DE GRUYTER Pure Appl. Chem. 2019; 91(7): 1149–1158

Conference paper

Lianjie Wang, Jia-Neng Tan, Mohammed Ahmar and Yves Queneau*

Solvent issues in the Baylis-Hillman reaction of 5-hydroxymethyl furfural (HMF) and 5-glucosyloxymethyl furfural (GMF). Towards no-solvent conditions

https://doi.org/10.1515/pac-2019-0215

Abstract: The possibility to apply solventless conditions for the Baylis-Hillman reaction of 5-hydroxymethyl furfural (HMF) and its glucosylated analog, glucosyloxymethyl furfural (GMF) has been investigated. This study shows that highly functionalized adducts can be obtained in fair to good yields, under the conditions combining the renewability of the substrates, the straightforwardness of the strategy, and the lowered cost and toxicity of the solvent conditions. The issue of the polarity of the furanic substrate is addressed by comparing HMF with furfural and GMF.

Keywords: carbohydrate; GMF; HMF; ICS-29; Morita-Baylis-Hillman reaction; no-solvent.

Introduction

Bio-based chemistry has evolved as a major field of research, which encompasses all sub-disciplines of chemistry and chemical engineering and offers extraordinary opportunities for innovation in all sectors of chemistry. Carbohydrate resources account for the major part of renewable feedstocks. Most of them are cheap and easily available using effective methods involving chemical, physical, and biological technologies. Significant efforts devoted to their use as renewable raw materials have resulted in the design of many examples of functional carbohydrate-based small molecules or macromolecules in the past decades, covering bulk, commodity and specialty chemicals, including surfactants and polymers [1–11].

Once limited to native sugars, this strategy now extends more and more to some of their immediate derivatives, so-called platform molecules. Many of such molecules have been listed as promising chemicals for the future [12–14]. Among them, furfural or HMF are furanic systems resulting from the direct dehydration of carbohydrates. The processes for their preparation and manufacture on a larger scale improve continuously [15–26]. Being available, these biobased furanic systems are relevant starting chemicals for the design of more elaborated functional molecules, benefiting notably from the versatility of the aldehyde function chemistry [15, 16, 27–32].

Article note: A collection of invited papers based on presentations at the 29th International Carbohydrate Symposium (ICS-29), held in the University of Lisbon, Portugal, 14–19 July 2018.

***Corresponding author: Yves Queneau,** Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Univ Lyon, CNRS, Université Lyon 1, INSA Lyon, CPE Lyon, ICBMS, UMR 5246, Université Claude Bernard, Bâtiment Lederer, 1 Rue Victor Grignard, 69622 Villeurbanne Cedex, France, e-mail: yves.queneau@insa-lyon.fr
Lianjie Wang and Mohammed Ahmar: Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Univ Lyon, CNRS, Université Lyon 1, INSA Lyon, CPE Lyon, ICBMS, UMR 5246, Université Claude Bernard, Bâtiment Lederer, 1 Rue Victor Grignard, 69622 Villeurbanne Cedex, France
Jia-Neng Tan: Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Univ Lyon, CNRS, Université Lyon 1, INSA Lyon, CPE Lyon, ICBMS, UMR 5246, Université Claude Bernard, Bâtiment Lederer, 1 Rue Victor Grignard, 69622 Villeurbanne Cedex, France; and Tobacco Research Institute of the Chinese Academy of Agricultural Sciences, Qingdao 266101, P.R. China

We have been interested for years in the use of carbohydrates as organic raw materials, focusing notably on the two disaccharides sucrose and isomaltulose [33–39]. More recently we also extended the scope of our work on biobased chemistry to the chemistry of HMF, in particular with respect to its use towards fine chemicals, outside its classical fields of applications. Up to now, most of HMF chemistry is focused on a short selection of intermediates like furan dicarboxylic acid, dimethyl furan, 2,5-diaminofuran, 2,5-dimethyltetrahydrofuran, which are the most promising ones economically speaking, being directly applicable in solvent and polymer industry. For extending this use to more complex targets with applications in fine chemistry, we have investigated several reactions such as the Morita-Baylis-Hillman (MBH) reaction, its *aza*-version, the Biginelli reaction, the Kabachnik-Fields reaction, leading to α-hydroxyacrylates, α-aminoacrylates, dihydropyrimidinones and α-aminophosphonates, respectively (Fig. 1) [40–43]. These reactions were chosen because they combine the advantages of leading to novel functional derivatives and elaborated structural architectures while exhibiting favorable atom economy.

With respect to the Morita-Baylis-Hillman reaction, we have earlier investigated its application to HMF and its corresponding glucosylated analog GMF (Fig. 1), available in one step from the commercial disaccharide isomaltulose. GMF, containing the furan, glucose and aldehydic entities, is able to undergo a remarkably wide range of transformations [44–49]. Strangely, applications of HMF and GMF in the Morita–Baylis–Hillman reaction were only scarcely investigated, though this route can afford interesting hydroxyacrylates with additional hydroxylated appendages. This innovative design combining polymerizable functions and possible multiple presence of hydroxyl groups might find possible uses as monomers or surfactants. This is why we revisited this topic, notably by investigating the issue of the medium in which the reaction is conducted [40, 50].

