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A new type of rearrangement in branched-chain carbohydrates: isomerization of 3-C-branched aldoses

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Dedicated to the memory of Professor S. J. Angyal (1914–2012)

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ABSTRACT

A new type of rearrangement is described for 3-C-branched chain aldoses. The studied transformation is based on the Mo(VI)-catalyzed isomerization of carbohydrate carbon skeleton and allows preparation of C-3 isomers of 3-C-branched aldoses in a simple way without formation of side products. This rearrangement at C-3 carbon differs from the previously described epimerization at C-2 of aldoses catalyzed by Mo(VI) ions, known as Bílik reaction. The potential of this new transformation is illustrated on the preparation of new, 3-*C*-methyl-D-glucose and 3-*C*-vinyl-D-glucose from 3-*C*-methyl-D-allose and 3-*C*-vinyl-D-allose, respectively.

1. Introduction

Branched-chain sugars represent a rare class of naturally occurring carbohydrates. They are all characterized by modification at one of the non-terminal carbon atoms of the sugar chain. Such derivatives often show unique structural characteristics that are associated with notable biolological activity.[1,2] The oldest and the best-known examples of branched-chain sugars are D-apiose (3-*C*-hydroxymethyl-D-glycero-tetrose) and D-hamamelose (2-*C*-hydroxymethyl-D-ribose) which were isolated from plants as a structural component of apiin[3] and hammamelitannin.[4] Subsequently, numerous other compounds have been isolated from natural sources or synthesized.[5–7] Especially 3-*C*-methyl-branched sugars, such as L-mycarose,[8] D-evalose, L-streptose, and D-virenose, are glycosidic components of antibiotics[9] and have stimulated extensive research on their synthesis. Methods of introducing a carbon chain at branching carbon atom require several steps. In spite of strong demands for higher stereoselectivities, an interesting and potentially valuable alternative is the stereospecific isomerization of carbohydrate carbon skeleton catalyzed by transition-metals. Such reactions allow even transformations of complex organic molecules.

During the past decade we have demonstrated the advantages and effectiveness of Mo(VI)-catalyzed rearrangement of carbohydrate carbon skeleton in microwave field.[10,11] Unsubstituted monosaccharides create various types of complexes with molybdate ions in aqueous solutions.[12] Comprehensive studies of acyclic dimolybdate–saccharide complexes carried out by Bílik led to preparative method for the synthesis of rare aldoses.[13,14] The Bílik reaction applied to 2-ketoses yielded 2-*C*-hydroxymethyl-aldoses and vice versa. Epimerization reaction, during which C-1 to C-2 transposition occurs,[14] must involve catalytically productive complexes. Apart from these highly reactive, catalytically active complexes a variety of other, non-active complexes exist in aqueous solution as well.

Recent works from our laboratory have shown that microwave irradiation has a great impact on this type of transformations. The finding that the use of molybdate ions as catalyst in combination with microwave irradiation improves the stereoselectivity markedly and shortens the reaction time significantly has rendered these reactions attractive for synthetic purposes. The methodology is reliable for the preparation of many sugar derivatives and led to the efficient preparation of epimeric aldoses,[10] ketoses,[11] deoxyaldoses,[15] and (1→6)-linked disaccharides,[16] but it is also effective in the case of aldoses bearing nitrogen in the branch.[17]

The biological importance of 3-C-branched chain aldoses and the unexplored potential of this transformation prompted us to investigate whether *C-3* isomerization could be performed to synthesize biologically important saccharides. The feasibility of such transformation employing Mo(VI) catalyst in combination with microwave field has been verified on various 3-C-branched chain aldoses preparing their isomeric structures.

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Table 1
Comparison of microwave and conduction-heated samples of the Mo(VI) catalyzed isomerization of 3-C-branched aldoses. Conversions are shown also for conventional heating to demonstrate vast differences between microwave and conventional approaches in reaction kinetics and amounts of isomeric product formation

3-C-Branched aldose	Microwave field		Oil-bath heating		Changes in reaction rate
	Time (min)	3-*C*-Aldose (%)	Time (h)	3-*C*-Aldose (%)	
3-*C*-Methyl-D-allose (**6**)	5	19	10	9	120×
3-*C*-Vinyl-D-allose (**7**)	5	14	12	8	144×
3-*C*-Phenyl-D-allose (**8**)	10	—	15	—	—
3-*C*-Nitromethyl-D-glucose (**9**)	10	—	15	—	—
3-*C*-Cyano-D-glucose (**10**)	10	—	15	—	—

2. Results and discussion

2.1. Synthesis of model 3-C-branched chain aldoses

Five model 3-C-branched chain aldoses with different structures were synthesized using Grignard reaction, which has the potential to cause branching of the carbohydrate skeleton. The corresponding 1,2: 5,6-di-*O*-isopropylidene-3-*C*-methyl-D-allose (**1**), 1,2: 5,6-di-*O*-isopropylidene-3-*C*-vinyl-D-allose (**2**) and 1,2: 5,6-di-*O*-isopropylidene-3-*C*-phenyl-D-allose (**3**) was thus prepared in 84%, 81% and 87% yield respectively. Another two 3-C-branched sugars, 1,2: 5,6-di-*O*-isopropylidene-3-*C*-nitromethyl-D-glucofuranose (**4**) and 3-*C*-cyano-1,2: 5,6-di-*O*-isopropylidene-D-glucofuranose (**5**), were prepared according to literature.[18,19] The structures of **4** and **5** were confirmed by spectroscopic methods. Acid-catalyzed hydrolysis of the isopropylidene derivatives **1**–**5** led exclusively to the corresponding 3-C-branched aldoses **6**–**10** respectively in very good yields (Scheme 1).

Two characteristic doublet resonances at 5.09 ppm and at 4.79 ppm originated from anomeric protons of α- and β-pyranose forms in ^{1}H NMR spectrum of 3-*C*-methyl-D-allose (**6**). The ratio of these forms was determined from the ^{1}H resonance intensities and indicated that the β-pyranose form is more stable than the α-form in aqueous solution (17% α-pyranose, 83% β-pyranose). The presence of the methyl group at C-3 was confirmed by the characteristic ^{1}H resonance (1.31 ppm) (*CH*$_3$ (C-3)); ^{13}C resonance (*C*H$_3$ (C-3)) was at 20.99 ppm. Three bond proton-proton coupling constant between H-1 and H-2 ($^3J_{1,2}$) was 8.1 Hz for the β-pyranose form, thus in a good agreement with $^4C_1$ form of the pyranose ring. The structure of **6** has been confirmed by 2D COSY, HSQC, and HMBC methods. Similarly, the β-pyranose form is more stable than the α-form (15% α-pyranose, 85% β-pyranose) also in 3-*C*-vinyl-D-allose (**7**). ^{1}H chemical shift of anomeric proton of the prevailing β form is at 4.89 ppm; chemical shift of proton of the α form is at 5.15 ppm. Three characteristic multiplets at lower field (5.84 ppm, 5.42 ppm, and 5.39 ppm) are due to the vinyl group linked to C-3 carbon. Corresponding vinyl carbon resonances are at 138.66 ppm (CH) and 117.39 (CH$_2$).

