominantly one stereoisomer. Thus, this operationally simple cascade transformation gives an access to optically pure branched ketoses.[1] Generated by the retro-aldol reaction an acetyl fragment of the acetylacetone is transferred to the primary hydroxyl group. To avoid the "loss" of this acetyl fragment we explored the utility of unactivated methyl ketones in this novel amine-mediated cascade reaction with unprotected ketoses (Scheme 1).



Scheme 1. Proline-catalyzed reactions of L-sorbose (after acetylation of reaction-products)

Results and Discussion

In initial experiments we tested dihydroxyacetone and acetone as substrates under reaction conditions described for the amine-catalyzed Knoevenagel / ketalization / retro-aldol cascade (catalytic amounts of DBU, water, r.t.).[1] No reactions were observed under these conditions. After a careful optimization equimolar amounts of proline were required to initiate the reaction. The 1,4-diketone **3a** was the only product we observed under these conditions (35% yield). Further investigation indicated an increase of yields by the application of 20 mol% *N*,*N*,*N'*-trimethylethane-1,2-diamine (trimethylethylenediamine) (45%, Scheme 2).

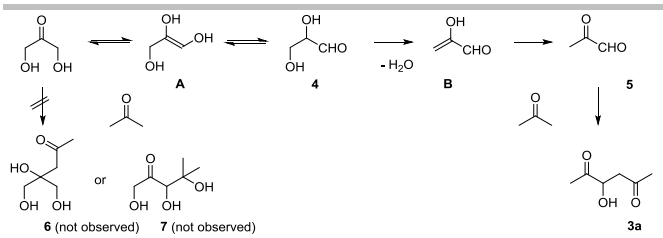


Scheme 2. Amine-mediated cascade reaction of dihydroxyacetone with acetone.[2]

The surprising and unexpected formation of the isolated hydroxy-1,4-diketone **3** can be explained by a de-Bruyn-Ekenstein rearrangement [3] / dehydration / aldol cascade. By treatment of dihydroxyacetone with proline and DBU the formation of glyceraldehyde **4** can be assumed via the enediol-species **A**. Subsequent dehydration yields the enol **B** of 2-oxopropanal **5** (pyruvic aldehyde, methylglyoxal).

[a] Humboldt-University, Department of Chemistry, Brook-Taylor Str. 2, 12489 Berlin, Germany
E-Mail: rainer.mahrwald@rz.hu-berlin.de
https://www.chemie.hu-berlin.de/de/forschung/mahrwald

Supporting information for this article is given via a link at the end of the document.

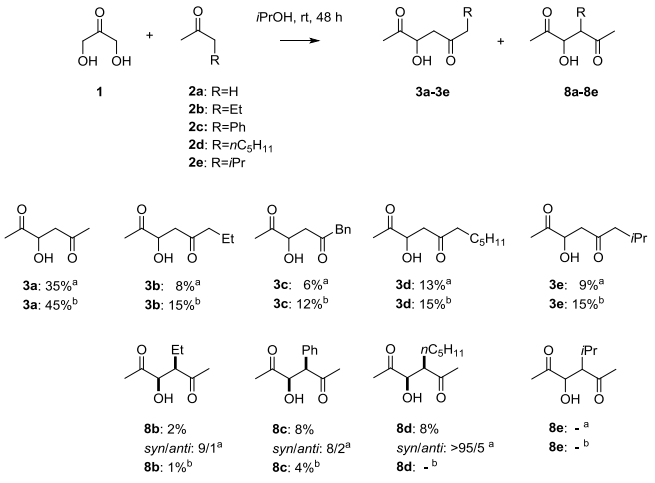


Scheme 3. Proposed reaction mechanism (enamine intermediates are not indicated for the sake of simplicity)

Cross-aldol adducts **6** or **7** on the other hand were not detected. To prove these considerations we reacted acetone with methylglyoxal **5** under the same conditions. As expected hydroxy-1,4-diketone **3a** was isolated in identical yields under the same conditions (Scheme 3).

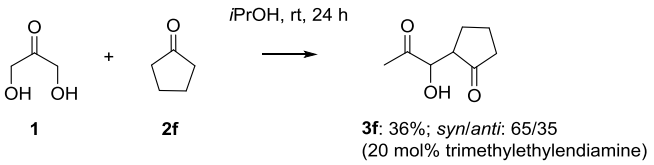
The enzymatic formation of methylglyoxal **5** from dihydroxyacetone **1** is well-known [4] and is the subject of intensive investigation as the "dark side of glycolysis".[5] Moreover, chemical transformations of dihydroxyacetone **1** to methylglyoxal **5** were reported. However, the harsh conditions reported for these chemical-induced tautomerizations are not compatible with the physiological conditions of an organocatalyzed transformation. [6] Indications for an amine- or amino acid-catalyzed transformation of dihydroxyacetone to pyruvic aldehyde were published.[7] Nonetheless, a preparative-useful organocatalyzed protocol for this tautomerization have not been reported so far.

To test the general applicability of these initial results, we reacted a set of different methyl ketones **2a**-**2e** with dihydroxyacetone under the optimized reaction conditions. The steric bulkiness of substituent R of methyl ketones dictates the dimension of yields and the regioselectivity of the aldol step (e.g. compare results of reaction with **2a** and **2e**, Scheme 4).



Scheme 4. Amine-mediated cascade reactions of dihydroxyacetone with methyl ketones. Reaction conditions: [a] 100% proline, [b] 20 mol% trimethylethylenediamine.

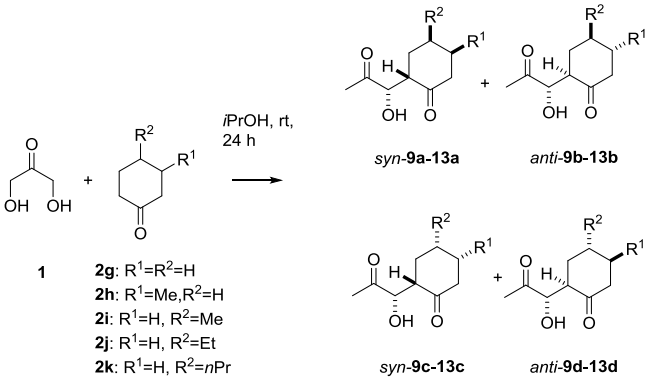
In further experiments we tested cyclic ketones as substrates in these cascade reactions. Initially, we reacted cyclopentanone with dihydroxyacetone under the optimized conditions. No reaction however was observed, when used with proline. In contrast to that the expected 1,4-diketone **3f** was isolated with 36 % yields as a mixture of *syn* and *anti* diastereoisomers (Scheme 5).



Scheme 5. Amine-catalyzed cascade reaction of dihydroxyacetone with cyclopentanone

Next, cyclohexanones **2g**-**k** were tested as substrates in these reactions. Higher yields were detected again, when used with catalytic amounts of trimethylethylenediamine instead of proline (Table 1). Interestingly, a reversal of the internal diastereoselectivity is observed in BINAM-prolinamide-catalyzed reactions of 4-methylcyclohexanone **2i** (R^1=H, R^2=Me) with methylglyoxal **5** (compare entry 6 with results reported in reference 8a: main product by this cascade is **11b**, whereas **11d** is described as the main product in reference 8a).

Table 1. Amine-catalyzed cascade reaction of dihydroxyacetone with cyclohexanones

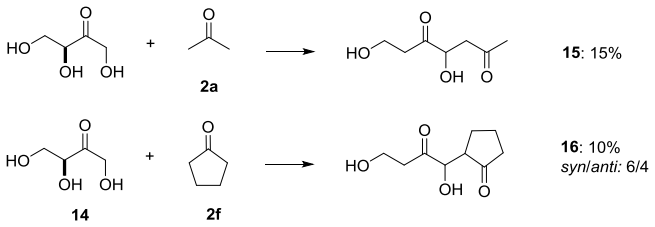


entry	compound	*syn*-**a**	*anti*-**b**	*syn*-**c**	*anti*-**d**	yield[%]
1	**9**: R^1=R^2=H	33	66			30[a]
2		54	46			53[b]
3	**10**: R^1=Me, R^2=H	17	-	55	28	8[a]
4		12	-	22	66	27[b]
5	**11**: R^1=H, R^2=Me	14	27	42	18	17[a]
6		12	70	14	2	34[b]
7	**12**: R^1=H, R^2=Et	10	19	46	25	20[a]
8		17	56	21	3	25[b]
9	**13**: R^1=H, R^2=*n*Pr	12	20	40	28	21[a]
10		10	51	34	6	38[b]

Reaction conditions: [a] equimolar amounts of proline; [b] 20 mol% trimethylethylenediamine. For the determination of configuration see reference 9.

The yields of products could not be improved by longer reaction times. It is assumed, that a competing Maillard-reaction and consecutive reactions inactivate proline or trimethylethylenediamine.

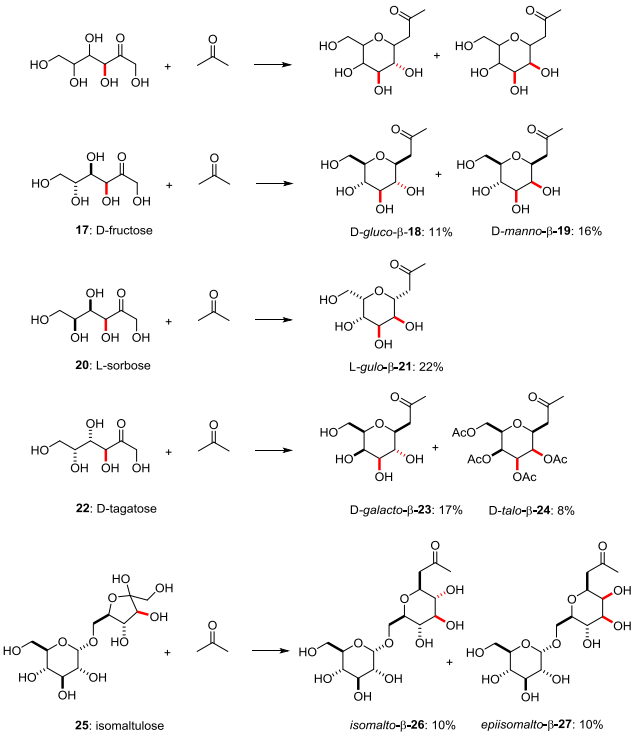
Since organocatalyzed, enantioselective direct aldol additions of methylglyoxal **5** with cyclohexanones or acetone have been reported,[8] we explored the deployment of substituted hydroxyacetones - namely unprotected ketoses – as substrates in these cascade reactions. We started these investigations with amine-catalyzed reactions of acetone or cyclopentanone with L-erythrulose **14**. The expected 1,4-diketones **15** or **16** were isolated under the same reaction conditions.