The MBH reaction is an efficient addition reaction between an aldehyde (or other types of electrophilic functions) and an activated olefin or other Michael acceptors, forming a C–C bond. It proceeds in the presence of a nucleophilic promoter such as a tertiary amine (so called Baylis-Hillman reaction) or a tertiary phosphine (referred to as the Morita reaction, actually the first one to be reported) [51–56]. The MBH reaction is an atom-economical access towards elaborated new systems, overall being a simple addition reaction. Its mechanism has been deeply investigated and one commonly accepted mechanism (Fig. 2) includes: (1) Michael type nucleophilic addition of the promoter onto the activated alkene, leading to an intermediate enolate; (2) Nucleophilic attack of this enolate on the electrophile (here the aldehyde), the C–C bond forming step, producing an alcoholate; (3) Proton migration resulting in an hydroxy-enolate intermediate (actually a rate-determining step); (4) Elimination of the tertiary amine leading to the MBH adduct. Kinetic and modeling studies have shown that the intermediate alcoholate could react with a second molecule of aldehyde leading to a hemiacetalate which facilitates the rate-determining proton transfer step [57–59].

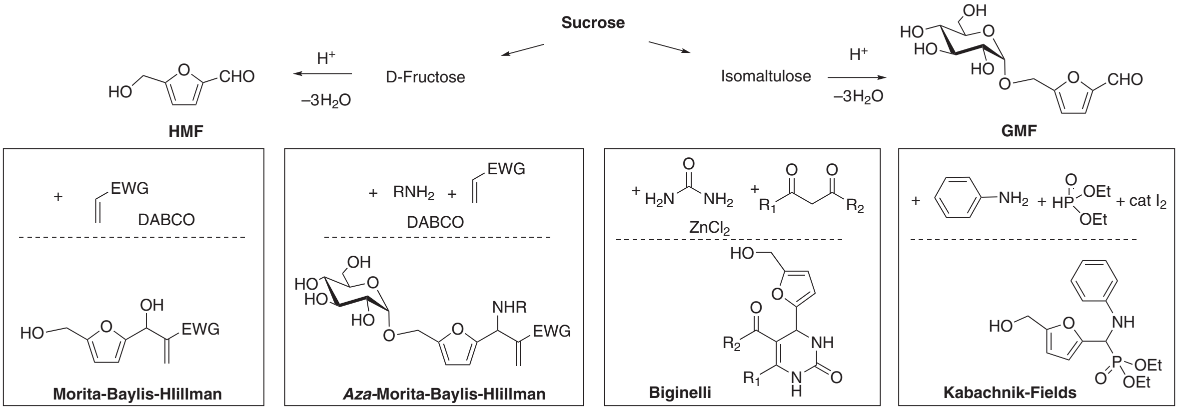

Fig. 1: Recent uses of HMF and GMF by our group.

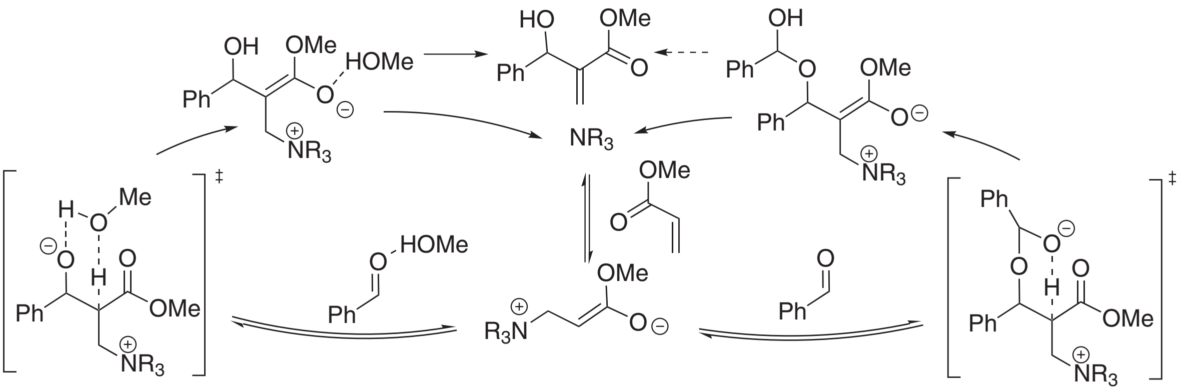

Fig. 2: MBH commonly accepted mechanism.

The nucleophilic promoter is often referred to as a “catalyst” because it is not consumed in the overall process and because its presence is indispensable, involved covalently in the intermediate Michael adduct. However, the amount of nucleophilic promoter is rarely less than 20 mol.% quantities, and often larger quantities of nucleophile are used to overcome the renowned slowness of the MBH reaction. In some specific solvents, nearly stoichiometric quantities are necessary for observing practical rates and yields [50]. A proton donor solvent like water and MeOH plays an important role in the reaction process, as it is able to intervene as a relay in the rate-determining proton transfer step [60]. Under aqueous conditions, the intermediate Michael addition adduct formed between DABCO and methyl acrylate can be hydrolyzed to a betaine resulting in a waste of both the promoter and the activated alkene, explaining why higher amounts of promoter and of activated alkene are generally required. However, aqueous or hydroalcoholic media are preferable in terms of cost and toxicity as compared to the often used THF or dioxane. This is why an earlier stage of this study [40, 50] focused on the use of either pure water or mixed aqueous-organic systems, including biobased solvents, showing, as summarized in Table 1, their ability to promote the reaction of HMF or GMF. The presence of water in mixed aqueous-bio-based organic solvents systems was favorable for HMF and furfural, whereas GMF, did not need the assistance of water, having his numerous OH within its structure for serving as relay in the reaction rate-determining step.

