

Correction

Correction: Gao, W., *et al.* Efficient One-Pot Synthesis of 5-Chloromethyl-furfural (CMF) from Carbohydrates in Mild Biphasic Systems. *Molecules* 2013, 18, 7675-7685

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We have recently been made aware by Prof. Mark Mascal (University of California Davis) and the *Molecules* Editorial Offices of some errors and omissions in the Introduction section of our recent paper. The third paragraph of said Introduction currently reads as follows:

“The conventional synthesis of CMF involves the treatment of HMF or cellulose with dry hydrogen halide. More specifically, the hydroxyl group in HMF undergoes a facile halogen substitution reaction. Examples in the literature include those of Sanda et al. who obtained CMF from the reaction of ethereal gaseous hydrogen chloride with HMF [13]. Furthermore, while the conversion of cellulose into CMF was low (12%) [14,15], a substantially higher yield (48%) was obtained for the preparation of BMF when dry HBr was employed [16]. Considering the importance of these compounds, Mascal et al. recently reported the synthesis of CMF from cellulose treated by HCl-LiCl and successive continuous extraction [2]. Unfortunately, 5-(chloromethyl)furfural, 2-(2-hydroxyacetyl)-furan, 5-(hydroxymethyl)furfural and levulinic acid were also produced with this system. More recently, Kumari et al. reported the preparation of BMF from cellulose by a modified procedure using HBr-LiBr involving continuous extraction [17].

Despite the numerous efforts aimed at these transformations, each of them suffers from at least one of the following limitations: diverse by-products in significant yields that reduce the selectivity of the reaction and its economics, low conversions and yields, harsh reaction conditions (dry hydrogen halide, relative high temperature), requirements for large amounts of costly reagents (LiCl, LiBr), prolonged reaction times and tedious operations with complex set ups (continuous extraction) [18]. These drawbacks seriously hamper their potential industrial applications. Consequently, as part of our program aimed at developing new biofuels and fine chemicals based on biomass, we embarked on research for the development of efficient and economical methods aimed at converting carbohydrates to CMF under mild reaction conditions”.

To set straight the scientific record we would like to make the following corrections:

- Concerning the sentences “Examples in the literature include those of Sanda *et al.* who obtained CMF from the reaction of ethereal gaseous hydrogen chloride with HMF [13]. Furthermore, while the conversion of cellulose into CMF was low (12%) [14,15], a substantially higher yield (48%) was obtained for the preparation of BMF when dry HBr was employed [16].” We must now state that our references 14 and 15 were incorrect or irrelevant in this context. Furthermore, the yield mentioned for our reference 16 should be 56%, and not 48%. We attribute this last error to the fact that we used a figure (wrongly) quoted for this method in a secondary source, our reference 17, rather than the correct value given in the primary reference. Consequently, these sentences should be changed to: “Examples in the literature include those of Sanda *et al.* who obtained CMF from the reaction of ethereal gaseous hydrogen chloride with HMF [13]. Additionally, Sanda *et al.* also developed a method of producing CMF by direct chlorination of HMF with Vilsmeier reagents [14]. Furthermore, while the conversion of cellulose into CMF was low (12%) [15], a substantially higher yield (56%) was obtained for the preparation of BMF when dry HBr was employed [16].” with a new reference 15 as shown below:

15. Fenton, H.J.H.; Gostling, M. LXXXV.—Derivatives of methylfurfural. *J. Chem. Soc. Trans.* **1901**, 79, 807–816.

- While we cited a paper by Mascal *et al.* (our reference 2) and discussed some of the perceived shortcomings of that method, unfortunately in our literature search in preparation for writing this paper we missed a follow-up paper by the same authors that needs to be cited now as new reference 18 (see below), wherein the authors addressed all the problems we had identified for their method. This is an omission for which we apologize.

18. Mascal, M.; Nikitin, E.B. Dramatic advancements in the saccharide to 5-(chloro-methyl)furfural conversion reaction. *ChemSusChem* **2009**, 2, 859–861.

- We cited our original reference 18 in describing operations with complex set-ups, specifically mentioning continuous extraction as an example. While reference 18 does describe the preparation of CMF, that method involves a continuous flow reactor, and not continuous extraction, which was used in our references 2 and 17. Consequently reference 18 needs to be changed to new reference 18 and be cited along with references 2 and 17.
- In the reference section of the original text, references numbered 21 to 33 need to be renumbered as 19 to 31 and reference numbers 19 and 20 become references 32 and 33. This occurred due to a last minute rearrangement of our experimental section due to journal requirements that actually missed our critical reading of the galley proofs.
- Footnote (a) to Table 6 should state 1.0 g not 1.0 mg.
- The revised References section based on all these corrections is now provided below.

Revised References Section

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- Finally, in summarizing we would like to offer the following rewrite of the Conclusions section of our paper:

In summary, this note describes an optimized biphasic system (HCl-H₃PO₄/CHCl₃) that may pave the way for the development of a mild, and cost-effective protocol for the conversion of various carbohydrates to CMF. The systematic optimization effort undertaken here delineates the structural features of carbohydrate residues that may eventually offer optimum CMF yields.

The authors would like to apologize to the readership of *Molecules* for these errors, and welcome this opportunity to correct the scientific record.

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