Scheme 6. Amine-catalyzed cascade reaction of L-erythrulose with acetone or cyclopentanone. Reaction conditions: 40 mol% trimethylethylenediamine, MeOH, rt, 48 h.

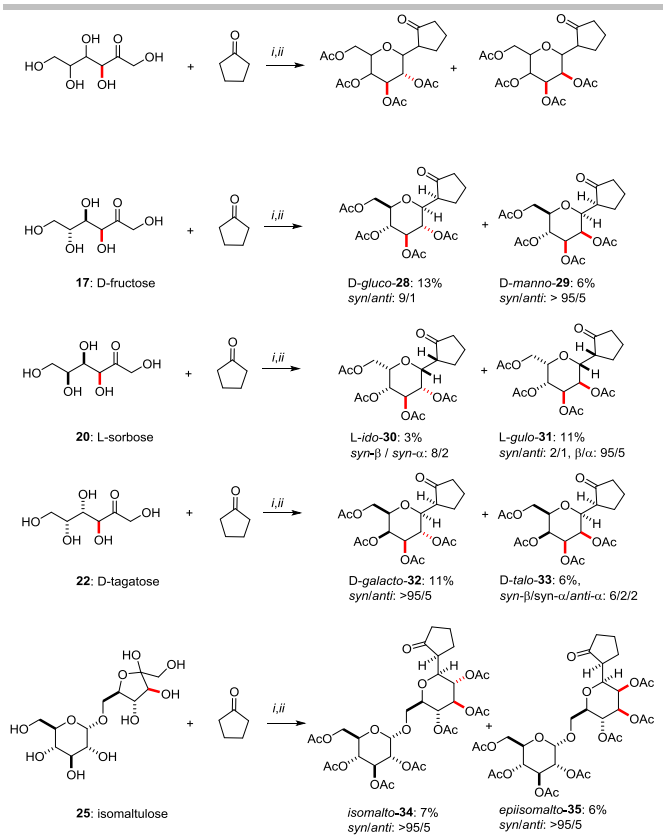
Based on the reaction mechanism this transformation is associated with the loss of the optical activity of the starting erythrulose **14**. In order to get an access to chiral products by this cascade transformation we reacted in a further series several ketohexoses with acetone. The utilization of these substrates required a further optimization of the reaction conditions. No reactions were observed when used with proline or trimetylethylenediamine as catalysts or in equimolar amounts. Instead, reactions were detected only when used by a combination of equimolar amounts of proline and DBU. The reaction was carried out in MeOH at 64°C. The change of reaction conditions resulted in a change of the cascade. Under these conditions C-glycosides were detected as a result of a de-Bruyn-Ekenstein rearrangement / aldol condensation / intramolecular oxa-Michael cascade (Scheme 7). These findings are at variance with those obtained by the de-Bruyn-Ekenstein rearrangement / dehydration / aldol cascade (compare Scheme 3 with Scheme 9). Support for these considerations is given by NMR-experiments. By treatment of fructose with proline and DBU, glucose and mannose can be detected. [9] High stereoselectivities were observed in these experiments. The formation of the corresponding β-configured C-glycosides was observed only in this reaction. In reactions of fructose a 1:1 ratio of *gluco*-C-glycoside **18** and *manno*-C-glycoside **19** was observed as a result of an unselective de-Bruyn-Ekenstein rearrangement. An increase of stereoselectivity is observed in the tagatose-series. The *galacto*-**23** and *talo*-C-glycoside **24** were isolated in a ratio of 2/1. When using L-sorbose a complete stereoselectivity is observed. The *gulo*-C-glycoside **21** is the only product which was observed in these reactions. The corresponding *ido*-C-glycoside on the other hand was not detected.

Also, unprotected disaccharides containing the ketose-unit are useful substrates in these cascade reactions, as this is shown by the utilization of isomaltulose **25** (α-glucopyranosyl-D-fructose). When used with isomaltulose **25** in reactions with acetone, the expected *gluco*- and *manno*-configured C-glycosides **26** and **27** were isolated in a ratio of 1 /1 (Scheme 7).



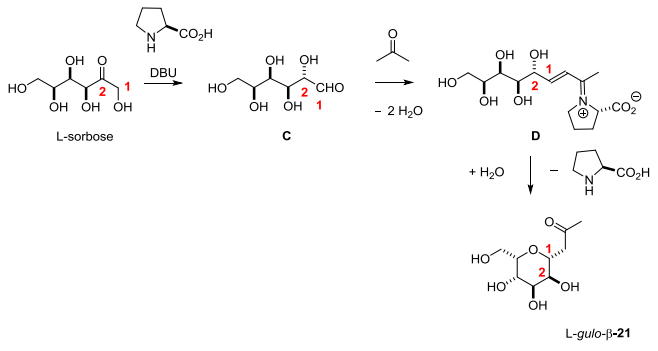
Scheme 7. Amine-mediated cascade reaction of ketohexoses with acetone. The acyclic structures of starting ketohexoses are depicted for reasons of simplification. Reaction conditions: 100 mol% L-proline, 100 mol% DBU, MeOH, 64°C, 24 h.

In a further series we tested cyclopentanone as the enol-component in these cascade reactions with several unprotected ketohexoses. Once more high stereoselectivities were detected. The ß-C-glycosides were the major products which were obtained. Moreover, the additional stereogenic center at C2-carbon atom of cyclopentanone was created with high degrees of *syn*-stereoselectivity (Scheme 8). The purification and analysis of the products of this series were carried out with their acetylated derivatives.



Scheme 8. Amine-mediated cascade reaction of ketohexoses with cyclopentanone. Reaction conditions: *i* = 100 mol% L-proline, 100 mol% DBU, MeOH, 64°C, 24 h, *ii* = Ac_2O, pyridine, rt.

A tentative working model for the mechanism of this cascade reaction is depicted in Scheme 9. L-Gulose (**C**) is intermediately formed by a de Bruyn-Ekenstein rearrangement of L-sorbose in the presence of equimolar amounts of proline and DBU. A further reaction with the enamine of acetone gives rise to the iminium-species **D**. Finally, a subsequent intramolecular oxa-Michael addition yields the *gulo*-C-glycoside **21**.



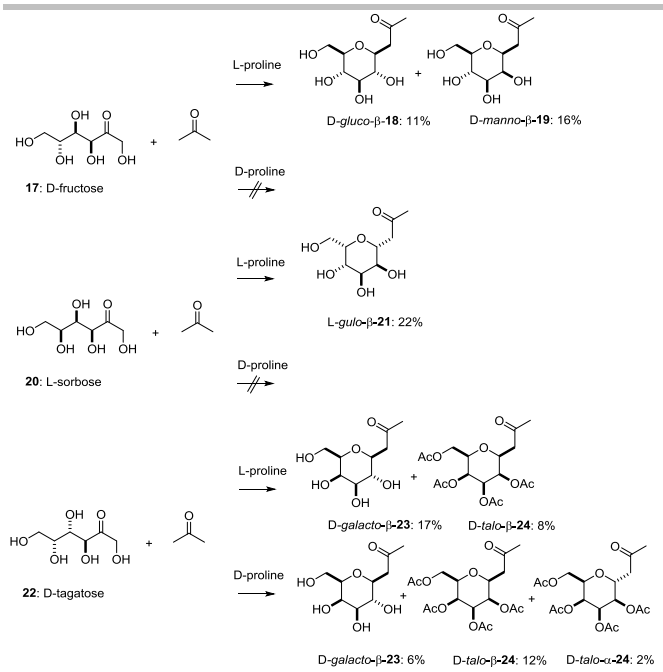
Scheme 9. Proposed reaction mechanism

Several remarkable stereochemical observations have been made in these investigations. The de-Bruyn / Ekenstein rearrangement, the aldol condensation and the oxa-Michael addition are equilibrium reactions. Secondary amine-catalyzed retro-aldol-condensations were reported.[10] In addition, the proline-catalyzed anomerization of protected C-glycosides was published.[11] This process was carried out at 120°C and based on the intramolecular retro-oxa-Michael addition. Thus, the high stereoselectivity that was obtained by the formation of ß-C-glycosides can be explained as a result of thermodynamically controlled intramolecular oxa-Michael addition.

To verify the exceptionally high diastereoselectivity, the corresponding unprotected aldohexoses, which deliver from the de-Bruyn-Ekenstein rearrangement of D-fructose, glucose and mannose were reacted with acetone under the same conditions (proline, DBU, MeOH, 64°C). In these direct C-glycosylations the corresponding *manno*-C-glycoside and *gluco*-C-glycoside were detected with excellent diastereoselectivities (β/α: >95/5). These results strongly contrast those which were obtained at room temperature.[12] In these experiments unselective mixtures of alternating configurations at the pseudo-anomeric carbon atom were detected.[9]

Next, the configuration at the C2-carbon atom of the carbohydrate does not influence the installation of configuration of the pseudo-anomeric carbon atom. ß-C-glycosides were detected as the only products in all reactions we carried out. In cascade reactions of D-fructose the β-configured C-glycosides **18** of D-glucose (*S*-C2) and **19** of D-mannose (*R*-C2) were obtained as the only products (Scheme 7).

And thirdly, notable and strong interactions between the configuration of proline and the deployed ketohexoses were detected. A matched case is noticed in reactions of D-fructose with L-proline, whereas no reaction was observed with D-fructose and D-proline. Moreover, a mismatched situation is observed in reactions of D-proline and L-sorbose. On the other hand the influence of configuration of proline is essentially smaller in reactions with tagatose. Similar results were obtained when used with D- or L-proline in reactions with tagatose (Scheme 10).