After our work on aqueous and biobased solvents [40, 50], we have explored the possibility to go further towards cheaper and cleaner processes by simply using solventless conditions for MBH reactions using HMF and GMF. Indeed, no-solvent is even more appropriate with respect to economic and green chemistry issues [61–64]. The purpose of this article is to see how far no-solvent conditions can be applied to the specific case of HMF and GMF and the results are reported herein. In the study were notably investigated the influence of

Table 1: Reported solvent systems for the DABCO promoted MBH reaction of HMF and GMF [40, 50, 57].[a,b]

Entry	Aldehyde	Acrylate/equiv.	Solvent	Time/h	MBH product yield (%)
1	HMF	Ethyl acrylate/2	H_2O	24	33
2	HMF	Ethyl acrylate/2	$EtOH/H_2O$	24	75
3	HMF	Ethyl acrylate/2	$THFA/H_2O$	24	72
4	HMF	Methyl acrylate/3	$Dioxane/H_2O$	36	62
5	HMF	Methyl acrylate/3	DMI/H_2O	36	63
6	GMF	Ethyl acrylate/2	H_2O	24	35
7	GMF	Ethyl acrylate/2	EtOH	24	65
8	GMF	Ethyl acrylate/2	$EtOH/H_2O$	24	50
9	GMF	Ethyl acrylate/2	$THFA/H_2O$	24	60
10	GMF	Methyl acrylate/3	$Dioxane/H_2O$	36	35
11	GMF	Methyl acrylate/3	DMI/H_2O	36	56

[a]Binary solvent ratio: 1:1 (v/v). [b]THFA, Tetrahydrofurfuryl alcohol; DMI, isosorbide dimethyl ether.

(1) the nature of the base, (2) quantity of base, (3) the stoichiometry between aldehyde and Michael acceptor, (4) the reaction time. This allowed defining a preferred set of conditions which were then applied to furfural and GMF, as well as other Michael acceptors, for comparison.

Results and discussion

The model reaction used in this study is the reaction of HMF with methyl acrylate in presence of DABCO. The formation of the desired MBH adduct (methyl 3-[2-(5-hydroxymethylfuryl)]-3-hydroxy-2-methylenepropionate **1**, Fig. 3) was fully assessed after isolation and comparison with an authentic sample. The product shows the typical pattern for the CHOH group at δ 5.50 ppm in ^{1}H NMR, combined with the δ 65.9 ppm corresponding carbon signal on HSQC spectrum, characteristic of the newly formed C–C bond. Isolated yields were measured, and in some cases, the conversion was determined after recovery of unreacted HMF.

We first focused on the nucleophilic promoter, by screening a range of typical BH promoters classically reported in literature (Table 2). The conditions chosen for this screening were 1:1 molar ratio of HMF and methyl acrylate, 0.7 equivalent of catalyst at room temperature. What was found is that DABCO appeared to be the best promoter, leading to total consumption of HMF after 7 h and a 69 % yield of the desired adduct. TMEDA and urotropine gave also good yields, but the reactions were much slower, 56 % yield after 30 days and 50 % yield after 5 days, respectively. For these examples, as the reaction was very clean (only HMF or BH product in the crude mixture), HMF conversion was easily measured, showing a 79 % conversion using TMEDA, and 70 % conversion using urotropine. Other classical BH catalysts like DBU, DMAP and TMG gave no BH reaction products in reasonable time, and the reaction was not clean enough for measuring HMF conversion, principally because of the formation of the other possible Michael addition product **2** (Fig. 3) arising from the addition of the HMF hydroxy group onto methyl acrylate (Fig. 3). Imidazole led to a complex mixture

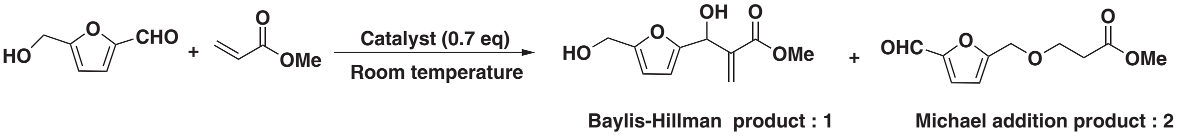

Fig. 3: MBH and Michael addition products from HMF and methyl acrylate.

Table 2: Catalyst screening for the MBH reaction of HMF with methyl acrylate.[a,b,c]

Entry	Catalyst	1	2
1	DABCO	69 %	–
2	DMAP	–	23 %
3	Imidazole	Complex mixture	
4	TMG	–	16 %
5	TMEDA	56 %	–
6	DBU	–	14 %
7	PPh_3	–	6 %
8	PPh_2Me	Complex mixture	
9	PCy_3	–	10 %
10	3-Quinuclidinol	41 %	–
11	Quinuclidine	Trace	–
12	Urotropine	50 %	–

[a] Reaction conditions: all reactions were conducted using 1 mmol HMF, 1 mmol methyl acrylate, 0.7 mmol of catalyst, magnetic stirring at room temperature, no solvent. [b] TMEDA, Tetramethylethylenediamine; TMG, 1,1,3,3-tetramethylguanidine. [c] Isolated yields.

of products. Quinuclidine led to only trace amounts of BH adduct, however triethylamine, *N*-methyl morpholine, 3-quinuclidinone, L-proline, also reported BH propoters, were unsuccessful. Triphenylphosphine and tricyclohexylphosphine led only to the Michael product with low conversion, whereas messy mixtures resulted from the use of PPh_2Me and no reaction using PBU_3.

