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Accepted Article

Title: Towards Improved Biorefinery Technologies: 5-Methylfurfural as a Versatile C6-Platform for Biofuels Development

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201802126

Link to VoR: http://dx.doi.org/10.1002/cssc.201802126



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Towards Improved Biorefinery Technologies: 5-Methylfurfural as a Versatile C₆-Platform for Biofuels Development

Konstantin I. Galkin and Valentine P. Ananikov*

Abstract: Low chemical stability and high oxygen content limits utilization of bio-based platform chemical 5-(hydroxymethyl)furfural (HMF) in biofuels development. In this work, Lewis-acid-catalyzed conversion of renewable 6-deoxy sugars leading to formation of more stable 5-methylfurfural (MF) is carried out with high selectivity. Besides its higher stability, MF is a deoxygenated analogue of HMF with increased C:O ratio. A highly selective synthesis of the innovative liquid biofuel 2,5-dimethylfuran starting from MF under mild conditions is described. Superior synthetic utility of MF against HMF in benzoin and aldol condensation reactions leading to long-chain alkane precursors is demonstrated.

Integration of renewable resources into sustainable energy cycle is one of the key challenges of modern chemical science and technology.^[1] Conversion of lignocellulosic biomass to liquid biofuels, fully compatible with petroleum-based fuels, provides great opportunities to replace the fossil-derived energy with the carbon neutral energy concept.[2] Direct utilization of plant biomass as a source of alternative energy is inefficient due to the high oxygen content and the low energy density of carbohydrates.^[3] A possible approach to increase the energy characteristics is to carry out catalytic dehydration of carbohydrates into platform chemical 5-(hydroxymethyl)furfural (HMF), possessing many applications as a biofuel precursor.^[4] Direct utilization of HMF as a biofuel is limited by its high boiling point, high oxygen content, relative chemical instability and insolubility in hydrocarbons.^[5] To access more suitable liquid further biofuels. deoxygenation by direct catalytic hydrodeoxygenation or other chemical modifications of HMF are required. However, these approaches have a number of disadvantages associated with difficult hydrogenation of hydroxyl groups in HMF (and related biofuel precursors) resulting in harsh reaction conditions and low selectivity of reduction.^[6] In addition, chemical instability and high polarity of HMF complicates its efficient preparation from renewable feedstocks.^[5a-c, 7] In this regards, development of reliable renewable chemical platforms for biofuels production is of paramount importance.

In the present work, we demonstrate that deoxygenated analogue of HMF, 5-methylfurfural (MF), is a promising platform for biofuels development (Scheme 1). MF is an industrially available product that can be considered as a perspective biofuel candidate due to its reduced oxygen content, chemical stability, high energy density, low volatility and solubility in hydrocarbons (Scheme 1).^[8] The existing methods of MF

[*] Dr. K. I. Galkin, Prof. Dr. V. P. Ananikov Zelinsky Institute of Organic Chemistry Russian Academy of Sciences Leninsky Prospekt, 47, Moscow, 119991 (Russia) E-mail: val@ioc.ac.ru synthesis from carbohydrates are associated with modification of platform chemicals furfural and HMF using step-by-step or onepot procedures.^[8] Direct synthesis of MF involving formation of HMF from various hexoses followed by iodination and hydrogenation processes was recently described,^[8d] but direct conversion of carbohydrates without formation of unstable HMF as intermediate would be a more advantageous approach. In this work, Lewis-acid-catalyzed dehydration of renewable 6-deoxy hexoses into MF is implemented with high selectivity, and the advantages of MF utilization against HMF for development of liquid biofuels are illustrated.



- x insoluble in hydrocarbon fuel components
- difficult deoxygenation
- x poor selectivity towards formation of
- biofuel precursors

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Scheme 1. Direct Lewis-acid-catalyzed conversion of 6-deoxy carbohydrates into MF and the advantages of its utilization, in comparison to HMF, for biofuels development are described in this work.

Synthesis of MF from renewable feedstocks. We started our investigations with MF synthesis by using the catalytic dehydration of commercially available L-rhamnose (6-deoxy-Lmannopyranose), which is abundant in plants and produced on industrial scales.^[9] Dehydration of carbohydrates into furanic products is a well-studied process mediated mainly by BrØnsted or Lewis acids.^[2d, 4b, 10] Catalytic systems based on BrØnsted acids are poorly adaptable to conversion of hexoses due to side processes involving oligomerization and decomposition,^[5c, 11] whereas Lewis acids show superior efficiency for dehydration of aldohexoses.^[2d, 4b, 12] We conducted conversion of L-rhamnose using various Lewis acid catalysts in a biphasic system 1-butyl-3-methylimidazolium chloride/methyl isobutyl ketone ([BMIM]CI/MIBK) according to the general methods of highyielding dehydration of aldohexoses (Table 1).^[12b, 13] Catalysis by Lewis acids demonstrated full conversion of the initial 6-deoxy carbohydrate, and the maximal yield of MF was obtained by using chromium chlorides (Table 1, Entries 1-8). The influence of reaction conditions such as reaction temperature, type of catalyst and reaction time was also investigated (see the Table 1, Entries 1-13 and the Supporting Information for details). Under the optimized reaction conditions, (Table 1, Entry 8) formation of