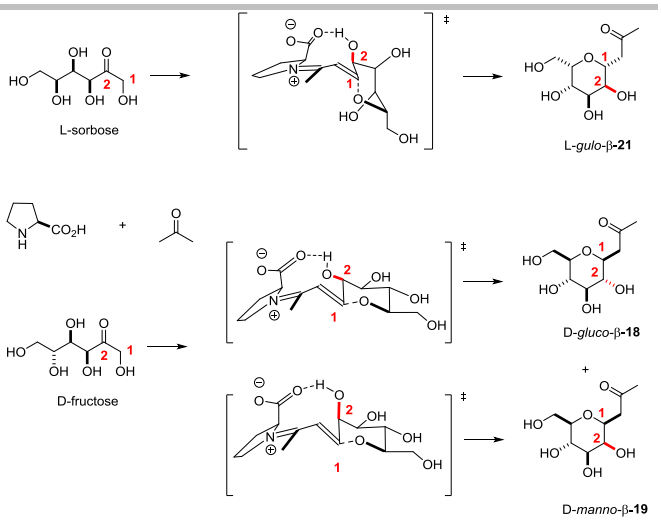
Scheme 10. Matched- and mismatched-cases in proline-mediated cascade reaction of ketohexoses with acetone. D-*talo*-β-**24** and D-*talo*-α-**24** were isolated and characterized with their corresponding tetraacetates.

Based on these results and considerations the following model for the stereochemical course of this cascade reaction was developed (Scheme 11).

The configuration of the hydroxyl groups of the starting ketohexoses dictates the installation of configuration at C2 carbon atom during the de-Bruyn-Ekenstein rearrangement. A comparison of the configurative course of the subsequent intramolecular oxa-Michael reaction is depicted in Scheme 10 for cascade reactions of sorbose and fructose with acetone.

The *S*-configured C5-hydroxyl group of L-sorbose dictates a clear *Re*-side attack at the pseudoanomeric carbon atom (C1) during the oxa-Michael process. This process proceeds with an extremely high degree of stereoselectivity. As a consequence the installation of the *S*-configured hydroxyl group at C2 is the favoured one.

In contrast, a *Si*-side attack at C1 is observed during the oxa-Michael process when used with D-fructose. To avoid steric interactions with the C-glycosidic bond at C1 the hydroxyl group at C2 is installed partially in the α- and β-configuration (**18**: *R*-configuration at C2, **19**: *S*-configuration at C2). This process is guided by hydrogen bonds of the carboxylic group of proline with the C2-hydroxyl group (see matched and mismatched case when used with L- or D-proline, Scheme 10). For a complete analysis of all conformations in the fructose-series see Supporting Informations.



Scheme 11. Comparison of the reaction of L-sorbose and D-fructose with L-proline

Conclusions

These reported cascade reactions of unprotected ketoses with proline are new, as they do not undergo the classical Amadori-pathway.[13] Amine-mediated de-Bruyn-Ekenstein rearrangements have not been reported so far, with the exception of deployment of secondary or primary amines, to obtain the corresponding α-amino ketones.[14] This combination of the de-Bruyn-Ekenstein process with the C-C bond formation of unprotected carbohydrates provides an elegant and highly stereoselective access to β-C-glycosides. By the utilization of these operationally simple cascade reactions an approach to C-glycosides of rare carbohydrates is given, as was demonstrated for the unnatural *gulo*-C-glycoside **21**.

Experimental Section

General Information: ^{1}H-NMR, ^{13}C-NMR, DEPT and correlation experiments H, H-COSY, HSQC, NOESY and JRES were carried out at 600, 500 MHz and 125 MHz. The residual protonated solvent was used as the internal standard: ^{1}H-NMR: 7.26 ppm for $CDCl_3$, ^{13}C-NMR: 77.0 ppm for $CDCl_3$, ^{1}H-NMR: 3.31 ppm for MeOD, ^{13}C-NMR: 49.0 ppm for MeOD and ^{1}H-NMR: 2.05 ppm for acetone-d_6, ^{13}C-NMR: 206.3 / 29.8 ppm for acetone-d_6, ^{1}H-NMR: 4.79 ppm for D_2O. Chemical shifts are given in ppm, coupling constants in Hz. High resolution mass spectroscopy was performed out on a LTQ-FT-ICR machine (ESI-MS). Purification of products was accomplished by flash chromatography (particle size 0.04 - 0.063 mm). Yields were determined after column chromatography. The solvent mixtures of CH_2Cl_2 (DCM) and methanol in ratio 80/20 → 95/5 and hexane/acetone 8/2 → 1/1 were used as eluent. Development was performed with cer(IV) sulfate / phosphormolybdic acid.

General Procedure for the Synthesis of 1,4-Diketones 3a-f, 8a-d and 9-13: Ketones **2a**-**2k** (10.0 mmol), L-proline (230 mg, 2.0 mmol) were added to a suspension of dihydroxyacetone (180 mg, 2.0 mmol) in isopropanol (9.0 mL). The resulting

mixture was stirred for 48 h at room temperature. Volatile compounds were removed under reduced pressure and the residue was directly purified by column chromatography. The 1,4-diketones **3a-f**, **8a-d** and **9-13** were isolated as colorless oils.

3-Hydroxyhexane-2,5-dione (**3a**):[15] Yield: 91.0 mg; 35 %; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (ddd, J = 6.3, 5.0, 3.6 Hz, 1H), 3.76 (d, J = 5.1 Hz, 1H), 2.94 (dd, J = 17.3, 3.8 Hz, 1H), 2.81 (dd, J = 17.2, 6.5 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 207.1, 73.7, 46.2, 30.8, 25.5; HRMS (ESI) calcd for $C_6H_{11}O_3^+$ $[M+H]^+$: 131.0703, found: 131.0703.

3-Hydroxyoctane-2,5-dione (**3b**):[16] Inseparable mixture **3b**/**8b**: 93/7. Overall yield: 50.0 mg; 16 %.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (td, J = 5.9, 3.9 Hz, 1H), 3.72 (d, J = 5.4 Hz, 1H), 2.94 (dd, J = 17.2, 3.8 Hz, 1H), 2.82 (dd, J = 17.1, 6.3 Hz, 1H), 2.45 (t, J = 7.3 Hz, 2H), 2.26 (s, 3H), 1.61 (sext, J = 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 209.5, 74.0, 45.7, 45.4, 25.5, 17.1, 13.7.

4-Hydroxy-1-phenylhexane-2,5-dione (**3c**):[17] Yield: 46.2 mg; 12 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, J = 1.6 Hz, 1H), 7.32 (t, J = 1.8 Hz, 1H), 7.28 (dt, J = 4.7, 1.9 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.18 – 7.17 (m, 1H), 4.32 (dt, J = 5.9, 4.2 Hz, 1H), 3.75 (s, 2H), 3.70 (d, J = 5.4 Hz, 1H), 2.98 (dd, J = 17.3, 3.9 Hz, 1H), 2.85 (dd, J = 17.3, 6.4 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.2, 206.9, 133.3, 129.6, 129.0, 127.4, 73.8, 50.9, 44.7, 25.5. HRMS (ESI) calcd for $C_{12}H_{14}O_3Na^+$ $[M+H]^+$: 229.0835, found: 229.0837.

3-Hydroxyundecane-2,5-dione (**3d**):[18] For L-proline: Inseparable mixture **3d**/**8d**: 62/38. Overall yield: 81.3 mg; 21 %.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (ddd, J = 6.2, 5.5, 4.0 Hz, 1H), 3.72 (d, J = 5.4 Hz, 1H), 2.94 (dd, J = 17.2, 3.8 Hz, 1H), 2.82 (dd, J = 17.2, 6.3 Hz, 1H), 2.45 (t, J = 7.5 Hz, 2H), 2.25 (s, 3H), 1.59 – 1.52 (m, 2H), 1.30 – 1.22 (m, 6H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 209.5, 74.0, 45.4, 43.9, 31.7, 28.9, 25.5, 23.5, 22.6, 14.1.

3-Hydroxy-7-methyloctane-2,5-dione (**3e**): Yield: 49.6 mg; 15 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (dd, J = 6.3, 3.8 Hz, 1H), 2.92 (dd, J = 17.3, 3.8 Hz, 1H), 2.81 (dd, J = 17.3, 6.3 Hz, 1H), 2.33 (m, 2H), 2.26 (s, 3H) 2.13 (h, J = 6.9 Hz, 1H), 0.91 (d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.5, 209.4, 74.0, 52.7, 45.8, 25.5, 24.6, 22.6. HRMS (ESI) calcd for $C_9H_{16}O_3Na^+$ $[M+Na]^+$: 195.0992, found: 195.0991.

***Syn*-2-(1-hydroxy-2-oxopropyl)cyclopentan-1-one** (*syn*-**3f**):[8a] Inseparable mixture *syn*/*anti*: 65/35. Overall yield: 112.4 mg; 36 %.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (dd, J = 4.7, 2.3 Hz, 1H), 3.49 (d, J = 4.7 Hz, 1H), 2.55 – 2.49 (m, 1H), 2.22 (s, 3H), 2.20 – 2.05 (m, 4H), 1.85 – 1.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.8, 208.7, 75.7, 50.7, 38.4, 25.2, 21.8, 20.8.

***Anti*-2-(1-hydroxy-2-oxopropyl)cyclopentan-1-one** (*anti*-**3f**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (t, J = 3.4 Hz, 1H), 3.85 (d, J = 3.5 Hz, 1H), 2.79 – 2.73 (m, 1H), 2.37 – 2.30 (m, 4H), 2.27 (s, 3H), 1.85 – 1.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.6, 208.0, 76.4, 51.5, 38.8, 26.4, 25.4, 21.2.

HRMS (ESI) calcd for $C_8H_{13}O_3^+$ $[M+H]^+$: 157.0859, found: 157.0856.

3-Hydroxy-4-ethylhexane-2,5-dione (**8b**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (dd, J = 4.2, 3.4 Hz, 1H), 3.52 (d, J = 4.5 Hz, 1H), 2.87 – 2.84 (m, 1H), 2.27 (s, 6H), 1.83 (ddd, J = 14.2, 9.0, 7.4 Hz, 1H), 1.39 (ddd, J = 14.1, 7.5, 5.0 Hz, 1H), 0.92 (t, J = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5, 208.9, 77.3, 57.0, 29.8, 26.3, 19.4, 12.6. HRMS (ESI) calcd for $C_8H_{14}O_3Na^+$ $[M+Na]^+$: 181.0835, found: 181.0839.