Based on this preliminary promoter screening, DABCO was selected and kept throughout the study. We then studied the influence of its quantity on the reaction outcome. HMF (1 mmol), methyl acrylate (1 mmol) and DABCO (from 0.1 equivalent to 1.4 equivalent) were stirred at room temperature for 7 h. The MBH adducts were isolated in each set of conditions and the yields were measured. As depicted in the graph shown in Fig. 4, a consistent yield increase with increasing DABCO amount from 0.1 to 0.8 equiv. was observed, in particular up to 0.5 equiv. Adding more than 0.8 equiv. did not improve the yield which reached a plateau. Over 1.2 equivalent of DABCO, an heterogeneous mixture with remaining solid DABCO was formed. Based on this set of experiments, a 0.8 equiv. amount DABCO was selected and used in the next steps of the study.

We then turned to the influence of stoichiometry between HMF and methyl acrylate. For this aim, the amount of methyl acrylate was increased from 1.0 to 3.0 equivalents, keeping the reaction time constant as 7 h. The results are shown in Fig. 5. A consistent increase in the reaction yield with excess acrylate is obvious up to 2.0 equivalents. Further excess of methyl acrylate did not prove useful. By checking the remaining quantity of unreacted HMF, the influence of the acrylate excess appears as a rate issue. So, the preferable quantity

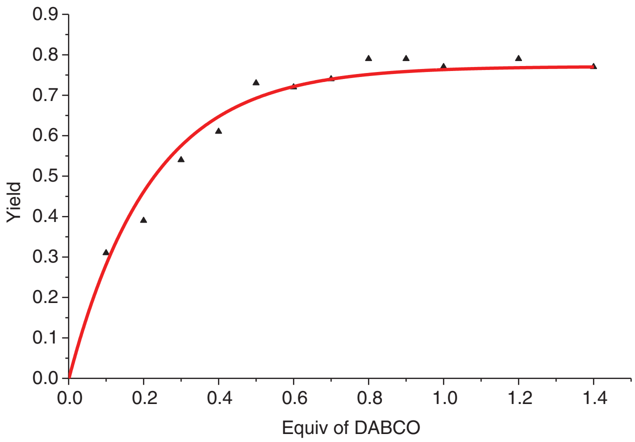

Fig. 4: Influence of the quantity of DABCO on the MBH reaction of HMF (1 equiv. of methyl acrylate, r.t., 7 h) to adduct **1**.

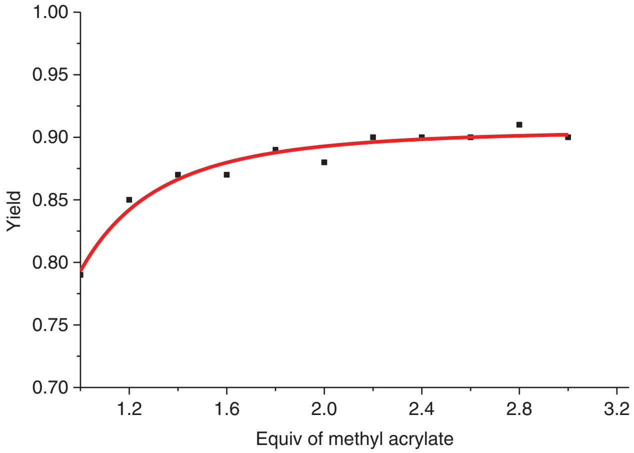

Fig. 5: Influence of the HMF vs. methyl acrylate stoichiometry on MBH reaction (0.8 equiv. DABCO, r.t., 7 h) to adduct **1**.

of acrylate should be chosen between 1.0 equiv. to 2.0 equiv, depending on a preference for a slightly better yield and faster reaction, or a better balance in terms of consumption of starting materials in keeping with green chemistry principles. Therefore, three values, namely 1.0, 1.5 and 2.0 equiv. of acrylate, were used in the next part of the study.

A short kinetic investigation was conducted using either 1.0, 1.5 or 2.0 equiv. of methyl acrylate, a fixed quantity of DABCO (0.8 equiv.) at room temperature. The reaction was stopped after a given time (from 2 to 16 h) by introduction of the crude mixture on a silica gel column, allowing purification of the products and measurement of the isolated yields of MBH adduct **1** (Fig. 6). Using only 1.0 equiv. of acrylate, the no-solvent MBH reaction proceeded slowly but provided a quite satisfactory 80 % yield after 10 h. A faster reaction rate was observed using 1.5 equiv. of acrylate, with good yields obtained after only 4 h, and yield up to 90 % upon extending the reaction time to 10 h. Increasing further the amount of methyl acrylate led to a much faster reaction reaching rapidly high yields. However, extending the time led to a slight decrease of the yield, though it was not possible to detect specific by products.

Overall, considering the balance between rate, yields and starting material consumption, a reasonable set of conditions can be fixed as 0.8 equiv. of DABCO, 1.5 equiv. of acrylate, at room temperature and 8 h. The influence of the polarity of the starting aldehyde was then checked by comparing HMF to furfural and GMF, and this was done for methyl acrylate, ethyl acrylate and acrylonitrile as electron deficient alkenes (Fig. 7).