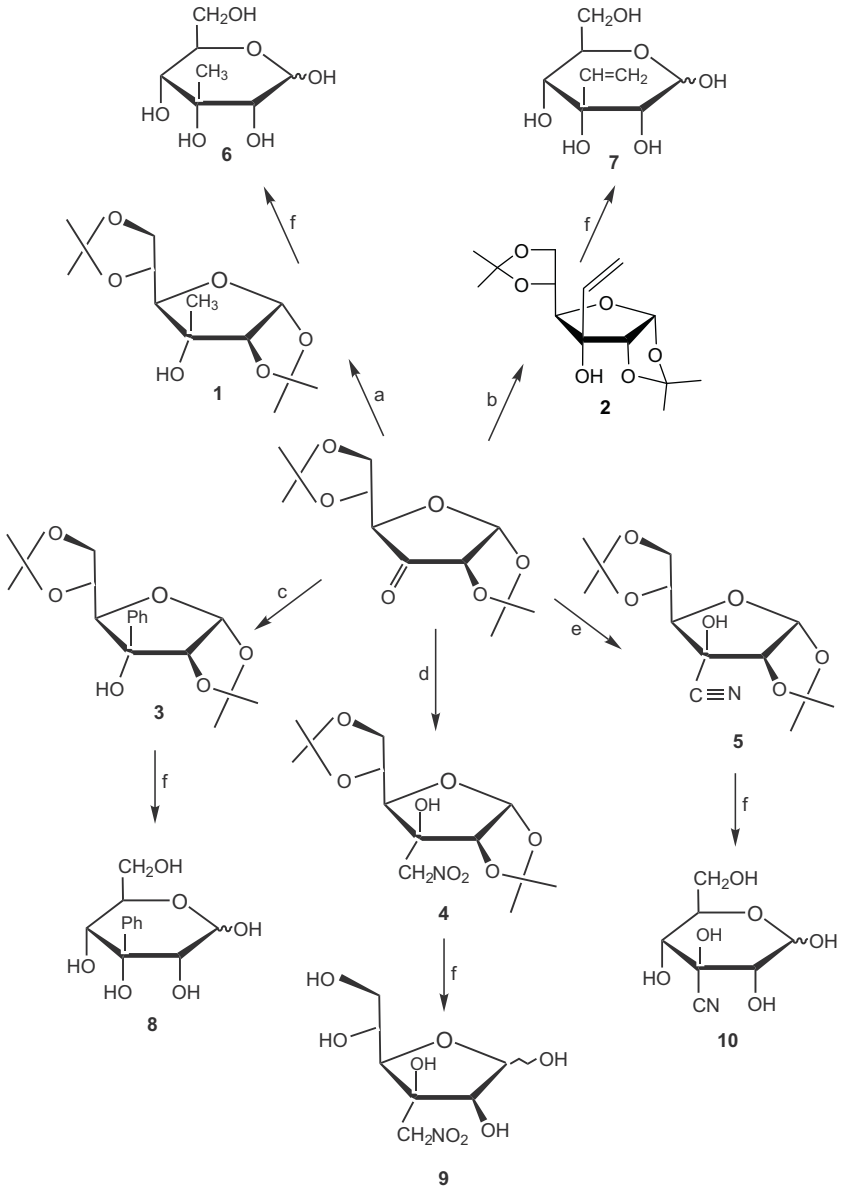
Slightly higher population of the α-pyranose form (21% α-pyranose, 79% β-pyranose), compared to previous compounds, in 3-*C*-phenyl-D-allose (**8**) has been determined from ^{1}H NMR spectra. The bulky phenyl group affected not only the mentioned anomeric ratio but in part also chemical shifts of anomeric protons (α-anomer, 5.25 ppm; β-anomer 5.04 ppm). Three multiplets at 7.36-7.55 ppm (^{1}H spectrum) and four resonances namely, 128.56, 127.67, 125.86, and 120.99 ppm in ^{13}C spectrum arose from the phenyl group linked to C-3 carbon. Unlike to above mentioned derivatives **6–8**, all four forms were identified in 3-*C*-nitromethyl-D-glucofuranose (**9**) in solution (31% α-pyranose, 19% β-pyranose, 22% α-furanose, 28% β-furanose)). Relatively high population of α-pyranose form (31% α-pyranose, 69% β-pyranose) was observed also in 3-*C*-cyano-D-glucofuranose (**10**). The assignments of NMR spectra were carried out using 2D NMR spectroscopy.

2.2. Mo(VI)-catalyzed isomerization reaction

Due to the multiple donor sites of nearly equivalent oxygen atoms and due to the equilibria between several isomers, branched-chain aldoses are versatile ligands. They may exist in aqueous solution in pyranose and furanose forms but in acyclic form as well. Furthermore, different conformers of furanose and pyranose rings provide different modes for metal binding.[20] Molybdate ions could form catalytically active species promoting stereospecific rearrangement of the saccharide carbon skeleton. Complexes with sugars are formed only when three or more hydroxyl groups are available in the current relative positions. The acyclic hydrated aldehyde forms of aldoses are linked in the binuclear molybdate core as tetradentate ligands via their hydrated carbonyl group and three adjacent hydroxyls (bound on carbons C$_{(2)}$, C$_{(3)}$, and C$_{(4)}$) (Fig. 1). Only these forms are active and mediate the stereospecific rearrangement.

Model compounds **6–10** were used to investigate Mo(VI)-catalyzed stereospecific isomerizations with C-3 branched sugars. The experiments were carried out with controlled microwave irradiation under sealed vessel conditions. The influence of microwave irradiation on conversion, selectivity, and product distribution was examined using multimode microwave reactor consisting of a continuous focused microwave power delivery system with operator-selectable power. The 3-C-branched chain aldose was suspended in 0.2% aqueous solution of molybdic acid and the mixture was exposed to microwave radiation at a controlled power (300 W). A homogenous blue solution was obtained indicating the complex formation. We have observed that 3-*C*-methyl-D-allose (**6**) and 3-*C*-vinyl-D-allose (**7**) are rapidly interconverted to their isomers, 3-*C*-methyl-D-glucose (**11**) and 3-*C*-vinyl-D-glucose (**12**) under present experimental conditions. The equilibruim mixtures favored in both cases the *allo*-isomer. Highly stereoselective reaction could be accomplished with a catalytic amount of Mo(VI) ions in few minutes (Scheme 2). It should be stressed that the reaction proceeded without significant formation of secondary products. Transformation must involve the formation of catalytically active dimolybdate species as intermediates which enable the stereospecific rearrangement in catalytic cycle. Experimental data have shown that 3-C-branched aldoses gave rise to new stereoisomeric branched compounds.