***Syn*-3-hydroxy-4-phenylhexane-2,5-dione** (*syn*-**8c**): Inseparable mixture *syn*/*anti*: 8/2. Overall Yield: 16.1 mg; 4 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 3H), 7.24 – 7.22 (m, 2H), 4.78 (dd, J = 4.3, 3.4 Hz, 1H), 4.11 (d, J = 4.2 Hz, 1H), 3.39 (d, J = 3.5 Hz, 1H), 2.13 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 208.2, 133.4, 129.9, 129.1, 128.4, 77.6, 61.1, 29.5, 26.9. HRMS (ESI) calcd for $C_{12}H_{14}O_3Na^+$ $[M+Na]^+$: 229.0835, found: 229.0837.

***Anti*-3-hydroxy-4-phenylhexane-2,5-dione** (*anti*-**8c**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 3H), 7.28 – 7.24 (m, 1H), 7.18 – 7.15 (m, 1H), 4.28 (dd, J = 8.0, 5.2 Hz, 1H), 4.13 (d, J = 5.2 Hz, 1H), 3.82 (d, J = 8.2 Hz, 1H), 2.04 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.26, 209.22, 134.89, 129.39, 129.26, 128.38, 79.52, 61.34, 30.01, 27.08.

3-Hydroxy-4-n-pentylhexane-2,5-dione (**8d**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (dd, J = 4.3, 3.3 Hz, 1H), 3.54 (d, J = 4.5 Hz, 1H), 2.92 – 2.88 (m, 1H), 2.26 (s, 6H), 1.82 – 1.73 (m, 1H), 1.59 – 1.52 (m, 1H), 1.33 – 1.27 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 208.9, 76.9, 55.5, 32.0, 29.7, 27.7, 26.3, 26.9, 22.5, 14.1. HRMS (ESI) calcd for $C_{11}H_{20}O_3Na^+$ $[M+Na]^+$: 223.1305, found: 223.1305.

***Syn*-2-(1-hydroxy-2-oxopropyl)cyclohexan-1-one** (*syn*-**9a**): Inseparable mixture *syn*/*anti*: 33/66. Overall yield: 100.0 mg; 30 %.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.62 (dd, J = 4.2, 2.4 Hz, 1H), 3.33 (d, J = 4.7 Hz, 1H), 2.81 – 2.76 (m, 1H), 2.47 – 2.42 (m, 1H), 2.39 – 2.26 (m, 1H), 2.19 (s, 3H), 1.77 – 1.70 (m, 3H), 1.69 – 1.57 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 210.5, 75.5, 53.1, 42.1, 26.8, 26.5, 26.5, 24.5. HRMS (ESI) calcd for $C_9H_{14}O_3Na^+$ $[M+Na]^+$: 193.0835, found: 193.0833.

***Anti*-2-(1-hydroxy-2-oxopropyl)cyclohexan-1-one** (*anti*-**9a**):[8a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (dd, J = 7.5, 2.9 Hz, 1H), 3.57 (d, J = 7.7 Hz, 1H), 3.02 (dddd, J = 12.8, 5.9, 3.0, 1.1 Hz, 1H), 2.39 – 2.26 (m, 2H), 2.24 (s, 3H), 2.12 – 2.00 (m, 3H), 1.96 – 1.80 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.2, 210.1, 77.9, 53.8, 42.0, 30.3, 26.9, 25.8, 24.8.

***Syn*-2-(1-hydroxy-2-oxopropyl)-5-methylcyclohexan-1-one** (*syn*-**10a**): Inseparable mixture: *syn*-**a**/*syn*-**c**/*anti*-**d**: 12/22/66. Overall yield: 99.1 mg ; 27 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (br. s, 1H), 3.33 (br. s, 1H), 2.80 – 2.76 (m, 1H), 2.35 (dd, J = 14.1, 5.4 Hz, 1H), 2.35 – 2.31 (m, 1H), 2.26 – 2.22 (m, 1H), 2.22 (s, 3H), 1.99 – 1.91 (m, 2H), 1.68 – 1.58 (m, 2H), 0.95 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.1, 210.4, 76.2, 52.4, 48.7, 31.5, 30.2, 26.6, 21.9, 19.3.

***Syn*-2-(1-hydroxy-2-oxopropyl)-5-methylcyclohexan-1-one** (*syn*-**10c**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.65 (br. s, 1H), 3.24 (br. s, 1H), 2.77 – 2.72 (m, 1H), 2.45 (ddd, *J* = 13.8, 3.8, 2.4 Hz, 1H), 2.22 (s, 3H), 2.06 (dd, *J* = 5.7, 3.1 Hz, 2H), 1.95 – 1.79 (m, 2H), 1.80 – 1.70 (m, 1H), 1.47 – 1.34 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) *δ* 211.0, 210.7, 75.5, 52.4, 50.4, 34.8, 33.4, 26.7, 25.5, 22.5.

***Anti*-2-(1-hydroxy-2-oxopropyl)-5-methylcyclohexan-1-one** (*anti*-**10d**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 3.85 (br. s, 1H), 3.54 (br. s, 1H), 2.99 (dddd, *J* = 13.1, 5.9, 3.0, 1.2 Hz, 1H), 2.36 (ddd, *J* = 13.8, 3.9, 2.2 Hz, 1H), 2.26 (s, 3H), 2.03 – 1.97 (m, 1H), 1.95 – 1.79 (m, 4H), 1.47 – 1.34 (m, 1H), 1.02 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.1, 210.4, 77.9, 53.1, 50.3, 34.9, 33.7, 29.3, 26.0, 22.5. HRMS (ESI) calcd for $C_{10}H_{17}O_3^+$ $[M+H]^+$: 185.1172, found: 185.1173.

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-methylcyclohexan-1-one** (*syn*-**11a**): Inseparable mixture *syn*-**a**/*anti*-**b**/*syn*-**c**/*anti*-**d**: 12/70/14/2. Overall yield: 122.7 mg; 34 %. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.62 (br. s, 1H), 3.39 (br. s, 1H), 2.92 – 2.85 (m, 1H), 2.53 – 2.43 (m, 1H), 2.21 (s, 3H), 2.06 – 1.88 (m, 3H), 1.72 – 1.33 (m, 3H), 1.09 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.1, 210.0, 76.7, 48.9, 41.4, 38.5, 32.4, 32.3, 26.3, 19.1.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-methylcyclohexan-1-one** (*anti*-**11b**): [8a] ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 3.82 (br. s, 1H), 3.55 (br. s, 1H), 3.10 (ddd, *J* = 13.6, 5.4, 3.0 Hz, 1H), 2.35 (dd, *J* = 8.4, 3.6 Hz, 1H), 2.25 (s, 3H), 1.99 (m, 3H), 1.64 (m, 1H), 1.36 – 1.33 (m, 2H), 1.02 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.5, 210.1, 77.9, 53.1, 41.4, 38.4, 35.0, 31.8, 25.9, 21.5. HRMS (ESI) calcd for $C_{10}H_{17}O_3^+$ $[M+H]^+$: 185.1172, found: 185.1175.

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-methylcyclohexan-1-one** (*syn*-**11c**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.65 (br. s, 1H), 3.27 (br. s, 1H), 2.85 (dddd, *J* = 13.0, 5.8, 2.3, 1.0 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.21 (s, 3H), 2.06 – 1.88 (m, 3H), 1.72 – 1.33 (m, 3H), 0.98 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 211.4, 210.7, 75.6, 52.3, 34.9, 34.5, 31.5, 27.0, 26.7, 21.6.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-methylcyclohexan-1-one** (*anti*-**11d**): ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.86 (d, *J* = 3.0 Hz, 1H), 3.22 - 3.12 (m, 1H), 2.51 – 2.35 (m, 1H), 2.28 (s, 3H), 2.04 – 1.91 (m, 2H), 1.72 – 1.60 (m, 3H), 1.47 – 1.36 (m, 2H), 1.17 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.7, 209.8, 78.6, 49.3, 36.2, 32.3, 29.8, 29.4, 24.0, 18.6.

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-ethylcyclohexan-1-one** (*syn*-**12a**): Inseparable mixture *syn*-**a**/*anti*-**b**/*syn*-**c**/*anti*-**d**: 17/56/21/3. Overall yield: 97.5 mg; 25 %. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.64 (dd, *J* = 4.7, 2.6 Hz, 1H), 3.35 (d, *J* = 4.8 Hz, 1H), 2.89 – 2.85 (m, 1H), 2.51 – 2.42 (m, 1H), 2.21 (s, 3H), 2.14 – 2.04 (m, 2H), 1.95 – 1.87 (m, 1H), 1.86 – 1.79 (m, 1H), 1.80 – 1.69 (m, 2H), 1.56 – 1.47 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.2, 210.0, 76.6, 48.8, 38.5, 33.9, 29.8, 29.8, 26.3, 25.6, 12.2.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-ethylcyclohexan-1-one** (*anti*-**12b**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 3.84 (dd, *J* = 7.7, 2.9 Hz, 1H), 3.55 (d, *J* = 7.8 Hz, 1H), 3.09 (dddd, *J* = 13.3, 5.7, 2.9, 1.0 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.27 (s, 3H), 2.15 – 2.04 (m, 2H), 1.80 – 1.69 (m, 2H), 1.59 (m, 2H), 1.36 (q, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.7, 210.0, 78.0, 53.0, 41.3, 38.3, 36.0, 32.6, 28.8, 25.9, 11.9. HRMS (ESI) calcd for $C_{11}H_{18}O_3Na^+$ $[M+Na]^+$: 221.1148, found: 221.1146

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-ethylcyclohexan-1-one** (*syn*-**12c**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.67 (dd, *J* = 4.8, 2.3 Hz, 1H), 3.24 (d, *J* = 4.8 Hz, 1H), 2.86 – 2.82 (m, 1H), 2.51 – 2.42 (m, 1H), 2.23 (s, 3H), 2.14 – 2.04 (m, 2H), 1.95 – 1.87 (m, 2H), 1.80 – 1.69 (m, 2H), 1.47 (q, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) *δ* 211.6, 210.6, 75.6, 52.3, 41.3, 37.9, 32.4, 32.2, 28.9, 26.6, 11.8.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-ethylcyclohexan-1-one** (*anti*-**12d**): ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.89 – 3.84 (m, 1H), 3.15 – 3.07 (m, 1H), 2.53 – 2.35 (m, 2H), 2.28 (s, 3H), 2.15 – 2.02 (m, 2H), 1.97 – 1.82 (m, 2H), 1.74 – 1.65 (m, 2H), 1.58 – 1.46 (m, 2H), 0.98 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 212.9, 209.8, 78.6, 49.4, 38.2, 33.8, 33.8, 29.8, 28.8, 25.2, 12.3.