First, we could observe that ethyl acrylate and acrylonitrile also reacted well with HMF, leading to product **5** (88 %) and **8** (71 %), respectively. The simpler HMF analog furfural, which misses the CH_2OH moiety, produced the corresponding adducts **7** and **10** in high yields. However, using the polyhydroxylated GMF, much less miscible with acrylate in absence of any other solvent, only modest to fair yields were obtained. Acrylonitrile was comparatively a better activated alkene for the reaction, being at the same time more reactive, and contributing likely to a better overall homogeneity of the medium as compared to methyl acrylate. New derivatives **8** and **9** were prepared from HMF and GMF respectively. All resulting MBH adducts **3–10** were carefully checked with respect to their structure and purity (see SI). The already reported ones were compared to literature reports [40, 50, 65] and new products **8** and **9** arising from acrylonitrile were fully characterized. Since GMF is a chiral substrate, the GMF-based MBH products **3**, **6** and **9** are mixtures of two diastereoisomers at the newly created carbinol group, which are not separable. For the new product **9**, complete identification of all atoms was possible by analysis of 1D and 2D (COSY, HSQC and HMBC) NMR spectra (shown in SI). In the ^{13}C NMR spectrum, though most signals of both epimers are superimposed, three of them, namely C-2 and C-4 on the furan moiety at 154.4 and 111.6 ppm respectively, and the newly created carbinol at 68.7 ppm, exhibit a slight difference, allowing to consider a ratio close to 1:1 between the two diastereoisomers. The first stereogenic center being far away from the MBH reaction site, it has no effect on the selectivity of the reaction, consistently with previous observations on compounds **3** and **6**.

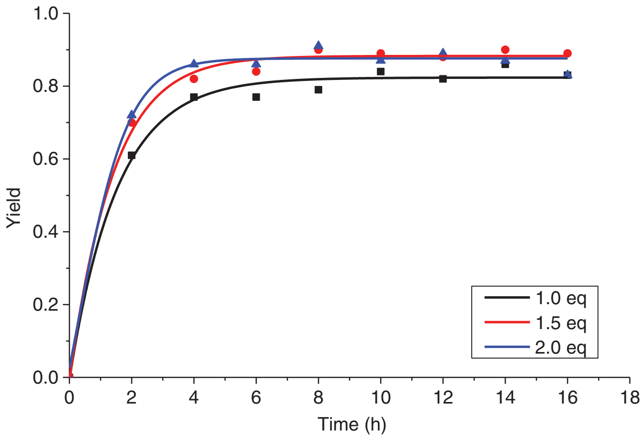

Fig. 6: Time course of the no-solvent MBH reaction (0.8 equiv. DABCO, r.t.) of HMF and methyl acrylate forming adduct **1**.

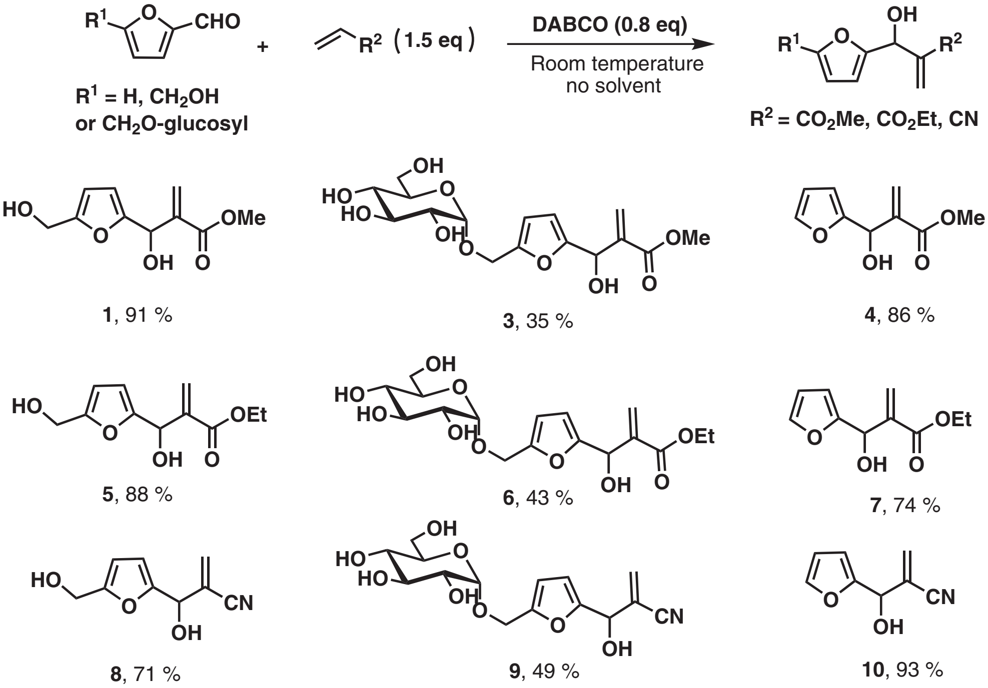

Fig. 7: Adducts from no-solvent MBH reactions using HMF, furfural and GMF.

Table 3: Influence of temperature on solvent-free MBH reaction between GMF and methyl acrylate.

