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Oxidation of diglycerol to diglycerose using hydrogen peroxide as a clean oxidant†

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The oxidation of diglycerol to diglycerose was developed using hydrogen peroxide as a clean oxidant and cerium bromide as a commercially available catalyst. Several parameters were investigated such as catalyst nature and loading, amount of oxidant, reaction time, solvent and concentration of starting material. This parametric study allows forming diglycerose on the gram scale. With a convenient access to diglycerose, several reactions were investigated such as acetylation and glycosylation in order to provide new biobased platform molecules.

Sustainability spotlight

Biomass constitutes an excellent reservoir of polyols. However, only a limited number of polyols are widely available and can be used as building-blocks to address high-volume applications. So, it is important to develop original biobased platform molecules that can bring new properties and address new applications. In this context, this study investigates the catalytic oxidation of diglycerol – a linear biobased starting material derived from vegetable oils – using hydrogen peroxide as a clean oxidant. The resulting cyclic product – named diglycerose – was prepared on the gram scale. Moreover, some derivatives were also prepared in order to study its reactivity. This work promotes the use of renewable resources and mainly aligns with the UN's Sustainable Development Goals 12 (SDG-12), responsible consumption and production.

Introduction

The use of renewable resources has been recognized as one of the ways to limit CO_2 emissions, and therefore, mitigate climate change. Contrary to petroleum resources, biomass has a high oxygen content due to the omnipresence of sugar derivatives and polyols. The transformation of these highly oxygenated molecules into valuable products offers many opportunities.[1] In the same time, it also raises tremendous challenges for chemists.

Among polyols, glycerol has been identified as one of the most interesting biobased platform molecule.[2] It is produced from vegetable oils and is obtained as a coproduct of biodiesel production.[3] Its current annual production is estimated around 6 million tons per year, so it is perfectly suitable to address high volume applications such as polymers, solvents and surfactants.[4] The fact that glycerol is a cheap, biobased and widely available molecule has attracted many chemists to develop its chemistry.[5]

The high functional density of glycerol (*i.e.* 3 alcohols for 3 carbons) offers many possibilities for its conversion to other valuable biobased platform molecules. For example, it can undergo carbonation, acetalization, peracetylation or permethylation leading to the formation of glycerol carbonate,[6] solketal,[7] triacetylglycerol[8] and 1,2,3-trimethoxypropane,[9] respectively. These compounds are usually used as biobased solvents. Others glycerol derivatives can also be produced such as acrolein,[10] glyceric acid,[11] 1,2-propanediol,[12] and others.[5] These compounds can be used as such or as intermediates to other biobased molecules.

Comparatively, the chemistry of diglycerol has been less explored. Diglycerol is produced by oligomerization of glycerol.[13] The reaction is usually performed at elevated temperatures, leading to a mixture of diglycerol, triglycerol and higher oligomers. This complexity has long been a hurdle for the development of its chemistry. However, some technologies now allow producing diglycerol with high selectivity,[14] making it an attractive renewable platform molecule. Although diglycerol is the main product, it also exists as a mixture of linear, branched and cyclic isomers, in which α,α-diglycerol and α,β-diglycerol are the main constituents, accounting for about 80 and 20%, respectively. Despite this complexity, diglycerol has also been valorized as biobased surfactants[15] and monomers.[16] Moreover, it can – most often – undergo similar transformations than glycerol, providing re-optimization due to its multifunctionality and its viscous nature, leading to solubility issues. Among diglycerol derivatives, diglycerol dicarbonate[17] is probably the

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most interesting as it can be used as a monomer for the preparation of polyhydroxyurethanes (PHUs).[18]

Selective oxidation of polyols is really challenging considering that several byproducts could be formed by overoxidation and C–C cleavage. The selective oxidation of 1,2-diols gives the corresponding α-hydroxyaldehydes or α-hydroxyketones that are useful synthetic intermediates.[19] More specifically, the oxidation of glycerol can lead to the formation of many products including dihydroxyacetone (DHA), glyceraldehyde, glyceric acid, hydroxypyruvic acid, and other C1–C3 compounds.[20] Among these possibilities, the selective oxidation of the secondary alcohol of glycerol is probably the most challenging but also the most interesting as it leads to the formation of DHA. This compound is used in cosmetics as a self-tanning agent but also as an intermediate in chemical and pharmaceutical industries.[21]