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-propylcyclohexan-1-one** (*syn*-**13a**): Inseparable mixture *syn*-**a**/*anti*-**b**/*syn*-**c**/*anti*-**d**: 10/51/34/6. Overall yield: 157.5 mg; 38 %. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.64 (dd, *J* = 4.7, 2.6 Hz, 1H), 3.35 (d, *J* = 4.8 Hz, 1H), 2.89 – 2.85 (m, 1H), 2.45 – 2.44 (m, 1H), 2.41 – 2.38 (m, 1H), 2.21 (s, 3H), 1.94 – 1.86 (m, 1H), 1.87 – 1.73 (m, 2H), 1.74 – 1.68 (m, 2H), 1.55 – 1.45 (m, 2H), 1.40 – 1.34 (m, 2H), 0.96 – 0.92 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.1, 210.0, 76.5, 48.9, 38.5, 35.0, 31.7, 30.2, 30.1, 26.3, 20.8, 14.3.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-propylcyclohexan-1-one** (*anti*-**13b**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 3.84 (dd, *J* = 7.7, 2.9 Hz, 1H), 3.55 (d, *J* = 7.8 Hz, 1H), 3.09 (ddd, *J* = 13.3, 5.7, 2.9 Hz, 1H), 2.38 – 2.35 (m, 1H), 2.26 (s, 3H), 2.12 – 2.02 (m, 2H), 1.87 – 1.73 (m, 2H), 1.63 – 1.54 (m, 2H), 1.40 – 1.23 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.6, 210.1, 77.9, 53.1, 41.3, 38.2, 36.3, 36.3, 33.0, 25.9, 20.4, 14.3. HRMS (ESI) calcd for $C_{12}H_{20}O_3Na^+$ $[M+Na]^+$: 235.1305, found: 235.1305.

***Syn*-2-(1-hydroxy-2-oxopropyl)-4-propylcyclohexan-1-one** (*syn*-**13c**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (dd, *J* = 4.8, 2.3 Hz, 1H), 3.24 (d, *J* = 4.8 Hz, 1H), 2.84 (dddd, *J* = 13.1, 5.7, 2.3, 0.9 Hz, 1H), 2.45 (dd, *J* = 4.5, 2.6 Hz, 1H), 2.40 (dd, *J* = 5.5, 2.8 Hz, 1H), 2.23 (s, 3H), 1.94 – 1.87 (m, 1H), 1.87 – 1.73 (m, 2H), 1.73 – 1.66 (m, 2H), 1.54 – 1.45 (m, 2H), 1.40 – 1.27 (m, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.55, 210.57, 75.55, 52.29, 41.33, 38.34, 35.96, 32.77, 32.56, 26.59, 20.36, 14.34.

***Anti*-2-(1-hydroxy-2-oxopropyl)-4-propylcyclohexan-1-one** (*anti*-**13d**): ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.86 (d, *J* = 2.8 Hz, 1H), 3.18 – 3.09 (m, 1H), 2.47 – 2.35 (m, 2H), 2.28 (s, 3H), 2.13 –

2.00 (m, 2H), 1.93 – 1.76 (m, 2H), 1.57 – 1.45 (m, 2H), 1.42 – 1.22 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 213.0, 209.9, 78.5, 49.5, 38.4, 34.6, 34.1, 31.9, 30.2, 26.6, 20.9, 14.3.

General Procedure for the Reactions of Ketoses with Acetone or Cyclopentanone: Ketones (10.0 mmol), L-proline (230 mg, 2.0 mmol) and DBU (304 mg, 2.0 mmol) were added to a suspension of ketoses (2.0 mmol) in methanol (20.0 mL). The resulting mixture was stirred for 24 h at 64°C. Volatile compounds were removed under reduced pressure and the residue was directly purified by column chromatography. The compounds were isolated as colorless oils.

4,7-Dihydroxyheptane-2,5-dione (**15**): Yield: 45.8 mg; 15%. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.34 (dd, *J* = 5.6, 4.0 Hz, 1H), 3.92 (td, *J* = 5.6, 3.5 Hz, 2H), 3.78 (s, 1H), 3.03 (dd, *J* = 17.6, 3.8 Hz, 1H), 2.91 (dd, *J* = 17.6, 6.1 Hz, 1H), 2.84 (t, *J* = 5.5 Hz, 2H), 2.47 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 212.1, 207.8, 73.9, 57.9, 46.2, 40.4, 30.9. HRMS (ESI) calcd for $C_7H_{12}O_4Na^+$ $[M+H]^+$: 183.0628, found: 183.0634.

***Syn*-2-(1,4-dihydroxy-2-oxobutyl)cyclopentan-1-one** (*syn*-**16**): Inseparable mixture of *syn*/*anti*: 6/4. Overall yield: 36.5 mg; 10 %. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.72 (d, *J* = 2.4 Hz, 1H), 3.99 – 3.93 (m, 2H), 2.74 (ddd, *J* = 13.4, 6.7, 4.2 Hz, 2H), 2.59 – 2.53 (m, 1H), 2.42 – 2.22 (m, 2H), 2.20 – 2.03 (m, 2H), 1.89 – 1.72 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) *δ* 218.3, 211.6, 75.6, 57.7, 51.0, 40.4, 38.4, 22.1, 20.7. HRMS (ESI) calcd for $C_9H_{14}O_4Na^+$ $[M+Na]^+$: 209.0784, found: 209.0790.

***Anti*-2-(1,4-dihydroxy-2-oxobutyl)cyclopentan-1-one** (*anti*-**16**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.16 (d, *J* = 3.4 Hz, 1H), 3.94 – 3.86 (m, 2H), 2.89 (ddd, *J* = 17.1, 6.7, 4.1 Hz, 1H), 2.84 – 2.78 (m, 1H), 2.70 (ddd, *J* = 17.1, 6.8, 4.1 Hz, 1H), 2.42 – 2.22 (m, 2H), 2.20 – 2.03 (m, 2H), 1.89 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 219.6, 210.8, 76.6, 58.0, 51.6, 40.5, 38.8, 26.3, 21.2.

1-C-(*β*-D-Glucopyranosyl)-propan-2-one (**18**):[19] Inseparable mixture of **18**/**19**: 40/60. Overall yield: 116.7 mg; 27 %. ^{1}H NMR (500 MHz, D_2O): *δ* 3.85 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.80 (ddd, *J* = 9.5, 9.2, 3.1 Hz, 1H), 3.68 (dd, *J* = 12.3, 5.0 Hz, 1H), 3.49 (dd, *J* = 9.3, 8.9 Hz 1H), 3.45-3.34 (m, 2H), 3.23 (dd, *J* = 9.5, 9.3 Hz, 1H), 3.04 (dd, *J* = 16.7, 3.1, 1H), 2.73 (dd, *J* = 16.7, 9.2 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, D_2O): *δ* 215.7, 82.1, 79.7, 77.8, 75.6, 72.3, 63.2, 48.2, 32.4. HRMS (ESI) calcd for $C_9H_{16}O_6Na^+$ $[M+Na]^+$: 243.0839, found: 243.0840.

1-C-(*β*-D-Mannopyranosyl)-propan-2-one (**19**):[20] ^{1}H NMR (500 MHz, D_2O): *δ* 4.03 (ddd, *J* = 8.4, 4.5, 0.6 Hz, 1H), 3.86 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.86-3.84 (m, 1H), 3.68 (dd, *J* = 12.2, 6.1 Hz, 1H), 3.67 (dd, *J* = 9.7, 3.8 Hz, 1H), 3.56 (dd, *J* = 9.7, 9.6 Hz, 1H), 3.36 (ddd, *J* = 9.6, 6.1, 2.3 Hz, 1H), 2.94 (dd, *J* = 17.2, 8.4 Hz, 1H), 2,80 (dd, *J* = 17.2, 4.5 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, D_2O): *δ* 213.3, 80.5, 74.6, 74.4, 71.3, 67.6, 61.7, 45.1, 30.4.

1-C-(*β*-L-Gulopyranosyl)-propan-2-one (**21**): Yield: 92.9 mg; 22 %. ^{1}H NMR (500 MHz, D_2O) *δ* 4.07 (td, *J* = 9.7, 3.1 Hz, 1H), 3.99 (t, *J* = 3.5 Hz, 1H), 3.87 (ddd, *J* = 6.8, 5.6, 1.2 Hz, 1H), 3.84 (dd, *J* = 3.8, 1.0 Hz, 1H), 3.66 (d, *J* = 2.4 Hz, 1H), 3.65 (d, *J* = 1.0 Hz, 1H), 3.63 (dd, *J* = 10.1, 3.3 Hz, 1H), 2.98 (dd, *J* = 16.6, 3.2 Hz, 1H), 2.69 (dd, *J* = 16.5, 9.4 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, D_2O) *δ* 213.7, 75.0, 71.7, 70.0, 69.6, 67.7, 61.1, 46.0, 29.8. $[\alpha]_D^{25}$ = +12 (c = 1, methanol). HRMS (ESI) calcd for $C_9H_{16}O_6Na^+$ $[M+Na]^+$: 243.0839, found: 243.0839

1-C-(*β*-D-Galactopyranosyl)-propan-2-one (**23**):[21] Yield: 74.0 mg; 17 %. ^{1}H NMR (500 MHz, D_2O): *δ* 3.93 (dd, *J* = 3.5, 0.5 Hz, 1H), 3.73 (td, *J* = 9.4, 3.1 Hz, 1H), 3.69 - 3.61 (m, 3H), 3.62 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.44 (dd, *J* = 9.6, 9.6 Hz, 1H) 3.00 (dd, *J* = 16.7, 3.0 Hz, 1H), 2.74 (dd, *J* = 16.6, 9.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, D_2O) *δ* 213.7, 78.9, 76.0, 74.1, 70.8, 69.4, 61.5, 46.1, 30.1. $[\alpha]_D^{25}$ = +2 (c = 1, methanol). HRMS (ESI) calcd for $C_9H_{16}O_6Na^+$ $[M+Na]^+$: 243.0839, found: 243.0835.