Temperature	0 °C	r.t.	40 °C	60 °C	80 °C
Yield of **3**	16 %	35 %	27 %	11 %	–

Table 4: Influence of the amount of acrylate in the solvent-free MBH reaction with GMF.

Acrylate	1.5 eq	2.0 eq	3.0 eq	4.0 eq	6.0 eq	9.0 eq
Yield of **3**	35 %	34 %	44 %	43 %	38 %	34 %

Efforts for increasing the solubility of GMF in the mixture by heating, resulted in no improvement, actually leading to lower yields, consistently with the known unfavorable effect of increasing temperature on MBH reactions (Table 3). Degradations were also observed, likely due to extensive acrylate polymerization. Since the excess methyl acrylate is actually a kind of solvent for the reaction, it was finally checked whether in the case of the less soluble GMF, increasing the methyl acrylate quantity would be of any use, and a slight improvement was observed when 3 or 4 equivalents are used (Table 4). The results likely reflect the balance between dilution effects, solubility effects, and side polymerizations or co-polymerization.

Conclusion

A solvent-free protocol for MBH reactions of bio-based platform molecules HMF and GMF was investigated. The reactions between HMF and acrylates or acrylonitrile run cleanly at room temperature. A 91 % yield of the MBH reaction adduct between HMF and methyl acrylate was obtained, actually the best as compared to previous reports in literature. Despite having much lower solubility in acrylates, GMF, as a polyhydroxylated analog of HMF, can also provide acceptable yield in these conditions.

Experimental

General methods

Reagents were purchased at the highest quality from Aldrich, Alfa Aesar, or TCI and used without further purification, unless otherwise noted. GMF was obtained through the acidic dehydration of isomaltulose, which is reported by Lichtenthaler *et al.* [44]. Eluents for chromatography and solvents were purchased from Carlo Erba reagents in high purity. NMR spectra were recorded on a Bruker DRX-300 spectrometer (^{1}H: 300 or 400 MHz; ^{13}C: 75 or 100 MHz). TLC was carried out on aluminum-backed plates pre-coated 0.2 mm silica gel 60. Flash chromatographies were performed on Merck Si 60 silica gel (40–63 μm). Structures were checked by comparison with authentic samples [40, 50, 65], except for compound **8** and **9** which are novel derivatives, and for which full characterization is given below.

General procedure for MBH reaction

A mixture of HMF (1.0 mmol) and methyl acrylate (1.5 mmol) was stirred at room temperature in the presence of 0.8 equivalent DABCO without the protection of an inert atmosphere. A colorless liquid system was formed at the beginning, due to the low melting point of HMF, then the transparent liquid became viscus and turned brown. Furfural, being liquid at room temperature, gave directly fully homogeneous mixtures. GMF, being a solid, was preferably first dissolved in MeOH, then reduced to a syrup by removal of MeOH under vacuum for easier mixing with the acrylate. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel directly without further workup process, using dichloromethane and diethyl ether (DCM/ether = 5/1) as eluent for HMF MBH reaction adducts, DCM/ether = 20/1 for furfural MBH reaction adducts, and DCM/MeOH = 5/1 for GMF MBH reaction adducts.

Data for new compounds

2-(hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)acrylonitrile 8

Yield 71 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (d, $J = 3.2$ Hz, 1H, H_4), 6.24 (d, $J = 3.2$ Hz, 1H, H_3), 6.16 (d, $J = 1.6$ Hz, 1H, $C{=}C\underline{H}_2$, a), 6.10 (d, $J = 1.3$ Hz, 1H, $C{=}C\underline{H}_2$, b), 5.26 (s, 1H, C$\underline{H}$-OH), 4.50 (s, 2H, $C\underline{H}_2$-OH), 4.24 (br s, 1H, OH), 3.27 (br s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (C_2), 151.6 (C_5), 131.7 ($C{=}\underline{C}H_2$), 123.1 ($\underline{C}{=}CH_2$), 116.8 (CN), 109.4 (C_4), 108.9 (C_3), 67.5 ($\underline{C}$H-OH), 57.0 ($\underline{C}H_2$-OH). HRMS (ESI) m/z: Calcd for $[M+Na]^+$ $C_9H_9NaO_3$ 202.0475; Found 202.0471.

2-(hydroxy(5-(α-D-glucopyranosyloxymethyl)-furan-2-yl)methyl)acrylonitrile 9 (mixture of two diastereoisomers)

Numbering of glucose hydrogen and carbon atoms are shown with a prime (3′, 5′, …). Two diastereoisomers are noted “R&S”.

Yield 49 % ^{1}H NMR (400 MHz, CD_3OD) δ 6.43 (d, $J = 3.2$ Hz, 1H, H_4), 6.38 (d, $J = 3.2$ Hz, 1H, H_3), 6.20 (d, $J = 1.1$ Hz, 1H, $C{=}CH_2$, a), 6.15 (d, $J = 1.0$ Hz, 1H, $C{=}CH_2$, b), 5.31 (s, 1H, C$\underline{H}$-OH), 4.90 (d, $J = 3.7$ Hz, 1H, $H_{1'}$), 4.66 (d, $J = 13.0$ Hz, 1H, $CH_{2(C\text{-}6)}$, a), 4.55 (dd, $J = 13.0$, 1.3 Hz, 1H, $CH_{2(C\text{-}6)}$, b), 3.83–3.77 (m, 1H, $H_{6'a}$), 3.72–3.57 (m, 3H, $H_{3'}$, $H_{5'}$, $H_{6'b}$), 3.40 (dd, $J = 9.7$, 3.8 Hz, 1H, $H_{2'}$), 3.34–3.30 (m, 1H, $H_{4'}$).