Despite that DHA is industrially produced through a fermentation process,[22] several chemical systems were also reported for the oxidation of glycerol to DHA. Stoichiometric methods using trichloroisocyanuric acid (TCCA)/AlCl$_3$·6H$_2$O[23] or DMSO/N$_2$H$_4$/I$_2$ (ref. 24) can be used but they generate a lot of waste. Consequently, they are not appropriate to address large-scale applications. Catalytic methods were also described using heterogeneous systems such as Pt–Bi/C[25] and Pd–Ag/C,[26] Au–Pd and Au–Pt supported on TiO$_2$,[27] Au/CuO[28] and Fe/zeolites.[29] Despite some exceptions, these methods give low yields of DHA but they have the advantage to use oxygen as a clean oxidant. Some homogeneous organometallic complexes were also reported. The Pd(OAc)$_2$/neocuproine complex described by Waymouth probably gives the best performances in terms of yield and selectivity using oxygen as an oxidant. However, it still relies on expensive palladium sources.[30] Another system based on Fe/bis(2-pyridinylmethyl)amine was reported by Crotti and Farnetti using H$_2$O$_2$ as a clean oxidant.[31] This system relies on more abundant iron source but only a moderate yield of DHA can be achieved. Finally, glycerol can be converted to DHA by electrochemical methods.[32] However, these methods give moderate selectivities and have never been implemented on the large scale.

Despite that many oxidation methods were reported on glycerol, there is, to the best of our knowledge, only one report on the oxidation of diglycerol. Indeed, our group has reported a catalytic oxidation of diglycerol giving the mono-oxidation product, which was found to mainly exist as a cyclic hemiketal form, that was named "diglycerose" (Scheme 1a).[33] The reaction is catalyzed by a palladium acetate/neocuproine complex using oxygen as a clean oxidant. For solubility reasons and to prevent the catalyst deactivation, hexafluoroisopropanol (HFIP) was used as a solvent and styrene as an additive.

Despite that diglycerose can be obtained in relatively good yield, the method presents several drawbacks: (1) the use of oxygen requires an autoclave; (2) the well-defined palladium complex is expensive and is not commercially available; (3) HFIP is an expensive fluorinated solvent; (4) the use of styrene makes the work-up quite complex. All these drawbacks prevent the preparation of diglycerose on the large scale and, therefore,
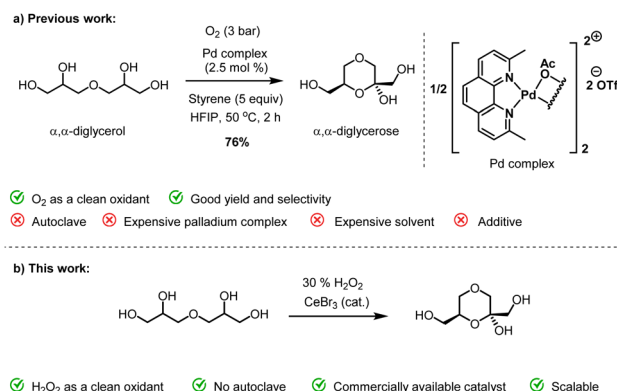
Scheme 1 Catalytic systems for the oxidation of diglycerol to diglycerose.

limit the development of this original platform molecule towards applications.

In this context, we now report another catalytic method for the oxidation of diglycerol to diglycerose. This method uses cerium bromide as a commercially available catalyst and H$_2$O$_2$ as a clean oxidant (Scheme 1b). Moreover, it does not require the use of an autoclave. For these reasons, the synthesis of diglycerose can be now easily scale-up, allowing exploring further transformations towards new biobased molecules.

Results and discussion

The oxidation of diglycerol **1** to diglycerose **2** was evaluated with hydrogen peroxide as an oxidant with various catalysts (Table 1).

Inspired by the conditions developed by Martín and Garrone for the oxidation of aliphatic 1,2-diols,[34] the use of FeBr$_3$/H$_2$O$_2$ (20 mol% in CH$_3$CN) was first investigated (Table 1, entry 1).