1-C-(2,3,4,6-Tetra-O-acetyl-*β*-D-talopyranosyl)-propan-2-one (β-**24**): Yield: 55.1 mg; 8 %. ^{1}H NMR (500 MHz, acetone) *δ* 5.28 (dt, *J* = 3.8, 1.0 Hz, 1H), 5.23 (t, *J* = 3.8 Hz, 1H), 5.21 – 5.19 (dt, *J* = 3.8, 1.0 Hz, 1H), 4.29 (ddd, *J* = 7.8, 5.1, 1.4 Hz, 1H), 4.13 – 4.05 (m, 3H), 2.78 (dd, *J* = 17.0, 7.8 Hz, 1H), 2.57 (dd, *J* = 17.0, 5.1 Hz, 1H), 2.12 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (126 MHz, acetone) *δ* 205.1, 170.9, 170.8, 170.6, 169.7, 75.5, 74.1, 69.4, 68.6, 66.5, 62.8, 44.9, 30.2, 20.7, 20.7, 20.6, 20.5. $[\alpha]_D^{25}$ = -8 (c = 1, acetone). HRMS (ESI) calcd for $C_{17}H_{24}O_{10}Na^+$ $[M+Na]^+$: 411.1262, found: 411.1263.

1-C-(2,3,4,6-Tetra-O-acetyl-*α*-D-talopyranosyl)-propan-2-one (α-**24**): Yield: 14.8 mg; 2 %. ^{1}H NMR (500 MHz, acetone) *δ* 5.34 (ddd, *J* = 7.3, 5.2, 4.0 Hz, 1H), 5.22 (dd, *J* = 3.8, 1.1 Hz, 1H), 5.04 (dd, *J* = 3.6, 1.1 Hz, 1H), 4.45 (ddd, *J* = 6.8, 6.4, 3.8 Hz, 1H), 4.31 (dd, *J* = 11.9, 4.0 Hz, 1H), 4.13 (dd, *J* = 11.9, 7.3 Hz, 1H), 3.98 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.87 (dd, *J* = 17.3, 6.7 Hz, 1H), 2.75 (dd, *J* = 17.3, 6.2 Hz, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, acetone) *δ* 205.4, 170.8, 170.5, 170.2, 170.1, 82.5, 79.0, 77.9, 77.1, 70.8, 63.4, 42.7, 20.9, 20.7, 20.7, 20.6. $[\alpha]_D^{25}$ = +7 (c = 0.7, acetone). HRMS (ESI) calcd for $C_{17}H_{24}O_{10}Na^+$ $[M+Na]^+$: 411.1262, found: 411.1261.

1-C-(*β*-D-Isomaltosyl)-propan-2-one (**26**): Inseparable mixture of **26**/**27**: 1/1. Overall Yield: 146.8 mg; 20 %. ^{1}H NMR (500 MHz, D_2O) *δ* 4.90 (d, *J* = 3.6 Hz, 1H), 3.89 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.86 – 3.78 (m, 3H), 3.76 – 3.57 (m, 9H), 3.55 – 3.49 (m, 2H), 3.49 – 3.44 (m, 2H), 3.44 – 3.36 (m, 2H), 3.25 – 3.18 (m, 1H), 3.03 (dd, *J* = 16.9, 2.9 Hz, 1H), 2.69 (dd, *J* = 16.9, 9.6 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, D_2O) *δ* 212.8, 97.8, 78.1, 77.4, 75.5, 73.2, 73.0, 71.7, 71.4, 69.5, 69.4, 65.7, 60.4, 45.5, 29.8. HRMS (ESI) calcd for $C_{15}H_{26}O_{11}Na^+$ $[M+Na]^+$: 405.1367, found: 405.1366.

1-C-(*β*-D-Epiisomaltosyl)-propan-2-one (**27**): ^{1}H NMR (500 MHz, D_2O) *δ* 4.90 (d, *J* = 3.6 Hz, 1H), 4.06 (ddd, *J* = 8.9, 4.0, 0.9 Hz, 1H), 3.93 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.83 – 3.78 (m, 2H), 3.72 – 3.53 (m, 9H), 3.55 – 3.49 (m, 2H), 3.47 – 3.42 (m, 2H), 3.41 – 3.38 (m, 2H), 3.25 – 3.18 (m, 1H), 2.93 (dd, *J* = 17.4, 8.8 Hz, 1H), 2.78 (dd, *J* = 17.5, 4.1 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, D_2O) *δ* 212.5, 97.8, 78.2, 74.3, 74.1, 73.1, 71.7, 71.4, 70.7, 69.5, 66.6, 65.8, 60.5, 44.4, 29.7.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-cyclopentan-2-one** (*syn*-β-**28**): Yield: 94.5 mg; 12 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (t, J = 9.4 Hz, 1H), 5.01 – 4.96 (t, J = 9.8 Hz, 1H), 4.95 (dd, J = 10.2, 9.4 Hz, 1H), 4.18 (dd, J = 12.3, 5.0 Hz, 1H), 3.97 (dd, J = 12.3, 2.3 Hz, 1H), 3.92 (dd, J = 10.2, 1.6 Hz, 1H), 3.61 (ddd, J = 10.1, 5.0, 2.3 Hz, 1H), 2.34 – 2.25 (m, 1H), 2.16 – 2.08 (m, 2H), 2.08 – 2.02 (m, 2H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.99 – 1.94 (m, 1H), 1.75 – 1.64 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.4, 170.7, 170.3, 169.8, 169.7, 75.7, 75.6, 74.4, 69.9, 68.6, 62.0, 48.9, 39.0, 22.5, 20.8, 20.8, 20.7, 20.7, 20.7. $[\alpha]_D^{25}$ = -42 (c = 1.0, acetone). HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1424.

***Anti*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-cyclopentan-2-one** (*anti*-β-**28**): Inseparable mixture of *anti*-β-**28**/*syn*-β-**29**: 2/8. Overall yield: 57.2 mg; 7 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (dd, J = 9.9, 9.3 Hz, 1H), 5.12 (t, J = 9.4 Hz, 1H), 5.02 (t, J = 9.7 Hz, 1H), 4.14 (dd, J = 12.3, 2.5 Hz, 1H), 4.08 (dd, J = 12.3, 4.9 Hz, 1H), 3.81 (dd, J = 10.0, 2.3 Hz, 1H), 3.64 – 3.62 (m, 1H), 2.42 – 2.32 (m, 1H), 2.23 – 2.17 (m, 1H), 2.09 – 2.04 (m, 2H), 2.04 (s, 3H), 2.00 (s, 3H), 2.01 – 1.96 (m, 2H), 1.97 (s, 3H), 1.94 (s, 3H), 1.92 – 1.85 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.1, 170.7, 170.5, 169.5, 169.5, 76.9, 76.0, 74.8, 69.3, 68.5, 62.2, 49.0, 39.2, 25.7, 23.9, 21.0, 20.7, 20.7, 20.6.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-mannopyranosyl)-cyclopentan-2-one** (*syn*-β-**29**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (dd, J = 3.4, 1.0 Hz, 1H), 5.17 (t, J = 10.0 Hz, 1H), 5.05 (dd, J = 10.1, 3.4 Hz, 1H), 4.21 (dd, J = 12.2, 5.8 Hz, 1H), 4.02 (dd, J = 12.2, 2.5 Hz, 1H), 3.98 (dd, J = 3.8, 1.0 Hz, 1H), 3.60 (ddd, J = 9.9, 5.8, 2.5 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.14 (s, 3H), 2.19 – 2.10 (m, 2H), 2.09 – 2.02 (m, 2H), 2.03 (s, 3H), 2.01 (s, 3H), 2.02 – 1.97 (m, 1H), 1.95 (s, 3H), 1.73 – 1.64 (m, 1H). **^{13}**C NMR (126 MHz, $CDCl_3$) δ 217.5, 170.7, 170.3, 170.1, 169.9, 76.4, 75.1, 72.4, 70.4, 66.2, 62.8, 50.4, 38.0, 24.8, 21.1, 20.9, 20.8, 20.8, 20.7. HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1422.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-L-idopyranosyl)-cyclopentan-2-one** (*syn*-α-**30**): Inseparable mixture of *syn*-α-**30**/*syn*-β-**31**: 1/9. Overall yield: 62.0 mg; 8 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 – 5.39 (m, 1H), 5.08 (dd, J = 9.9, 6.6 Hz, 1H), 4.95 – 4.91 (m, 2H), 4.62 (dd, J = 12.7, 8.2 Hz, 1H), 4.21 (dd, J = 10.2, 1.8 Hz, 1H), 4.08 – 4.05 (m, 1H), 2.31 – 2.26 (m, 1H), 2.19 – 2.15 (m, 2H), 2.14 (s, 3H), 2.14 (s, 3H), 2.13 – 2.09 (m, 2H), 2.03 (s, 3H), 2.02 (s, 3H), 2.03 – 1.97 (m, 1H), 1.80 – 1.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.9, 170.7, 169.9, 169.9, 169.8, 71.0, 70.6, 70.4, 69.8, 69.7, 60.3, 48.9, 39.0, 22.4, 21.0, 20.8, 20.8, 20.8, 20.7.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-L-idopyranosyl)-cyclopentan-2-one** (*syn*-β-**30**): Inseparable mixture of *syn*-β-**30**/*anti*-β-**31**: 45/55. Overall yield: 47.9 mg; 6 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (dd, J = 5.3, 3.5 Hz, 1H), 5.28 (dd, J = 6.2, 3.4 Hz, 1H), 4.53 (t, J = 5.1 Hz, 1H), 4.30 (dd, J = 5.7, 5.1 Hz, 1H), 4.06 – 4.03 (m, 1H), 4.05 – 4.02 (m, 1H), 3.99 (dd, J = 9.1, 5.5 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.10 – 2.03 (m, 2H), 2.09 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 2.01 – 1.95 (m, 2H), 1.96 (s, 3H), 1.90 – 1.80 (m, 1H), 1.77 – 1.66 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.7, 170.7, 170.0, 169.9, 169.4, 78.0, 77.2, 76.3, 76.3, 72.6, 62.3, 49.1, 38.3, 25.6, 21.1, 21.0, 21.0, 20.9, 20.8. HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1419.