^{13}C NMR (100 MHz, CD_3OD) δ 154.4 and 154.4 (C_2, R&S), 153.2(C_5), 132.0($\underline{C}{=}CH_2$), 125.7($C{=}\underline{C}H_2$), 118.0($\underline{C}$N), 111.6 and 111.6 (C_4, R&S), 109.7 and 109.7 (C_3, R&S), 99.2($C_{1'}$), 75.0($C_{5'}$), 73.8($C_{3'}$), 73.4($C_{2'}$), 71.7($C_{4'}$), 68.7 and 68.7($\underline{C}$H-OH, R&S), 62.6($C_{6'}$), 62.1 (C_6). HRMS (ESI) m/z: Calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO_8$ 364.1003; Found 364.0995.

Acknowledgements: The authors thank the Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation, Funder Id: http://dx.doi.org/10.13039/501100002717 (MESRI), the University of Lyon and CNRS, Funder Id: http://dx.doi.org/10.13039/501100004794 for financial support. They also gratefully acknowledge the support of the Chinese Scholarship Council, Funder Id: http://dx.doi.org/10.13039/501100004543 (UT-INSA-CSC call) by providing a fellowship to LW and JNT. The authors also thank Cargill Inc. for a gift of isomaltulose.

References

[1] R. A. Sheldon. *Green Chem.* **16**, 950 (2014).
[2] M. Besson, P. Gallezot, C. Pinel. *Chem. Rev.* **114**, 1827 (2014).
[3] P. Gallezot. *Chem. Soc. Rev.* **41**, 1538 (2012).
[4] A. J. J. Straathof. *Chem. Rev.* **114**, 1871 (2014).
[5] M. J. Climent, A. Corma, S. Iborra. *Green Chem.* **13**, 520 (2011).
[6] A. Corma, S. Iborra, A. Velty. *Chem. Rev.* **107**, 2411 (2007).
[7] *Carbohydrates in Sustainable Development I*, A. P. Rauter, P. Vogel, Y. Queneau (Eds), Springer Berlin Heidelberg, Berlin, Heidelberg (2010).
[8] *Carbohydrates in Sustainable Development II*, A. P. Rauter, P. Vogel, Y. Queneau (Eds), Springer Berlin Heidelberg, Berlin, Heidelberg (2010).
[9] N. Brun, P. Hesemann, D. Esposito. *Chem. Sci.* **8**, 4724 (2017).
[10] L. Wu, T. Moteki, Amit A. Gokhale, David W. Flaherty, F. D. Toste. *Chem* **1**, 32 (2016).
[11] L. Wang, Y. Queneau. "Carbohydrate-Based Amphiphiles: Resource for Bio-based Surfactants", in *Encyclopedia of Sustainability Science and Technology*, R. A. Meyers (Ed.), pp. 1, Springer New York, New York, NY (2018). Doi:10.1007/978-1-4939-2493-6_1009–1.
[12] T. Werpy, G. Petersen. National Renewable Energy Lab., Golden, CO (US) (2004).
[13] J. J. Bozell, G. R. Petersen. *Green Chem.* **12**, 539 (2010).
[14] L. T. Mika, E. Cséfalvay, Á. Németh. *Chem. Rev.* **118**, 505 (2018).
[15] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries. *Chem. Rev.* **113**, 1499 (2013).
[16] A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso. *Green Chem.* **13**, 754 (2011).
[17] M. E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik. *Chem. Rev.* **111**, 397 (2011).
[18] S. P. Teong, G. Yi, Y. Zhang. *Green Chem.* **16**, 2015 (2014).
[19] M. Dashtban, A. Gilbert, P. Fatehi. *RSC Adv.* **4**, 2037 (2013).
[20] F. Menegazzo, E. Ghedini, M. Signoretto. *Molecules* **23**, 2201 (2018).
[21] A. Sanborn, E. Hagberg, S. Howard, E. M. Rockafellon. Patent WO2014158554A1, Issued 2014-10-02 2014.
[22] B. Saha, M. M. Abu-Omar. *Green Chem.* **16**, 24 (2013).
[23] A. Chinnappan, C. Baskar, H. Kim. *RSC Adv.* **6**, 63991 (2016).
[24] S. Jiang, C. Verrier, M. Ahmar, J. Lai, C. Ma, E. Muller, Y. Queneau, M. Pera-Titus, F. Jerome, K. D. O. Vigier. *Green Chem.* **20**, 5104 (2018).
[25] K. Gupta, R. K. Rai, S. K. Singh. *ChemCatChem* **10**, 2326 (2018).
[26] R. F. A. Gomes, Y. N. Mitrev, S. P. Simeonov, C. A. M. Afonso. *ChemSusChem* **11**, 1612 (2018).
[27] F. A. Kucherov, L. V. Romashov, K. I. Galkin, V. P. Ananikov. *ACS Sustain. Chem. Eng.* **6**, 8064 (2018).
[28] S. Subbiah, S. P. Simeonov, J. M. S. S. Esperança, L. P. N. Rebelo, C. A. M. Afonso. *Green Chem.* **15**, 2849 (2013).
[29] L. Hu, L. Lin, Z. Wu, S. Zhou, S. Liu. *Renew. Sust. Energ. Rev.* **74**, 230 (2017).
[30] Z. Zhang, K. Deng. *ACS Catal.* **5**, 6529 (2015).
[31] M. Sajid, X. B. Zhao, D. H. Liu. *Green Chem.* **20**, 5427 (2018).
[32] D. Zhang, M.-J. Dumont. *J. Polym. Sci. Part A: Polym. Chem.* **55**, 1478 (2017).
[33] N. M. Xavier, A. P. Rauter, Y. Queneau. "Carbohydrate-Based Lactones: Synthesis and Applications", in *Carbohydrates in Sustainable Development II*, A. P. Rauter, P. Vogel, Y. Queneau (Eds.), p. 19, Springer Berlin Heidelberg, Berlin, Heidelberg (2010).
[34] J. Gagnaire, G. Toraman, G. Descotes, A. Bouchu, Y. Queneau. *Tetrahedron Lett.* **40**, 2757 (1999).
[35] S. Thévenet, A. Wernicke, S. Belniak, G. Descotes, A. Bouchu, Y. Queneau. *Carbohydr. Res.* **318**, 52 (1999).
[36] S. Trombotto, A. Bouchu, G. Descotes, Y. Queneau. *Tetrahedron Lett.* **41**, 8273 (2000).
[37] S. Trombotto, E. Violet-Courtens, L. Cottier, Y. Queneau. *Top. Catal.* **27**, 31 (2004).
[38] Y. Queneau, S. Chambert, C. Besset, R. Cheaib. *Carbohydr. Res.* **343**, 1999 (2008).
[39] Y. Queneau, S. Jarosz, B. Lewandowski, J. Fitremann. "Sucrose Chemistry and Applications of Sucrochemicals", in *Adv. Carbohydr. Chem. Biochem.* D. Horton (Ed.), p. 217, Academic Press, Amsterdam (2007).