Table 1 Oxidation of diglycerol with H$_2$O$_2$ using different catalysts[a]

Entry	Catalyst	Cat. loading (mol%)	Conv.[b] of **1** (%)	Yield[b] of **2** (%)
1[c]	FeBr$_3$	20	42	4
2	CeBr$_3$	40	85	8
3	Ce(OTf)$_3$	40	0	0
4	CeCl$_3$	40	0	0
5	FeBr$_2$	40	4	1
6	FeCl$_3$	40	58	0

[a] Reaction conditions: diglycerol **1** (2 mmol), H$_2$O$_2$ (30 wt% in H$_2$O, 10 mmol, 2 mmol in every 15 min, 5 equiv.), catalyst (0.4 or 0.8 mmol, 20 or 40 mol%), solvent (2 mL), 25 °C, 24 h. [b] Conversion and yield were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard. [c] CH$_3$CN as a solvent (5 mL).

However, despite that the conversion reached 42%, the desired product was formed in only 4% yield. The analogous CeBr₃/H₂O₂ system developed by Tong[35] was also tested under the reported conditions (40 mol% in dioxane). In that case, the conversion reached 85% and diglycerose **2** was obtained in 8% yield (Table 1, entry 2). Despite that diglycerose is formed using these two conditions, it is only obtained in very low yields. These results really contrast with those reported for the oxidation of aliphatic 1,2-diols (72–82% yield),[34,35] thus demonstrating the challenge to oxidize diglycerol to diglycerose. Indeed, considering the gap between the conversion and yield, it is clear that some by-products or intermediates are formed under these conditions (*vide infra*). Other iron and cerium catalysts were tested under the same conditions but no product was obtained (Table 1, entries 3–6). As a result, the CeBr₃/H₂O₂ combination was selected for further optimization.

The oxidation of diglycerol with H₂O₂ in the presence of CeBr₃ was next followed by GC (after derivatization) at various reaction times (Table 2). The reaction proved to be quite fast after the complete addition of H₂O₂ as the conversion reached 64% while the yield of **2** reached 15% (Table 2, entry 1). Increasing the reaction time to 4 hours did not significantly improve the conversion (Table 2, entry 2). However, the yield reached 31%, indicating that a reaction intermediate is probably transformed to the desired product during that time. No further improvement was obtained when the reaction time was increased to 8 hours (Table 2, entry 3). Prolonging the reaction to 24 hours increased the conversion to 85%, but significantly decreased the yield and selectivity to 6 and 8%, respectively, indicating over-oxidation and/or degradation of the product. Consequently, a reaction time of 4 hours was kept for investigating other parameters.

Considering that over-oxidation can negatively affects the selectivity, the amount of H₂O₂ was next investigated (Table 3). Using only 1 or 2 equivalents of H₂O₂ resulted in low yields and

Table 3 Influence of the amount of H₂O₂[a]

Entry	Equiv. H₂O₂	Conv.[b] of **1** (%)	Yield[b] of **2** (%)	Selectivity[b] of **2** (%)
1	1	61	2	4
2	2	61	1	2
3	3	73	37	51
4	4	64	26	41
5	5	63	28	45

[a] Reaction conditions: diglycerol **1** (0.2 mmol), H₂O₂ (30 wt% in H₂O, 0.2 mmol in every 15 min, x equiv.), CeBr₃ (0.08 mmol, 40 mol%), 1,4-dioxane (2 mL), 25 °C, 4 hours. [b] Conversion, yield and selectivity were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard.

selectivities, despite that the conversion already reached 61% (Table 3, entries 1 and 2). Strikingly, the use of 3 equivalents of H₂O₂ led to 73% conversion and 37% yield, while the selectivity reached 51% (Table 3, entry 3).

These conditions led to the formation of diglycerose quite cleanly as demonstrated by the GC chromatogram of the crude reaction mixture after derivatization (Fig. 1). Finally, further increasing the amount of H₂O₂ to 4 and 5 equivalents led to lower yields and selectivities, confirming the negative impact of excess H₂O₂ (Table 3, entries 4 and 5). The influence of solvents was next probed (Table 4).

Considering that dioxane gave encouraging results in the previous experiments, ethers were first considered (Table 4, entries 1–5). However, all the other tested ethers (THF, 2-MeTHF, CPME, MTBE) gave poor results for the desired product. Alcohols such as methanol, ethanol, *t*-butanol and *t*-amylalcohol were also tested (Table 4, entries 6–9).