***Anti*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-L-gulopyranosyl)-cyclopentan-2-one** (*anti*-β-**31**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (dd, J = 9.0, 3.4 Hz, 1H), 5.10 (dt, J = 7.2, 4.5 Hz, 1H), 4.88 (dd, J = 3.7, 1.4 Hz, 1H), 4.31 – 4.27 (m, 1H), 4.20 (dd, J = 11.8, 4.2 Hz, 1H), 4.03 (dd, J = 10.0, 2.1 Hz, 1H), 3.95 (dd, J = 11.8, 7.2 Hz, 1H), 2.34 (t, J = 10.1 Hz, 1H), 2.12 – 2.07 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.05 – 2.02 (m, 2H), 2.02 (s, 3H), 2.01 – 1.98 (m, 1H), 1.87 (s, 3H), 1.77 – 1.66 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.9, 170.7, 169.8, 169.6, 169.3, 73.7, 69.7, 68.5, 66.7, 66.5, 62.8, 48.8, 39.4, 25.7, 21.3, 21.0, 20.9, 20.9, 20.8.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*α*-L-gulopyranosyl)-cyclopentan-2-one** (*syn*-α-**31**): Yield: 5.0 mg; 1 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 (t, J = 2.7 Hz, 1H), 4.96 (ddd, J = 2.7, 1.6, 1.1 Hz, 1H), 4.81 – 4.79 (m, 3H), 4.19 – 4.13 (m, 1H), 4.09 – 4.04 (m, 1H), 2.36 – 2.24 (m, 1H), 2.15 (s, 3H), 2.17 – 2.12 (m, 2H), 2.11 (s, 3H), 2.10 (s, 3H), 2.12 – 2.07 (m, 2H), 2.07 – 2.01 (m, 1H), 2.03 (s, 3H), 1.79 – 1.69 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.3, 170.7, 169.7, 169.7, 168.4, 73.6, 73.0, 68.0, 66.4, 65.4, 62.3, 50.3, 38.4, 25.2, 21.1, 21.1, 21.0, 20.9, 20.9. $[\alpha]_D^{25}$ = +11 (c = 0.5, acetone). HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1418.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-L-gulopyranosyl)-cyclopentan-2-one** (*syn*-ß-**31**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (t, J = 3.5 Hz, 1H), 4.97 (dd, J = 10.6, 3.2 Hz, 1H), 4.94 (dd, J = 3.8, 1.1 Hz, 1H), 4.29 (dd, J = 10.6, 2.1 Hz, 1H), 4.09 (dd, J = 5.4, 1.4 Hz, 1H), 4.09 – 4.05 (m, 1H), 3.97 (dd, J = 10.3, 5.1 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.21 – 2.16 (m, 1H), 2.14 (s, 3H), 2.14 (s, 3H), 2.13 – 2.08 (m, 2H), 2.08 – 2.04 (m, 1H), 2.04 – 1.99 (m, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.78 – 1.67 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.4, 170.6, 169.8, 169.7, 169.4, 72.2, 72.0, 68.4, 66.7, 66.7, 61.7, 48.8, 39.3, 22.4, 21.0, 20.9, 20.8, 20.8, 20.8. HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1420.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-galactopyranosyl)-cyclopentan-2-one** (*syn*-β-**32**): Yield: 89.5 mg; 11 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (dd, J = 3.4, 1.1 Hz, 1H), 5.16 (t, J = 10.0 Hz, 1H), 5.03 (dd, J = 10.0, 3.4 Hz, 1H), 4.07 (dd, J = 11.2, 6.7 Hz, 1H), 3.97 (dd, J = 11.2, 6.7 Hz, 1H), 3.93 (dd, J = 10.0, 1.3 Hz, 1H), 3.86 (td, J = 6.7, 1.1 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.15 – 2.13 (m, 2H), 2.14 (s, 3H) 2.12 – 2.02 (m, 2H), 2.04 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.79 – 1.69 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.8, 170.6, 170.4, 170.2, 170.1, 76.3, 74.1, 72.4, 67.7, 67.4, 61.3, 49.0, 39.3, 22.7, 20.9, 20.8, 20.8, 20.8, 20.8. $[\alpha]_D^{25}$ = -42 (c = 1, acetone). HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1423.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-talopyranosyl)-cyclopentan-2-one** (*syn*-β-**33**): Inseparable mixture *syn*-β-**33**/*syn*-α-**33**/*anti*-α-**33**: 6/2/2. Overall yield: 45.6 mg; 6 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (dd, J = 4.1, 1.4 Hz, 1H), 5.32 (ddd, J = 7.1, 5.5, 3.9 Hz, 1H), 5.04 (dd, J = 3.6, 1.3 Hz, 1H), 4.35 (dd, J = 12.0, 3.9 Hz, 1H), 4.30 (dd, J = 4.7, 4.3 Hz, 1H),

4.09 (dd, *J* = 11.9, 7.2 Hz, 1H), 3.90 (dd, *J* = 5.6, 3.6 Hz, 1H), 2.14 – 2.11 (m, 2H), 2.11 (s, 3H), 2.09 (s, 3H), 2.10 – 2.05 (m, 2H), 2.07 (s, 3H), 2.03 (s, 3H), 2.04 – 2.00 (m, 2H), 1.83 – 1.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 217.6, 170.6, 170.1, 169.6, 169.5, 81.3, 79.0, 77.9, 77.4, 70.0, 62.8, 48.4, 38.0, 25.6, 21.0, 20.9, 20.9, 20.7, 20.7. HRMS (ESI) calcd for $C_{19}H_{26}O_{10}Na^+$ $[M+Na]^+$: 437.1418, found: 437.1422.

***Syn*-1-C-(2,3,4,6-tetra-O-acetyl-*α*-D-talopyranosyl)-cyclopentan-2-one** (*syn*-α-**33**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 5.33 (ddd, *J* = 6.7, 3.5, 1.1 Hz, 1H), 5.18 (ddd, *J* = 7.3, 4.8, 3.0 Hz, 1H), 5.09 (t, *J* = 3.5 Hz, 1H), 4.98 – 4.94 (m, 1H), 4.35 (dd, *J* = 6.7, 2.6 Hz, 1H), 4.18 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.99 – 3.94 (m, 1H), 2.31 – 2.25 (m, 1H), 2.13 – 2.06 (m, 1H), 2.07 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.03 – 1.97 (m, 2H), 1.97 – 1.90 (m, 1H), 1.81 – 1.70 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 218.1, 170.3, 170.1, 170.0, 169.9, 81.3, 80.1, 78.6, 72.0, 70.0, 62.4, 49.9, 38.8, 22.7, 20.9, 20.8, 20.8, 20.7, 20.7.

***Anti*-1-C-(2,3,4,6-tetra-O-acetyl-*β*-D-talopyranosyl)-cyclopentan-2-one** (*anti*-α-**33**): ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 5.25 – 5.23 (m, 1H), 5.14 (dd, *J* = 6.0, 3.2 Hz, 1H), 5.10 - 5.06 (m, 1H), 4.33 (dd, *J* = 6.1, 3.9 Hz, 1H), 4.27 – 4.24 (m, 1H), 4.10 – 4.06 (m, 1H), 4.06 – 4.03 (m, 1H), 2.40 – 2.33 (m, 1H), 2.13 – 2.06 (m, 1H), 2.03 (s, 3H), 2.03 – 1.97 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.97 – 1.90 (m, 1H), 1.81 – 1.70 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 217.6, 170.7, 170.7, 170.2, 170.0, 81.2, 79.2, 78.7, 71.6, 70.2, 62.7, 50.6, 38.8, 23.8, 21.0, 20.9, 20.9, 20.8, 20.7.

***Syn*-1-C-(2,3,4,6,8,9,10,12-octa-O-acetyl-*β*-D-isomatosyl)-cyclopentan-2-one** (*syn*-**34**): impure with 5 % *syn*-**35**, yield: 87.1 mg; 7 %. ^{1}H NMR (500 MHz, acetone) *δ* 5.39 (dd, *J* = 10.2, 9.5 Hz, 1H), 5.27 (t, *J* = 9.4 Hz, 1H), 5.07 (d, *J* = 3.6 Hz, 1H), 5.03 (d, *J* = 9.7 Hz, 1H), 4.99 (d, *J* = 9.5 Hz, 1H), 4.93 (dd, *J* = 9.8 Hz, 1H), 4.84 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.19 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.08 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.03 (dd, *J* = 10.3, 2.0 Hz, 1H), 3.99 (ddd, *J* = 10.2, 5.4, 2.4 Hz, 1H), 3.83 (ddd, *J* = 9.9, 5.5, 2.6 Hz, 1H), 3.73 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.61 (dd, *J* = 11.4, 2.6 Hz, 1H), 2.30 – 2.23 (m, 1H), 2.24 – 2.15 (m, 2H), 2.08 (s, 3H), 2.03 (s, 3H), 2.04 – 2.00 (m, 2H), 2.01 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.82 – 1.70 (m, 2H). ^{13}C NMR (126 MHz, acetone) *δ* 217.4, 170.8, 170.7, 170.4, 170.2, 170.1, 170.1, 170.1, 96.2, 76.9, 76.2, 75.1, 71.4, 70.7, 70.6, 70.0, 69.5, 68.3, 66.6, 62.7, 49.2, 39.2, 24.5, 23.2, 21.2, 20.8, 20.7, 20.6, 20.6. HRMS (ESI) calcd for $C_{31}H_{42}O_{18}Na^+$ $[M+Na]^+$: 725.2263, found: 725.2265.