The structure of 3-*C*-methyl-D-glucose (**11**) was identified on the basis of NMR chemical shifts, proton-proton coupling constant ($^3J_{H,H}$), NOEs and theoretical DFT analysis. ^{1}H NMR spectrum of the reaction mixture contained new doublets at 5.18 ppm and 4.66 ppm, respectively, which were assigned to the pyranose anomeric protons H-1 of the 3-*C*-methyl-D-glucose. Signal integration gave the ratio of α/β 15/85 in aqueous solution at 25 °C. $^3J_{1,2}$ value was 8.2 Hz and was compatible with antiperiplanar position of H-1 and H-2 in 3-*C*-methyl-β-D-glucose (Fig. 2). Theoretical analysis made possible further insight into the product structure. DFT-optimized molecular geometry using the 6-31+G* basis set enabled calculation of proton-proton coupling constants and inter-proton distances. Computed torsion angle between H-1 and H-2 was



Scheme 1. Reagents and conditions: (a) CH_3MgI, Et_2O, 0 °C→rt/4 h; (b) $CH{=}CH_2MgBr$, THF, 60 °C/3 h; (c) PhMgBr, Et_2O, reflux, 2 h; (d) CH_3NO_2, CH_3ONa, r t. 18 h; (e) NaCN, CH_3OH, rt 6 h; (f) H_2O, Dowex 50 W ×4, H^+ 75 °C, 7 h.

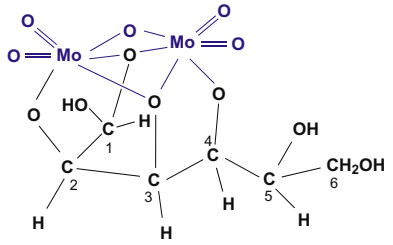
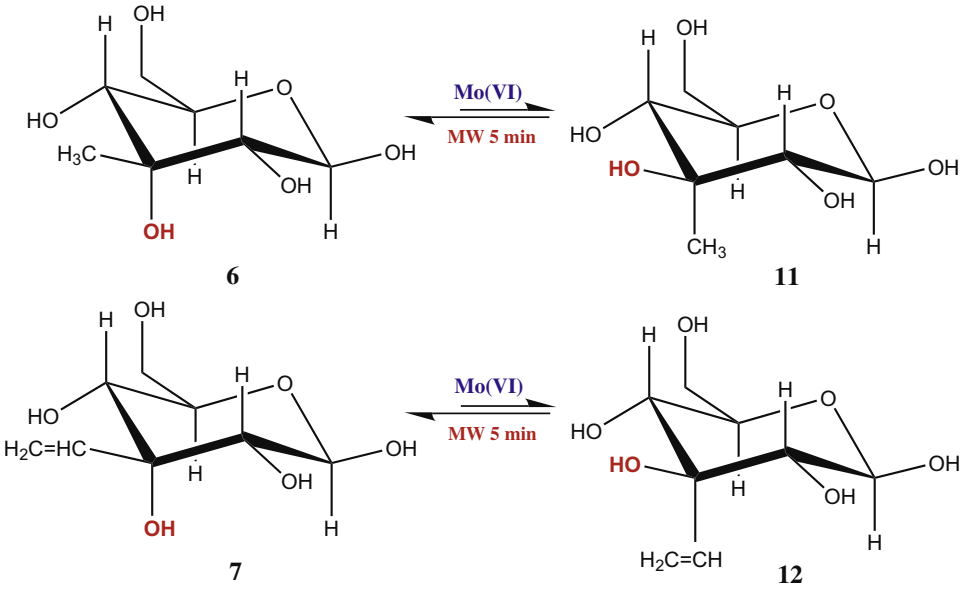


Figure 1. The acyclic forms of aldoses linked in the binuclear molybdate core as tetradentate ligands via their hydrated carbonyl group and three adjacent hydroxyls (bound on carbons $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$).

178.9°, the angle between H-4 and H-5 was −175.2°. Theoretical values of three-bond coupling constants for these proton pairs ($^3J_{1,2}$ = 7.9 Hz and $^3J_{4,5}$ = 9.0 Hz) agreed with experimental data and supported $^4C_1$ β-pyranose form of glucose derivative. The presence of the methyl group at C-3 was confirmed by the characteristic ^{1}H resonance (1.16 ppm) (*CH*$_3$ (C-3)). Further evidence of the *gluco* arrangement was found in NOESY spectra. Cross-peaks between 3-*C*-methyl group and anomeric proton as well as *C*-methyl and H-5 proton confirmed spatial closeness of these protons (computed distances were 2.3–2.4 Å). These NOEs could be observed only in case when methyl group is in the axial position. On the other hand, dipolar interactions seen in NOESY spectrum differed in 3-*C*-methyl-D-allose. In the latter case, cross-peaks between *C*-methyl group and H-2 and H-4 protons agreed with equatorial position of the *C*-methyl group (corresponding computed internuclear distances were 2.5–2.6 Å).

The β-pyranose form (H-1 at 4.80 ppm) is more stable than the α-form (H-1 at 5.21 ppm) also in 3-*C*-vinyl-D-glucose (**12**) (28% α-pyranose, 72% β-pyranose). The value of proton-proton coupling constant $^3J_{1,2}$ was 8.6 Hz and was thus comparable with the value in 3-*C*-methyl-β-D-glucose confirming the $^4C_1$ β-pyranose form of this branched glucose derivative. Three resonances at lower field (6.03 ppm, 5.56 ppm, and 5.53 ppm) originate from the vinyl group linked to C-3 carbon. Corresponding carbon resonances of vinyl



6 **11** **7** **12**

Scheme 2. Stereospecific Mo(VI)-catalyzed isomerisation of 3-*C*-methyl-D-allose (**6**) and 3-*C*-vinyl-D-allose (**7**) to 3-*C*-methyl-D-glucose (**11**) and 3-*C*-vinyl-D-glucose (**12**) in microwave field.