[40] J.-N. Tan, M. Ahmar, Y. Queneau. *RSC Adv.* **5**, 69238 (2015).
[41] W. Fan, Y. Queneau, F. Popowycz. *Green Chem.* **20**, 485 (2018).
[42] W. Fan, Y. Queneau, F. Popowycz. *RSC Adv.* **8**, 31496 (2018).
[43] C. Verrier, S. Moebs-Sanchez, Y. Queneau, F. Popowycz. *Org. Biomol. Chem.* **16**, 676 (2018).
[44] F. W. Lichtenthaler, D. Martin, T. Weber, H. Schiweck. *Eur. J. Org. Chem.* **1993**, 967 (1993).
[45] C. Ruß, C. Luff, A. H. Begli, B. Koenig. *Synth. Commun.* **42**, 3112 (2012).
[46] A. Brust, F. W. Lichtenthaler. *Green Chem.* **15**, 1368 (2013).
[47] J.-N. Tan, M. Ahmar, Y. Queneau. *Pure Appl. Chem.* **87**, 827 (2015).
[48] J.-N. Tan, M. Ahmar, Y. Queneau. *Curr. Org. Chem.* **18**, 1768 (2014).
[49] J.-N. Tan, M. Ahmar, Y. Queneau. *Curr. Org. Synth.* **15**, 430 (2018).
[50] J.-N. Tan, M. Ahmar, Y. Queneau. *RSC Adv.* **3**, 17649 (2013).
[51] K.-i. Morita, Z. Suzuki, H. Hirose. *Bull. Chem. Soc. Jpn.* **41**, 2815 (1968).
[52] M. Hillman, A. Baylis. Patent US3743669A, Issued 1973-07-03 1973.
[53] V. Declerck, J. Martinez, F. Lamaty. *Chem. Rev.* **109**, 1 (2009).
[54] D. Basavaiah, A. J. Rao, T. Satyanarayana. *Chem. Rev.* **103**, 811 (2003).
[55] D. Basavaiah, B. S. Reddy, S. S. Badsara. *Chem. Rev.* **110**, 5447 (2010).
[56] Y. Wei, M. Shi. *Chem. Rev.* **113**, 6659 (2013).
[57] C. Yu, B. Liu, L. Hu. *J. Org. Chem.* **66**, 5413 (2001).
[58] V. K. Aggarwal, S. Y. Fulford, G. C. Lloyd-Jones. *Angew. Chem. Int. Ed.* **44**, 1706 (2005).
[59] K. E. Price, S. J. Broadwater, B. J. Walker, D. T. McQuade. *J. Org. Chem.* **70**, 3980 (2005).
[60] V. K. Aggarwal, D. K. Dean, A. Mereu, R. Williams. *J. Org. Chem.* **67**, 510 (2002).
[61] K. Tanaka, F. Toda. *Chem. Rev.* **100**, 1025 (2000).
[62] G. Nagendrappa. *Resonance* **7**, 59 (2002).
[63] G. Nagendrappa. *Resonance* **7**, 64 (2002).
[64] C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl, J. P. Hallett. *Chem. Rev.* **118**, 747 (2018).
[65] S. Chandrasekhar, C. Narsihmulu, B. Saritha, S. Shameem Sultana. *Tetrahedron Lett.* **45**, 5865 (2004).

Supplementary Material: The online version of this article offers supplementary material (https://doi.org/10.1515/pac-2019-0215).