***Syn*-1-C-(2,3,4,6,8,9,10,12-Octa-O-acetyl-*β*-D-epiisomatosyl)-cyclopentan-2-one** (*syn*-**35**): impure with 5 % *syn*-**34**, yield: 80.5 mg; 6 %. ^{1}H NMR (500 MHz, acetone) *δ* 5.61 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.44 (dd, *J* = 10.2, 9.4 Hz, 1H), 5.17 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.11 (d, *J* = 9.9 Hz, 1H), 5.08 (d, *J* = 3.5 Hz, 1H), 5.01 (dd, *J* = 10.1, 9.4 Hz, 1H), 4.84 (dd, *J* = 10.3, 3.6 Hz, 1H), 4.17 – 4.15 (m, 2H), 4.11 (dd, *J* = 11.0, 3.1 Hz, 1H), 4.10 (dd, *J* = 5.5, 1.2 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.73 (dd, *J* = 10.8, 7.0 Hz, 1H), 3.59 (dd, *J* = 10.8, 2.6 Hz, 1H), 2.39 – 2.33 (m, 1H), 2.27 – 2.18 (m, 2H), 2.12 (s, 3H), 2.14 – 2.08 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.85 – 1.73 (m, 2H). ^{13}C NMR (126 MHz, acetone) *δ* 217.0, 170.7, 170.6, 170.6, 170.4, 170.3, 170.2, 170.1, 95.7, 77.4, 75.9, 73.1, 71.4, 71.0, 70.6, 69.6, 68.4, 67.3, 67.1, 62.8, 50.3, 38.4, 26.4, 21.3, 20.9, 20.8, 20.7, 20.6, 20.6. HRMS (ESI) calcd for $C_{31}H_{42}O_{18}Na^+$ $[M+Na]^+$: 725.2263, found: 725.2263.

Supporting Information (see footnote on the first page of this article): Conformation analysis, proof of configuration and copies of ^{1}H NMR and ^{13}C NMR spectra are available in the Supporting Information.

Acknowledgements

The authors thank Deutsche Forschungsgemeinschaft for financial support.

Keywords: amine-catalysis; cascade reaction; C-glycosides; mechanism

[1] C. Richter, B. Voigt, R. Mahrwald, *RSC Advances* **2015**, *5*, 45571-45574.

[2] Dihydroxyacetone exists in solid state as a dimeric structure. For reasons of simplification the monomeric structure is depicted.

[3] For reviews in this field, see: a) A. Jacobsen, J. Thiem, *Curr. Org. Chem*. **2014**, *18*, 2833-2841; b) L. A. Paquette, J. E. Hofferberth, *Org. React.* **2003**, *62*, 477-567; c) S. J. Angyal, *Top. Curr. Chem*. **2001**, *215*, 1-14; d) J. C. Speck jr., *Adv. Carb. Chem*. **1958**, *13*, 63-103; e) W. L. Evans, *Chem. Rev*. **1929**, *6*, 281-315.

[4] a) C. Angeloni, L. Zambonin, S. Hrelia, *Biomed Res. Int*. **2014**, 1-12; b) Y. Wang, C.-T. Ho, *Chem. Soc. Rev*. **2012**, *41*, 4140-4149; c) K. P. Subedi, I. Kim, J. Kim, B. Min, C. Park, *FEMS Microbiology Lett.* **2008**, *279*, 180-187; d) M. P. Kalapos, *Drug Metabol. Drug Interact*. **2008**, *23*, 69-91; e) R. A. Cooper, *Ann. Rev. Microbiol*. **1984**, *34*, 49-68; f) R. Iyengar, I. A. Rose, *J. Am. Chem. Soc*. **1983**, *105*, 3301-3303.

[5] I. Allaman, M. Belanger, P. J. Magistretti, *Neurosci*. **2015**, *9*, 1-12.

[6] a) J. Dijkmans, M. Dusselier, D. Gabriels, K. Houthoofd, P. C. M. M. Magusin, S. Huang, Y. Pontikes, M. Trekels, A. Vantomme, L. Giebeler, S. Oswald, B. F. Sels, *ACS Catalysis* **2015**, *5*, 928-940; b) tin phosphate / 140°C: X. Wang, F. Liang, C. Huang, Y. Li, B. Chen, *Cat. Science & Techn.* **2015**, *5*, 4410-4421; c) Hydrothermal decomposition at 210°C: X. Liang, A. Rahubadda, B. S. Haynes, A. Montoya, *Ind. & Eng. Chem. Res*. **2015**, *54*, 8437-8447; d) Zeolithes / 100°C: P. Y. Dapsens, B. T. Kusema, C. Mondelli, J. Perez-Ramirez, *J. Mol. Cat. A: Chem*., **2014**, *388-389*, 141-147; e) Lewis-acid / 100°C: Y. Koito, K. Nakajima, R. Hasegawa, H. Kobayashi, M. Kitano, M. Hara, *Catalysis Today*, **2014**, *226*, 198-203; f) Lewis-acid /140°C: C. B. Rasrendra, B. A. Fachri, I. Makertihartha, B. N. Gusti, S. Adisasmito, H. J. Heeres, *ChemSusChem* **2011**, *4*, 768-777; g) H_2SO_4 / 140°C: M. J. Antal, Jr., W. S. L. Mok, G. N. Richards, *Carb. Res*. **1990**, *199*, 111-115; h) H_2SO_4 / 100°C: B. Görlich, *Chem. Ber*. **1956**, *89*, 2145-2154; i) for a very first report - alkaline degradation of glucose, see: G. Pinkus, *Ber*. **1898**, *31*, 31-37.

[7] M. N. C. Grainger, M. Manley-Harris, J. R. Lane, R. Field, *J. Food Chem.* **2016**, *202*, 492-499.

[8] a) for organocatalyzed aldol additions of methylglyoxal with ketones see F. J. N. Moles, G. Guillena, C. Najera, *Synlett* **2015**, *26*, 656-660; b) aldol reactions of methylglyoxal with enolizable aldehydes: Y. Hayashi, Y. Yasui, M. Kojima, T. Kawamura, H. Ishikawa, *Chem. Comm*., **2012**, *48*, 4570-4572; c) for organocatalyzed aldol reactions of acetone with methylglyoxal see D. G. Alberg, T. B. Poulsen, S. Bertelsen, K. L. Christensen, R. D. Birkler, M. Johannsen, K. A. Jorgensen, *Bioorg. Med. Chem. Lett*. **2009**, *19*, 3888-3891; d) for Sc(III)-catalyzed aldol addition of α-keto aldehydes to 2-oxindoles see K. Shen, X. Liu, K. Zheng, W. Li, X. Hu, L. Lin, X. Feng, *Chem.-Eur. J.* **2010**, *16*, 3736-3741.

[9] see Supporting Information

[10] D. Enders, T. V. Nguyen, *Tetrahedron Lett.* **2012**, 53, 2091-2095.

[11] A. Massi, A. Nuzzi, A. Dondoni, *J. Org. Chem*. **2007**, *72*, 10279-19282.
[12] S. N. R. Witte, B. Voigt, R. Mahrwald, *Synthesis*, **2015**, *47*, 2249-2255.
[13] a) M. Hellwig, T. Henle, *Angew. Chem. Int. Ed.* **2014**, *53*, 10316-10329; b) R. J. Ferrier, R. Blattner, R. A. Field, R. H. Furneaux, J. M. Gardiner, J. O. Hoberg, K. P. R. Kartha, D. M. G. Tilbrook, P. C. Tyler, R. H. Wightman, *Carb. Chem*. **2002**, *33*, 126-143; c) V. A. Yaylayan, A. Huyghues-Despointes, *Crit. Rev. Food Sci. Nutr*. **1994**, *34*, 321-369.
[14] L. A. Paquette, J. E. Hofferberth, *Org. React.* **2003**, 62, 477-567.
[15] K. Gupta, D. Tyagi, A. D. Dwivedi, S. M. Mobin, S. K. Singh, *Green Chem*. **2015**, *17*, 4618-4627.
[16] C. Bongards, W. Gaertner, *Eur. J. Org. Chem*. **2007**, 5749-5758.
[17] M. Mikolajczyk, S. Grzejszczak, W. Midura, A. Zatorski, *Phos. Sulf. Rel. Elem.* **1983**, *18*, 175-178.
[18] S. K. Mukerji, K. K. Sharma, K. B. G. Torssell, *Tetrahedron* **1983**, *39*, 2231-2235.
[19] F. Peri, L. Cipolla, B. La Ferla, P. Dumy, F. Nicotra, *Glycoconjugate J.* **1999**, *16*, 399-404.
[20] F. Rodrigues, Y. Canac, A. Lubineau, *Chem. Comm*. **2000**, 2049-2050.
[21] N. Bragnier, M.-C. Scherrmann, *Synthesis* **2005**, 814-818.

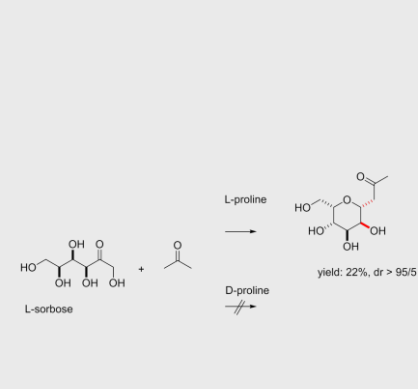
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

Amine-mediated cascade reactions of unprotected ketoses were elaborated. Extremely matched or mismatched cases were detected by deployment of D- or L-proline in these transformations.



Cascade reactions, carbohydrates

*Celin Richter, Michael Krumrey, Kristin Klaue, Rainer Mahrwald**

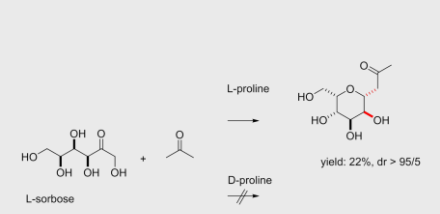
Page No. – Page No.

Title

*cascade reactions, carbohydrates

Layout 2:

FULL PAPER



Text for Table of Contents

Amine-mediated cascade reactions of unprotected ketoses were elaborated. Extremely matched or mismatched cases were detected by deployment of D- or L-proline in these transformations.

Cascade reactions, carbohydrates

*Celin Richter, Michael Krumrey, Kristin Klaue, Rainer Mahrwald**

Page No. – Page No.

Title

*cascade reactions, carbohydrates