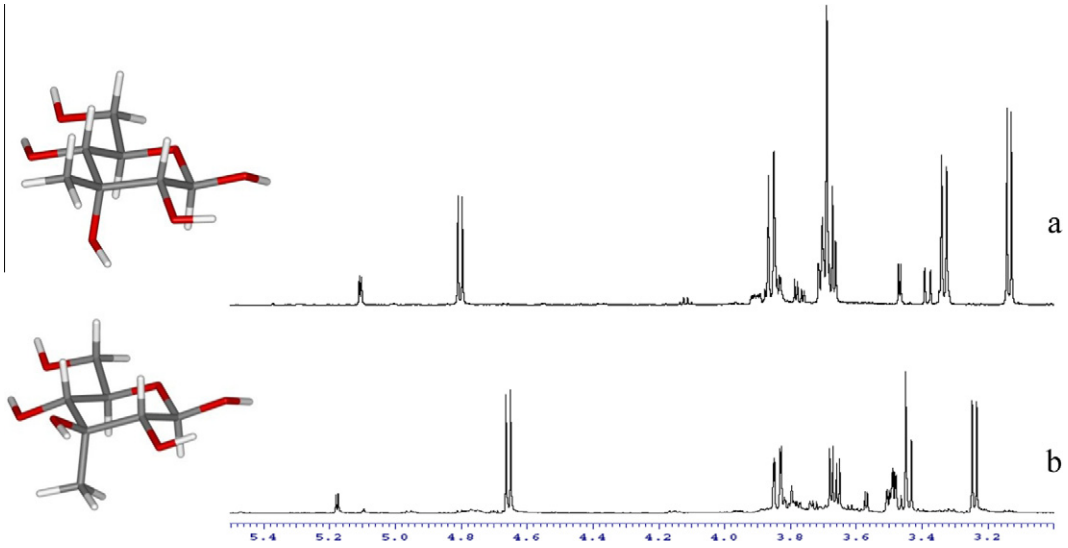


Figure 2. High-resolution 600 MHz ^{1}H NMR spectra of 3-*C*-methyl-D-allose (**a**) and 3-*C*-methyl-D-glucose (**b**) at 25 °C in D_2O. Insets show DFT-optimized structures of these branched aldoses.

group are at 131.82 (CH) and 120.80 ppm (CH_2). On the other hand, in the case of 3-*C*-phenyl-D-allose (**8**) any changes in the reaction mixture were observed even after prolonged reaction time. Similarly, there were no changes detected in the composition of the reaction mixture for 3-*C*-nitromethyl-D-glucose (**9**) and 3-*C*-cyano-D-glucose (**10**). Thus, bulkier substituents at the branching position prevent isomerisation at C-3 carbon.

The isomerization reaction progressed smoothly in microwave field and reached its thermodynamic equilibrium within 5 min, compared to conventional conditions, where these reactions took several hours to complete (Table 1). Transformation afforded desired 3-*C*-methyl-D-glucose and 3-*C*-vinyl-D-glucose 120–144-times faster than using conventional approach (90 °C, oil-bath). The reaction yields are markedly improved (~100%) as well. The best conversion was found with 3-*C*-methyl-D-allose (**6**) that isomerize to 3-*C*-methyl-D-glucose (**11**) (19%) using microwave irradiation. Similarly, 3-*C*-vinyl-D-allose (**7**) provided product 3-*C*-vinyl-D-glucose (**12**) in 14% yield. The yields of 3-*C*-methyl-D-glucose and 3-*C*-vinyl-D-glucose were markedly lower (9% and 8%) using conventional conditions. Furthermore, the analysis of ^{1}H NMR spectra indicated also formations of undesirable side products in the reaction mixture after long heating. These results suggest that molybdate ions can form catalytically active complexes with 3-C-branched chain aldoses thus promoting the isomerization process. Mo(VI) acts as a unique catalyst for isomerization of carbohydrate skeleton and study of this rearrangement provides a new route to the rare 3-C-branched chain aldoses. Alkyl groups such as methyl, vinyl might have less steric demands on the reaction transition state that leads to the desired isomeric molecule. Derivatives, 3-*C*-phenyl-D-allose, 3-*C*-nitromethyl-D-glucose, and 3-*C*-cyano-D-glucose were not suitable ligands for such transformation. Bulky substituents most likely prevent formations of active dimolybdate species. Consequently, isomeric aldoses were not formed.

As we explored the scope of this reaction, some limitations have been uncovered. Analysis of Bílik reaction showed that C-2 epimers are formed due to C1–O1 and C2–C3 bonds cleavage with

subsequent formations of C2–O1 and C1–C3 bonds via putative binuclear tetradendate Mo(VI)-aldose complex.[21] Present data indicate that a specific active molybdate complex is formed producing isomeric 3-*C*-methyl-branched aldose. This complex must be different to that one described for C-2 epimerization (Fig. 1). However, the structure of this complex and mechanism of this new type of isomerisation reaction is not clear. At present we can just consider that the presence of bulky substituent at $C_{(3)}$ carbon prevents formation of binuclear tetradendate complex due to steric effects. In this case, steric effects drive Mo(VI) ions to adopt a different complex structure contributing to rearrangement of chemical bonds linking $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ carbons. The analysis of structure of such complex will be subject of our further studies. The structure of the ligand thus seems to be a key issue for the catalytic process: Aldoses epimerize at C-2 carbon producing *epi*aldoses (Fig. 3a). Aldoses with substituents at $C_{(2)}$ carbon isomerize under the formation of 2-ketoses (Fig. 3b). 3-C-branched aldoses with sterically accessible substituents (methyl, vinyl) isomerize at C-3 carbon (Fig. 3c), whereas bulky substituents (phenyl or nitromethyl group) linked to $C_{(3)}$ carbon completely prevent any isomerization. They possibly inhibit formation of active complexes or block the isomerisation reaction by creating stable or nonreactive molybdate complexes.

These results also point out the important role of $C_{(3)}$ substitution in the pyranose ring, directing the new rearrangement pathway. The transformation probably occurs via intramolecular mechanism. This new type of isomerisation yielded only moderate yields at present and further refinement is in progress using different experimental conditions (pH, temperature, ligand/catalyst ratio). Study of mechanism of this transformation with ^{13}C-labeled compounds is currently under investigation and the results will be discussed in further publications.

3. Conclusion

We have demonstrated that isomeric products of 3-*C*-methyl- and 3-*C*-vinyl-branched chain aldoses can be prepared via *C*-3 isomerization utilizing the synergic effect of Mo(VI) ions and microwave field. Examples of chemical transformations producing reasonable yields are illustrated on the preparation of new 3-*C*-methyl-D-glucose and 3-*C*-vinyl-D-glucose from 3-*C*-methyl-D-allose and 3-*C*-vinyl-D-allose. The reaction is straightforward and leads to rare saccharides in a single step, but is limited to smaller substituents in the branch. This approach provides excellent alternative to conventional multistep methods in chemical synthesis of rare carbohydrates and acquired knowledge in this area may provide insight into the development of other stereoselective transformations used in the synthesis of natural products.