Table 2 Oxidation of diglycerol at various times[a]

Entry	Time[b] (h)	Conv.[c] of **1** (%)	Yield[c] of **2** (%)	Selectivity[c] of **2** (%)
1	1	64	15	24
2	4	68	31	45
3	8	68	30	44
4	24	85	6	8

[a] Reaction conditions: diglycerol **1** (1 mmol), H₂O₂ (30 wt% in H₂O, 5 mmol, 1 mmol in every 15 min, 5 equiv.), CeBr₃ (0.4 mmol, 40 mol%), 1,4-dioxane (10 mL), 25 °C. [b] Reaction time after the end of the addition of H₂O₂. [c] Conversion, yield and selectivity were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard.
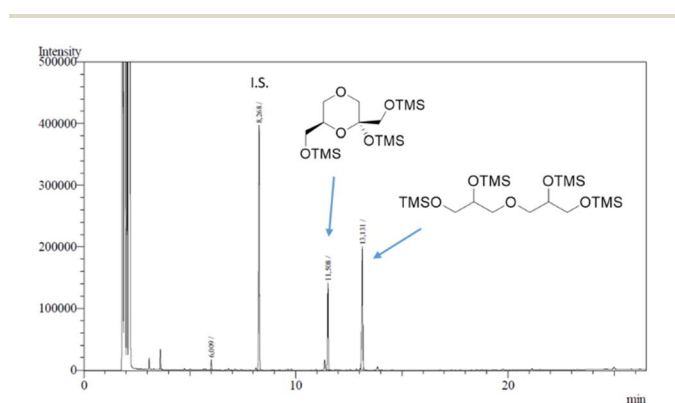

Fig. 1 GC chromatogram of a crude reaction mixture obtained after derivatization (experiment from Table 3, entry 3). I.S.: internal standard (1,3,5-trimethoxybenzene).

Table 4 Influence of solvents[a]

Entry	Solvent	Conv.[b] of 1 (%)	Yield[b] of 2 (%)	Selectivity[b] of 2 (%)
1	Dioxane	73	37	51
2	THF	37	5	14
3	2-MeTHF	39	0	0
4	CPME	34	4	11
5	MTBE	38	5	12
6	MeOH	77	6	8
7	EtOH	48	13	27
8	t-BuOH	67	22	32
9	t-amylOH	54	15	27
10	HFIP	42	12	27
11	TFE	65	16	25
12	CH$_3$CN	52	14	27
13	DMF	35	10	28
14[c]	Dioxane	57	27	47

[a] Reaction conditions: diglycerol **1** (0.2 mmol), H$_2$O$_2$ (30 wt% in H$_2$O, 0.6 mmol, 3 equiv.), CeBr$_3$ (0.08 mmol, 40 mol%), solvent (2 mL), 25 °C, 4 hours. [b] Conversion, yield and selectivity were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard. [c] FeBr$_3$ was used as a catalyst. 2-MeTHF: 2-methyltetrahydrofuran; CPME: cyclopentyl methyl ether; MTBE: *tert*-butyl methyl ether; *t*-BuOH: *tert*-butanol; *t*-amylOH: 2-methyl-2-butanol; HFIP: 1,1,1,3,3,3-hexafluoroisopropanol; TFE: 2,2,2-trifluoroethanol.

Table 5 Influence of diglycerol concentration[a]

Entry	Conc. of 1 (mol L^{-1})	Conv.[b] of 1 (%)	Yield[b] of 2 (%)	Selectivity[b] of 2 (%)
1	1	76	37	49
2	0.1	73	37	51
3	0.05	66	37	56
4	0.01	65	16	25

[a] Reaction conditions: diglycerol **1** (0.2 mmol), H$_2$O$_2$ (30 wt% in H$_2$O, 0.6 mmol, 3 equiv.), CeBr$_3$ (0.08 mmol, 40 mol%), solvent (2 mL), 25 °C, 4 hours. [b] Conversion, yield and selectivity were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard.