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MF was conducted with a good yield of 61%. Isolation of MF was performed by extraction from ionic liquid with MIBK during the reaction, followed by distillation leading to the desired product as a colorless oil of more than 99% purity. Only traces of MF were detected after the conversion process with BrØnsted acids as catalysts (Table 1, Entries 11-13). Conversion of other commercially available 6-deoxy sugars L-fucose (6-deoxy Lgalactose) and D-quinovose (6-deoxy D-glucose) was also studied. Under the same reaction conditions as had been used for L-rhamnose dehydration, MF was obtained with 12% and 60% yields from L-fucose and D-quinovose, respectively (Table 1, Entries 14, 15). The absence of the reactive hydroxymethyl group in C(6) position in the starting materials (6-deoxy carbohydrates) provided the higher selectivity of conversion as compared to D-glucose dehydration into HMF proceeded with only 48% yield at the same reaction conditions (Table 1, Entry 16). A significant decrease in the selectivity of L-fucose conversion is consistent with a cyclic reaction pathway (see Scheme S1 for the reaction mechanism in Supplementary Information).

Table 1. Catalytic conversion of 6-deoxy hexoses ^[a].



[a] Reaction conditions: 6-deoxy carbohydrate, catalyst (0.1 eq), [BMIM]CI/MIBK, 2h; [b] yield of HMF.

Comparison of chemical properties of MF and HMF. Generally, direct conversion of carbohydrates provides a pathway to rough HMF as an oil (usually of 80-90% purity, unless the high cost purification is performed). In our previous work it has been found that oily HMF undergoes rapid decomposition in the presence of acidic impurities (traces of acidi catalysts), and these processes complicate many applications of HMF in organic synthesis.^[5c] We compared stabilities of synthesized MF and oily HMF, both obtained by the CrCl₂ catalyzed dehydration of L-rhamnose and D-glucose, respectively, in [BMIM]CI medium. The samples of ~99% purity were stored at room temperature for 1 week, and their composition was monitored by NMR. After 7 days of storage, the color of the HMF sample changed from light yellow to dark brown (Figure 1a) and approximately 20 % of by-products insoluble in chloroform were formed. In contrast, the sample of MF maintained its light yellow color without significant changes in purity and solubility in *n*-hexane (Figure 1b).



Figure 1. a) Samples of pure MF and HMF (0 day) and after 7 days of storage; b) ¹H NMR spectra of aged HMF (top spectrum, no signals, insoluble) and aged MF (bottom spectrum, signals clearly visible, soluble); samples in *n*-hexane for solubility assessment.

Selective reduction of C6-furfurals, mostly HMF, is a general approach used for the synthesis of the innovative liquid biofuel 2,5-dimethylfuran (DMF) with combustion properties and physical characteristics comparable to gasoline.[14] Formation of DMF by hydrodeoxygenation of HMF usually proceeds via MF or methylfurfuryl alcohol (MFA) as intermediates.^[6b, 15] For this reason, milder and more selective formation of DMF was observed when MF or MFA instead of HMF were used as starting substrates.^[6a-c, 16] However, direct hydrodeoxygenation of hydroxymethyl or carbonyl moieties in furan-containing precursors is generally difficult and low selective, and occurs at high temperatures of around 100-250 °C.^[6, 15-17] To facilitate the suitability of this process, a substitution of oxygen-containing functional groups at the furan ring with more flexible substituents was performed, followed by a reduction stage. $^{\left[15e,\ 18\right]}$ We evaluated the convenient methodology of DMF synthesis by focusing on the mildest reaction conditions using the transfer hydrogenation of 5-methylfurfuryl acetate (MFAc) (Scheme 2).



Scheme 2. Selective synthesis of DMF from MF under mild conditions using the Ni-mediated transfer hydrogenation. Reaction conditions: (i) NaBH₄, MeOH, 0 °C; (ii) Ac₂O, Et₃N, DMAP; (iii) NiCl₂, NaBH₄, MeOH, 0 °C. For comparison, the transformation of HMF is also shown (for the reaction conditions see Supporting Information).

MFAc was synthesized using a two-stage methodology involving only renewable carbon sources: MF was treated with sodium borohydride to obtain MFA, followed by acetylation process (Scheme 2 and Supporting Information for details). Deoxygenation of MFAc was carried out using nickel boride^[19] prepared *in situ* from NiCl₂ and sodium borohydride in methanol. Reduction process was conducted at 0 °C for 3 hours and proceeded with 99 % conversion and 95 % yield of DMF (91 % overall yield starting from MF). Under the same reaction conditions, only 86 % conversion and 67 % yield of DMF was detected after deoxygenation of 2,5-bis(acetoxymethyl)furan (BAcMF) obtained from HMF^[20] (Scheme 2). It is important to point out, that the studied MF to DMF transformation is based on renewable, easy separable or recyclable reagents.