4. Experimental

4.1. General methods

Conversions and the purities of the products were determined by NMR spectroscopy. High-resolution NMR spectra were recorded

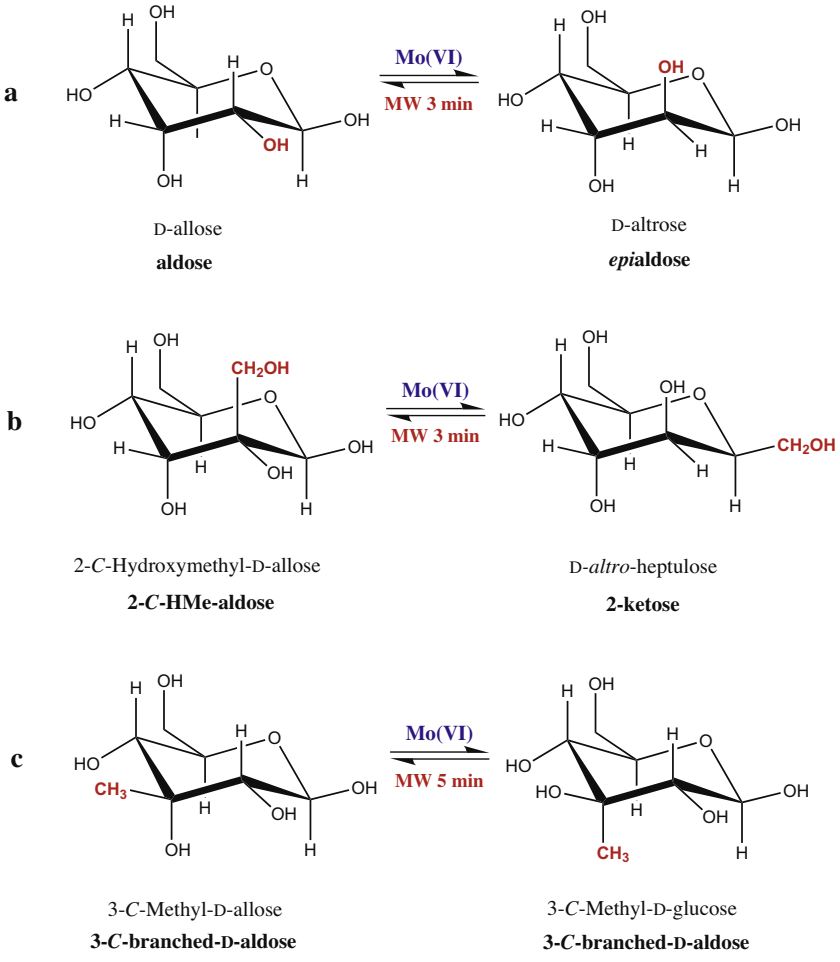


Figure 3. Isomerizations of aldoses and branched chain aldoses at $C_{(2)}$ and $C_{(3)}$ carbons catalyzed by Mo(VI). Aldoses epimerize at $C_{(2)}$ carbon producing corresponding epimer (a). 2-C-Hydroxymethyl-aldoses with substituted at $C_{(2)}$ carbon isomerize to 2-ketoses[14] (b). 3-C-branched aldoses with sterically accessible substituents (methyl, vinyl) isomerize at $C_{(3)}$ carbon producing isomeric 3-C-branched aldoses (c).

in a 5 mm cryoprobe at 25 °C in D_2O, acetone-d_6 or $CDCl_3$. The proton and carbon chemical shifts were referenced to external TSP. One-dimensional 600 MHz ^1H and 150 MHz ^{13}C NMR spectra as well as two-dimensional COSY, HSQC, and HMBC were used to determine ^1H and ^{13}C chemical shifts. Chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hertz. The geometry of compounds has been optimized with the GAUSSIAN09 program[22] using density functional theory (DFT) with the hybrid B3LYP functional and the 6-31+G* basis set. Solvent effect was evaluated using the IEFPCM approach.[23] NMR proton–proton spin–spin coupling constants were computed with the B3LYP functional. Microwave reactions were performed in a multimode microwave reactor CEM Discover consisting of a continuous focused microwave power delivery system with operator-selectable power from 0 to 300 W; microwave frequency source of 2.45 GHz. The reactions were performed in sealed glass tubes and were stirred magnetically. FT-IR spectra were measured on spectrometer Nicolet 6700 with DTGS detector and OMNIC 8.0 software using 128 scans at the resolution of 4 cm^{-1} with diamond ATR technique. MS were measured on ITQ 900 Thermo Fisher (EI, 70 eV). Optical rotations were determined at 20 °C with an automatic polarimeter Perkin–Elmer Model 141 using a 10 cm, 1-ml cell.

The progress of reactions was checked by thin layer chromatography (TLC) on Merck silica gel 60 glass plates. Detection was effected by spraying the chromatograms with 10% ethanolic sulfuric acid and heating them to 100 °C. Flash column chromatography was performed with silica gel (40–100 μm, Merck). Solvent A (ethyl acetate/hexane/acetone, 6:1:2, v/v/v); solvent B (ethyl acetate/chloroform, 1:1 v/v); solvent C (diethyl ether/hexane, 1:1, v/v); solvent D (ethyl acetate/benzene, 1:1, v/v). Separations of the free sugars were accomplished by column chromatography on Dowex 50 W X8 resin (Sigma–Aldrich) in the Ba^{2+} form (200–400 mesh). Paper chromatography was performed by the descending method on the Whatman No. 1 paper using ethyl acetate/pyridine/water (8:2:1) as the mobile phase. The chromatograms were made visible by means of alkaline silver nitrate. All chemicals were reagent grade and used without further purification. All concentrations were carried out under reduced pressure at a bath temperature not exceeding 50 °C.

4.2. 1,2: 5,6-Di-*O*-isopropylidene-3-*C*-methyl-D-*allo*-furanose (1)

To the mixture of 1,2: 5,6-di-*O*-isopropylidene-D-ribohex-3-ulose (1 g; 3.6 mmol) in dry diethyl ether (10 mL) cooled to 0 °C was added dropwise with stirring 3 M solution of methylmagnesium iodide in diethyl ether (4 mL; 12 mmol) and stirring continued (0 °C→rt) 30 min. Reaction mixture was refluxed for 4 h until the disappearance of starting material on TLC (solvent A). The complex was decomposed with water. After addition of saturated aq solution NH_4Cl (10 mL) the reaction mixture was extracted with $CHCl_3$ (3 × 25 mL). The combined organic layers were dried overnight ($MgSO_4$) and concentrated in vacuo. TLC of the reaction mixture indicated one major product which was purified by silica gel flash column chromatography (solvent A) to afford the compound **1** (832 mg; 84%) isolated as syrup. Yield (84%); R_f = 0.81 (solvent A); $[\alpha]_D^{20}$ +23.0 (c = 1, $CHCl_3$); ν_{max} (ATR, diamond): 3477 cm^{-1} (OH), ν_s 2981 (CH_3), ν_{as} 2885 (CH_3), δ 1458 (CH_3), δ 1373 (CH_3); MS (EI, 70 eV); m/z: 274 [M^+], 259 [M^+-CH_3], calcd for $C_{13}H_{22}O_6$ 274.3102; ^1H NMR (599.84 MHz, acetone-d_6): 5.73 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.15 (d, 1H, H-2), 4.12 (m, 1H, H-5), 4.00 (dd, 1H, $J_{5,6}$ = 6.1 Hz, $J_{6,6'}$ = 8.0 Hz, H-6), 3.88 (d, 1H, $J_{4,5}$ = 6.1 Hz, H-4), 3.83 (dd, 1H, $J_{5,6'}$ = 6.2 Hz, H-6′), 1.49 (s, 3H, CH_3 (Ip)), 1.34 (s, 3H, CH_3 (Ip)), 1.30 (s, 3H, CH_3 (Ip)), 1.29 (s, 3H, CH_3 (Ip)), 1.13 (s, 3H, CH_3 (C-3)). ^{13}C NMR (150.84 MHz, acetone-d_6): 114.50 (1,2; 5,6 CMe_2) 106.25 (C-1), 87.52 (C-2), 84.16 (C-4), 79.57 (C-3), 76.57 (C-5), 68.92 (C-6), 28.83, 28.71, 28.57, 27.42 (4 × CH_3 Ip), 21.70 (CH_3 (C-3)).

4.3. 1,2: 5,6-Di-*O*-isopropylidene-3-*C*-vinyl-D-*allo*-furanose (2)

To the cold 0 °C solution of 1,2: 5,6-di-*O*-isopropylidene-D-ribohex-3-ulose (1 g; 3.6 mmol) in dry THF (20 mL) was added dropwise with stirring a solution of 0.7 M vinylmagnesium bromide in THF (16.7 mL; 11.7 mmol). Stirring continued at room temperature for 30 min. The yellow reaction mixture was heated at 60 °C for 3 h. The mixture was cooled and complex was decomposed with water. After addition of saturated aq. solution NH_4Cl the reaction mixture was extracted with $CHCl_3$ (5 × 25 mL). The combined organic layers were dried overnight ($MgSO_4$). A syrupy derivative was purified by flash column chromatography on silica gel (solvent B). TLC indicated one major product **2** isolated as syrup. Yield 839 mg (81%); R_f = 0.88 (solvent B); $[\alpha]_D^{20}$ +32.0 (c = 1, $CHCl_3$); ν_{max} (ATR, diamond): 3101 cm^{-1} (=CH), 1638 cm^{-1} (C=C); MS (EI, 70 eV); m/z: 287 [M^++H], calcd for $C_{14}H_{22}O_6$ 286.3209; ^1H NMR (599.84 MHz, acetone-d_6): 5.83 (d, 1H, $J_{1',2'a}$ = 10.9 Hz, H-1′ vinyl), 5.78 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.57 (dd, 1H, $J_{2'a,2'b}$ = 1.3 Hz, H-2′a vinyl), 5.37 (dd, 1H, $J_{1',2'b}$ = 17.3 Hz, H-2′b vinyl), 4.27 (d, 1H, H-2), 4.10 (m, 1H, H-5), 4.03 (dd, 1H, $J_{5,6}$ = 6.2 Hz, $J_{6,6'}$ = 8.5 Hz, H-6), 3.92 (d, 1H, $J_{4,5}$ = 7.3 Hz, H-4), 3.92 (dd, 1H, $J_{5,6'}$ = 5.6 Hz, H-6′), 1.62 (s, 3H, CH_3 (Ip)), 1.44 (s, 3H, CH_3 (Ip)), 1.35 (s, 3H, CH_3 (Ip)), 1.32 (s, 3H, CH_3 (Ip)). ^{13}C NMR (150.84 MHz, acetone-d_6): 134.82 (–CH Vi), 116.82 (–CH_2 Vi), 113.13 (1,2 CMe_2), 109.41 (5,6 CMe_2), 103.81 (C-1), 83.68 (C-2), 81.41 (C-4), 80.33 (C-3), 73.83 (C-5), 67.08 (C-6), 26.71, 26.67, 26.44, 25.27 (4 × CH_3 Ip).

4.4. 1,2: 5,6-Di-*O*-isopropylidene-3-*C*-phenyl-D-*allo*-furanose (3)

To the cold 0 °C solution of 1,2: 5,6-di-*O*-isopropylidene-D-ribohex-3-ulose (300 mg; 1.1 mmol) in dry diethyl ether (6 mL) was added dropwise with stirring a solution of 2.8 M phenylmagnesium bromide in diethyl ether (1.3 mL; 3.6 mmol). Stirring continued at room temperature for 20 min. The yellow reaction mixture was refluxed for 2 h. The mixture was cooled and complex was decomposed with water. After addition of saturated aq solution NH_4Cl (5 mL) the reaction mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried overnight ($MgSO_4$) and syrupy derivative was purified by flash column chromatography on silica gel (solvent C). TLC indicated one major product **3** isolated as syrup. Yield 317 mg (87%); R_f = 0.60 (solvent C); $[\alpha]_D^{20}$ +42.0 (c = 1, $CHCl_3$); ν_{max} (ATR, diamond): 3091, 3061, 3037 cm^{-1} $(CH)_{Ar}$, 1603, 1583 cm^{-1} $(C–C)_{Ar}$; MS (EI, 70 eV); m/z: 337 [M^++H], 77 [$C_6H_5^+$], calcd. for $C_{18}H_{24}O_6$ 336.3796; ^1H NMR (599.84 MHz, $CDCl_3$): 7.37-6.82 (m, 5H, Ph (C-3)), 6.09 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.49 (d, 1H, H-2), 4.15 (d, 1H, $J_{4,5}$ = 5.3 Hz, H-4), 3.80 (m, 1H, H-5), 3.55 (dd, $J_{5,6}$ = 6.6 Hz, $J_{6,6'}$ = 8.6 Hz, H-6), 3.13 (dd, 1H, $J_{5,6'}$ = 6.7 Hz, H-6′), 1.67 (s, 3H, CH_3 (Ip)), 1.41 (s, 3H, CH_3 (Ip)), 1.38 (s, 3H, CH_3 (Ip)), 1.20 (s, 3H, CH_3 (Ip)). ^{13}C NMR (150.84 MHz, $CDCl_3$): 112.90 (1,2 CMe_2), 108.66 (5,6 CMe_2), 104.86 (C-1), 84.40 (C-2), 83.23 (C-4), 80.38 (C-3), 73.63 (C-5), 65.20 (C-6), 26.55, 26.55, 26.52, 25.36 (4 × CH_3 Ip).