Comparative study of suitability of MF and HMF for the preparation of diverse long-chain alkane precursors. Condensation of HMF and its derivatives with highly accessible carbonyl compounds followed by complete hydrodeoxygenation is a promising route to alkanes with high carbon chain lengths, highly suitable as a drop-in diesel and jet biofuels.^[4e, 21] We compared the synthetic potential of MF and HMF in the benzoin and aldol condensation reactions with ketones for the preparation of long-chain (C₉-C₁₈) alkane precursors. Benzoin condensation of MF and HMF with formation of *n*-dodecane precursors **1** and **2**, respectively, was conducted by the organocatalytic approach^[7c, 22] using common imidazolium salt [BMIM]Cl in presence of DBU (Table 2, Entry 1).

Table 2. Comparison of synthetic potentials of MF and HMF in ${\sf benzoin}^{[a]}$ and ${\sf aldol}^{[b]}$ condensation reactions.

Entry	Product	Initial ketone	Product, yield (%) from MF (R=CH ₃)	Product, yield (%) from HMF (R=CH ₂ OH)
1			1,60	2 , 19
2	R-CJ-C-R	acetone	3 , 87	4 , 42
3	R-OR	butanone	5 , 81	6 , 83
4	R-CJ-CJ-R	cyclo- pentanone	7 , 97/96 ^[c]	8 , 91/44 ^[c]
5	R-COTTO-R	cyclo- hexanone	9 , 94	10 , 89
6	R C	acetone	11 , 91	12 , 89



[a] Reaction conditions: furanic substrate, [BMIM]CI, DBU (0.1 eq), 80 °C, 2 h; [b] Reaction conditions: NaOH, MeOH or MeOH/H₂O 1:1, RT, 12 h; [c] Substrate aged for 7 days was used

Under the similar reaction conditions, the yield of the furoin **1** obtained by self-condensation of MF was significantly higher than the yield of product **2** obtained from HMF (60 % and 19 %, respectively). In addition, isolation of the highly hydrophilic compound **1** by extraction from water was unsuccessful, and the resulting product was purified by column chromatography of the crude reaction mixture. In contrast, the more hydrophobic compound **2** was easily separated from the reaction mixture by extraction with ethyl acetate followed by flash chromatography on silica gel (see Supporting Information for details).

Evaluation of synthetic potential of MF and HMF in the base-catalyzed aldol condensation leading to a number of known and new compounds 3-22 was conducted using highly accessible bio-derived acyclic and cyclic ketones under green conditions (Table 2).^[3, 23] Product **4** obtained by di-aldol condensation of HMF with acetone was isolated in a low yield (42%) due to its decomposition in solution during the reaction and isolation processes. In contrast, the deoxygenated derivative 3 was stable and obtained with a high selectivity (Table 2, Entry 2). Products 5-10 of di-aldol condensation of furfurals with butanone and cyclic ketones (Table 2, Entries 3-5), as well as mono-aldol adducts 11-18 (Table 2, Entries 6-9) were obtained in similar yields from both MF and HMF. In contrast, the mono-aldol condensation with cyclopentanone and mesityl oxide leading to products 19-22 showed much higher selectivity when using MF as a starting substrate (Table 2, Entries 9, 11).

Synthetic utility of aged MF and HMF for the synthesis of alkane precursors formed from cyclopentanone and MIBK was also studied. Approximately a two-fold decrease in yield and complications of the isolation process were observed for adducts **8** and **16** obtained from HMF, while utilization of aged MF did not lead to any significant decrease in the selectivity of condensation process (Table 2, Entries 4, 7). Therefore, MF will be much more tolerant to conventional logistics of transportation to fuel-producing plants, while transportation of HMF would require special considerations to avoid further obstacles (reputification, drop in yield, etc.).

In conclusion, a selective model synthesis of the promising biofuel candidate MF directly from renewable feedstocks by the Lewis-acid-catalyzed dehydration of 6-deoxy carbohydrates was carried out. Under the optimized reaction conditions, MF was obtained in good yields by using an easily accessible catalytic system. The advantageous higher stability of MF allows its integration into a biofuel production cycle after synthesis/storage

without extensive purification. A new approach was evaluated to achieve highly selective synthesis of the important liquid biofuel candidate DMF starting from MF under rather mild conditions using a transfer hydrogenation process and avoiding expensive catalysts. Comparison of synthetic utility of MF and HMF in benzoin and aldol condensation reactions yielding long-chain alkane precursors showed higher efficiency in the case of MF. To summarize, the lower oxygen content, better stability and excellent synthetic utility reflect the highly promising potential of MF as a bio-derived platform for biofuels development.

Acknowledgements

This study was supported by the Russian Science Foundation (Grant RSF 17-13-01176).

Keywords: plant biomass · deoxy carbohydrates · biofuels · 5-(hydroxymethyl)furfural • 5-methylfurfural • alkanes • 2,5dimethylfuran

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Development of renewable sources for biofuels production is a critical task for carbon neutral economy. Comparison of the synthetic utility of bio-based platform chemical HMF and deoxygenated analogue MF (obtained by Lewis-acid-catalyzed dehydration of renewable 6-deoxy hexoses) showed much higher utility of MF in biofuels development.



more stable, increased C/O ratio, higher selectivity towards synthesis of biofuels

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