4.5. 1,2: 5,6-Di-*O*-isopropylidene-3-*C*-nitromethyl-D-*gluco*-furanose[18] (4)

Yield 260 mg (75%); R_f = 0.86 (solvent B); $[\alpha]_D^{20}$ +32.0 (c = 1, $CHCl_3$); ν_{max} (ATR, diamond): 3454 cm^{-1} (OH), ν_{as} 1566 cm^{-1} (NO_2); ν_s 1377 cm^{-1} (NO_2); in accordance with lit.[18] MS (EI, 70 eV); m/z: 320 [M^++H] calcd for $C_{13}H_{21}O_8N$ 319.3077. Following NMR data are given for the sake of completeness: ^1H NMR (599.84 MHz, $CDCl_3$): 5.92 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.92 (d, 1H,

$J_{CH2a,\ CH2b}$ = 13.4 Hz, CH_{2a} (NMe)), 4.73 (d, 1H, CH_{2b} (NMe)), 4.59 (d, 1H, H-2), 4.38 (m, 1H, $J_{4,5}$ = 8.8 Hz, $J_{5,6}$ = 2.9 Hz, $J_{5,6'}$ = 7.7 Hz H-5), 4.15 (dd, $J_{6,6'}$ = 8.7 Hz, H-6), 3.99 (dd, 1H, H-6′), 3.68 (d, 1H, H-4), 1.52 (s, 3H, CH_3 (Ip)), 1.43 (s, 3H, CH_3 (Ip)), 1.35 (s, 3H, CH_3 (Ip)), 1.31 (s, 3H, CH_3 (Ip)).^{13}C NMR (150.84 MHz, $CDCl_3$): 113.07 (1,2 CMe_2), 109.84 (5,6 CMe_2), 104.86 (C-1), 85.36 (C-2), 81.33 (C-4), 79.67 (C-3), 71.76 (C-5), 67.31 (C-6), 26.93, 26.83, 26.28, 24.95 (4 × CH_3 Ip).

4.6. 3-*C*-Cyano-1,2: 5,6-Di-*O*-isopropylidene-D-*gluco*-furanose[19] (5)

Yield 421 mg (41%); R_f = 0.79 (solvent D); $[\alpha]_D^{20}$ +42.0 → +47.0 (*c* = 1, acetone);[19] Following analytical data are given for the sake of completeness: ν_{max} (ATR, diamond): 3365 cm^{-1} (OH), 1375 cm^{-1} (CN); MS (EI, 70 eV); *m*/*z*: 286 [M$^+$+H] calcd for $C_{13}H_{19}O_6N$ 285.2931; ^{1}H NMR (599.84 MHz, $CDCl_3$): 5.97 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.69 (d, 1H, H-2), 4.34 (m, 1H, $J_{4,5}$ = 7.6 Hz, $J_{5,6}$ = 4.3 Hz, $J_{5,6'}$ = 6.3 Hz, H-5), 4.15 (d, 1H, H-4), 4.09 (dd, $J_{6,6'}$ = 8.8 Hz, H-6), 3.95 (dd, 1H, H-6′), 1.51 (s, 3H, CH_3 (Ip)), 1.41 (s, 3H, CH_3 (Ip)), 1.33 (s, 3H, CH_3 (Ip)), 1.30 (s, 3H, CH_3 (Ip)). ^{13}C NMR (150.84 MHz, $CDCl_3$): 112.92 (1,2 CMe_2), 109.32 (5,6 CMe_2), 105.11 (C-1), 85.85 (C-2), 82.75 (C-4), 74.22 (C-3), 71.91 (C-5), 66.34 (C-6), 26.29, 26.12, 25.77, 24.62 (4xCH_3 Ip).

4.7. Typical procedure for acid hydrolysis

A mixture of isopropylidene derivative of 3-C-branched chain aldose in water and Dowex 50 W X4 resin in the H$^+$ form was stirred at 75 °C for 7 h. The resin was filtered off, the filtrate was purified with charcoal, and evaporated to afford syrupy derivative.

4.8. 3-*C*-Methyl-β-D-*allo*-pyranose (6)

Yield 96%; $[\alpha]_D^{20}$ +9.6 → +11.0 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3299 cm^{-1} (OH), ν_s 2976 (CH_3), ν_{as} 2887 (CH_3), δ 1454 (CH_3), δ 1373 (CH_3); MS (EI, 70 eV); *m*/*z*: 195 [M$^+$+H], calcd for $C_7H_{14}O_6$ 194.1825; ^{1}H NMR (599.84 MHz, D_2O): 4.79 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 3.86 (m, 1H, H-6), 3.70 (m, 1H, H-5), 3.67 (m, 1H, H-6′), 3.33 (d, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 3.13 (d, 1H, H-2), 1.31 (s, 3H, CH_3 (C-3)). ^{13}C NMR (150.84 MHz, D_2O): 93.98 (C-1), 74.75 (C-2), 74.49 (C-5), 73.83 (C-3), 70.16 (C-4), 61.44 (C-6), 20.99 (CH_3 (C-3)).

4.9. 3-*C*-Vinyl-β-D-*allo*-pyranose (7)

Yield 93%; $[\alpha]_D^{20}$ +4.0 → +4.5 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3315 cm^{-1} (OH), 2996 (=CH), 1641 cm^{-1} (C=C); MS (EI, 70 eV); *m*/*z*: 207 [M$^+$+H], calcd. for $C_8H_{14}O_6$ 206.1932; ^{1}H NMR (599.84 MHz, D_2O): 5.84 (dd, 1H, $J_{1',2'a}$ = 11.0 Hz, $J_{1',2'b}$ = 17.4 Hz, H-1′ vinyl), 5.42 (dd, 1H, $J_{2'a,2'b}$ = ∼0.4 Hz, H-2′a vinyl), 5.39 (dd, 1H, H-2′b vinyl), 4.89 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 3.86 (dd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 3.79 (m, 1H, H-5), 3.69 (dd, 1H, $J_{5,6'}$ = 5.8 Hz, H-6′), 3.52 (d, 1H, $J_{4,5}$ = 8.0 Hz, H-4), 3.30 (d, 1H, H-2). ^{13}C NMR (150.84 MHz, D_2O): 138.66 (–CH Vi), 117.39 (–CH_2 Vi), 93.92 (C-1), 77.30 (C-3), 74.37 (C-2), 73.28 (C-5), 68.92 (C-4), 61.38 (C-6).

4.10. 3-*C*-Phenyl-β-D-allose (8)

Yield 92%; $[\alpha]_D^{20}$ +12.0 → +8.0 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3293 cm^{-1} (OH), 3064, 3029, 2935 cm^{-1} $(CH)_{Ar}$, 1601, 1547 cm^{-1} $(C–C)_{Ar}$; MS (EI, 70 eV); *m*/*z*: 257 [M$^+$+H], 77 [$C_6H_5^+$], calcd for $C_{12}H_{16}O_6$ 256.2518; ^{1}H NMR (599.84 MHz, D_2O): 7.55–7.36 (m, 5H, Ph (C-3)), 5.04 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 3.94 (m, 1H, H-5), 3.89 (m, 1H, H-6), 3.88 (m, 1H, H-4), 3.73 (m, 1H, H-6′), 3.66 (d, 1H, H-2). ^{13}C NMR (150.84 MHz, D_2O): 128.56, 127.67, 125.86, 120.99 (C_6H_5 (C-3)), 94.37 (C-1), 78.59 (C-3), 75.32 (C-2), 74.85 (C-5), 71.07 (C-4), 61.43 (C-6).

4.11. 3-*C*-Nitromethyl-D-glucose (9)

Yield 95%; $[\alpha]_D^{20}$ +26.0 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3336 cm^{-1} (OH); ν_{as} 1549 cm^{-1} (NO_2); ν_s 1379 cm^{-1} (NO_2); MS (EI, 70 eV); *m*/*z*: 241 [M$^+$+H], calcd for $C_7H_{13}O_8N$ 240; ^{13}C NMR (150.84 MHz, D_2O): 102.43 (C-1β*f*), 96.82 (C-1α*f*), 93.77 (C-1β*p*), 91.27 (C-1α*p*), 81.02 (C-4β*f*), 81.02 (C-3α*f*), 80.27 (C-3β*f*), 79.82 (C-2β*f*), 78.77 (C-4α*f*), 76.86 (CH_2β*f*), 76.86 (CH_2α*f*), 76.64 (C-3β*p*), 76.18 (C-2β*p*), 76.02 (CH_2α*p*), 75.80 (C-3α*p*), 75.64 (CH_2β*p*), 75.47 (C-2α*f*), 74.27 (C-5β*p*), 72.74 (C-4α*p*), 71.86 (C-4β*p*), 71.43 (C-2α*p*), 71.04 (C-5α*p*), 69.46 (C-5β*f*), 68.70 (C-5α*f*), 63.56 (C-6β*f*), 63.56 (C-6α*f*), 61.04 (C-6β*p*), 60.67 (C-6α*p*).

4.12. 3-*C*-Cyano-D-*gluco*-pyranose (10)

Yield 93%; $[\alpha]_D^{20}$ +20.0 → +15.0 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3288 cm^{-1} (OH),1485 (CN); MS (EI, 70 eV); *m*/*z*: 206 [M$^+$+H], calcd for $C_7H_{11}O_6N$ 205.1653; ^{1}H NMR (599.84 MHz, D_2O): 5.23 (d, 1H, H-1α), 4.79 (d, 1H, H-1β), 3.90 (m, 1H, H-5α), 3.87 (dd, 1H, H-6β), 3.81 dd, 1H, H-6α), 3.79 (dd, 1H, H-6′α), 3.72 (m, 1H, H-6′β), 3.77 (m, 1H, H-2α), 3.72 (m, 1H, H-5β), 3.71 (m, 1H, H-4β), 3.71 (m, 1H, H-4α), 3.41 (d, 1H, H-2β). ^{13}C NMR (150.84 MHz, D_2O): 117.24 (s, CN (C-3)), 94.81 (C-1β), 91.41 (C-1α), 77.95 (C-3β), 75.32 (C-3α), 74.94 (C-5β), 74.32 (C-2β), 72.13 (C-2α), 70.30 (C-4α), 70.29 (C-4β), 69.76 (C-5α), 60.34 (C-6β), 60.16 (C-6α).

4.13. Typical procedure for Mo(VI) catalyzed isomerization of the 3-C-branched chain aldoses

4.13.1. In microwave field

To the mixture of branched-chain aldose **6–10** dissolved in water molybdic acid was added (molar ratio 1:10). The reaction mixture was exposed to microwave irradiation (300 W) for different lengths of time. Samples (0.5 mL) were taken at selected intervals (1, 2, 3, 4, 5, 10 min), treated with Amberlite IRA-400 in the HCO_3^- form (3 mL) to remove the catalyst. The composition of the reaction mixture was determined by ^{1}H NMR spectroscopy. The rest of the reaction mixture was also treated batch-wise with an excess of the ion-exchange resin, filtered off, washed with water, and combined filtrates were evaporated. Fractionization of the syrupy residue by column chromatography on Dowex 50 W X8 in the Ba^{2+} form, eluted with water at a flow rate 5 mL/h, afforded two isomeric 3-C-branched derivatives that were fully characterized.

4.13.2. Conventional conditions

To the aqueous solution of 3-C-branched chain aldose **6–10** molybdic acid was added (molar ratio 1:10). Reaction mixture was heated in oil-bath at 90 °C for 10–15 h. The composition of the reaction mixture was examined by ^{1}H NMR spectroscopy until the equilibrium mixture was reached. The reaction mixture was stirred with Amberlite IRA-400 in the HCO_3^- form (15 mL). The filtrates were concentrated to syrup that was fractionated by column chromatography.

4.14. 3-*C*-Methyl-β-D-*gluco*-pyranose (11)

Yield 19%; $[\alpha]_D^{20}$ +8.6 → +7.1 (*c* = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3315 cm^{-1} (OH), ν_s 2982 (CH_3), ν_{as} 2866 (CH_3), δ 1454 (CH_3), δ 1371 (CH_3); MS (EI, 70 eV); *m*/*z*: 195 [M$^+$+H], calcd for $C_7H_{14}O_6$ 194.1825; ^{1}H NMR (599.84 MHz, D_2O): 4.66 (d, 1H,

$J_{1,2}$ = 8.2 Hz, H-1), 3.84 (dd, 1H, $J_{5,6}$ = 2.2 Hz, $J_{6,6'}$ = 12.3 Hz, H-6), 3.67 (dd, 1H, $J_{5,6'}$ = 5.6 Hz, H-6′), 3.49 (ddd, 1H, $J_{4,5}$ = 10.2 Hz, H-5), 3.44 (d, 1H, H-4), 3.24 (d, 1H, H-2), 1.16 (s, 3H, CH_3 (C-3)). ^{13}C NMR (150.84 MHz, D_2O): 94.59 (C-1), 76.52 (C-2), 75.47 (C-3), 74.87 (C-5), 72.02 (C-4), 61.27 (C-6), 12.74 (CH_3 (C-3)).

4.15. 3-*C*-Vinyl-β-D-*gluco*-pyranose (12)

Yield 14%; $[\alpha]_D^{20}$ +8.0 (c = 1, H_2O) (24 h); ν_{max} (ATR, diamond): 3323 cm^{-1} (OH), 2991 (=CH), 1620 cm^{-1} (C=C); MS (EI, 70 eV); m/z: 207 [M^++H], calcd. for $C_8H_{14}O_6$ 206.1932; ^{1}H NMR (599.84 MHz, D_2O): 6.03 (dd, 1H, $J_{1',2'a}$ = 11.0 Hz, $J_{1',2'b}$ = 17.0 Hz, H-1′ vinyl), 5.56 (d, 1H, H-2′a vinyl), 5.53 (d, 1H, H-2′b vinyl), 4.80 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 3.85 (dd, 1H, $J_{5,6}$ = 1.0 Hz, $J_{6,6'}$ = 11.2 Hz, H-6), 3.69 (dd, 1H, $J_{5,6'}$ = 5.7 Hz, H-6′), 3.63 (m, 1H, H-5), 3.52 (d, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.33 (d, 1H, H-2). ^{13}C NMR (150.84 MHz, D_2O): 131.82 (-*C*H Vi), 120.80 (-*C*H_2 Vi), 94.41 (C-1), 78.40 (C-3), 76.50 (C-2), 74.78 (C-5), 71.96 (C-4), 61.13 (C-6).

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