In these cases, the conversion of diglycerol was improved by comparison with ethers and a 22% yield was reached with *t*-butanol (Table 4, entry 8). Fluorinated solvents such as HFIP and TFE were also considered as they proved to be excellent solvents in our previous work using palladium acetate/neocuproine complex (Table 4, entries 10 and 11). However, the poor results obtained indicate that these solvents are not appropriate for the use of CeBr$_3$ as a catalyst. Finally, CH$_3$CN and DMF were also tested for comparison purposes but neither the conversion of diglycerol nor the yield of diglycerose were improved under these conditions (Table 4, entries 12 and 13). From all these results, no improvement can be obtained using alternative solvents, so dioxane was kept for further investigation. At that stage of the study, we have also re-investigated the use of FeBr$_3$ as a catalyst under the same conditions (40 mol% in dioxane). In that case, the conversion of diglycerol reached 57% while diglycerose was obtained in 27% yield (Table 4, entry 14). These results confirm the better catalytic activity – initially observed – of CeBr$_3$ over FeBr$_3$.

The effect of diglycerol concentration in dioxane was next studied (Table 5). Increasing the initial concentration from 0.1 to 1 M did not have a significant impact on the results (Table 5, entries 1 and 2). Decreasing the concentration to 0.05 M led to slight decrease of the conversion but both the yield and

selectivity were not significantly affected (Table 5, entry 3). However, a further decrease to 0.01 M led to a drastic decrease in yield (Table 5, entry 4).

Finally, the impact of the amount of CeBr$_3$ was also investigated (Fig. 2). Reducing the amount from 0.4 to 0.2 equivalent led to a decrease of conversion, yield and selectivity. On the opposite, gradually increasing the CeBr$_3$ quantity from 0.4 to 2 equivalents led to an increase of conversion. However, both the yield and selectivity drastically drop and no product was obtained with 2 equivalents of CeBr$_3$. These results indicate that excess CeBr$_3$ is deleterious for the reaction, leading to the formation of species that could not be detected by GC (after derivatization).

Thus, we hypothesized that diglycerose has been either degraded or oligomerized to give heavier products. In order to detect potential oligomers, the crude mixture of diglycerose was treated with excess acetic anhydride in the presence of 4-DMAP (see ESI† for details). The resulting mixture was analysed by
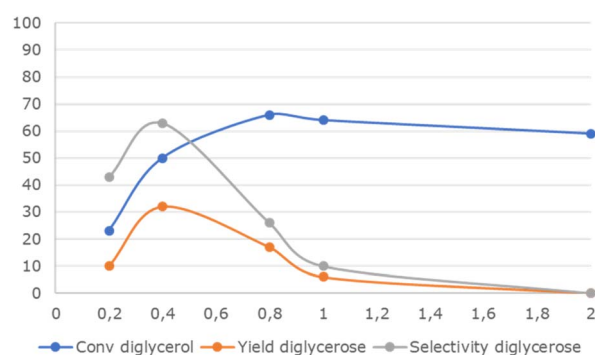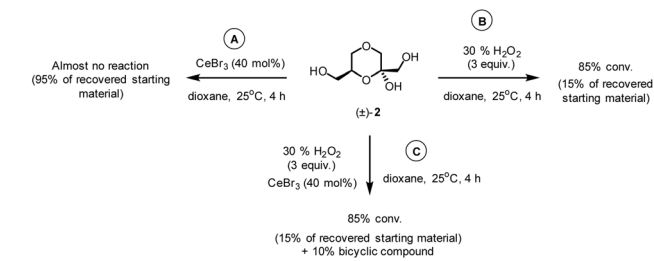

Fig. 2 Effect of the amount of CeBr$_3$. Reaction conditions: diglycerol **1** (0.2 mmol), H$_2$O$_2$ (30 wt% in H$_2$O, 0.6 mmol, 3 equiv.), CeBr$_3$ (*x* equiv., *x* mol%), dioxane (1 mL), 25 °C, 4 hours. Conversion, yield and selectivity were measured by GC after derivatization, using 1,3,5-trimethoxybenzene as an internal standard.
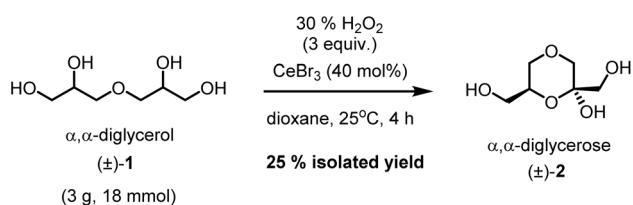
Scheme 2 Diglycerose stability studies.
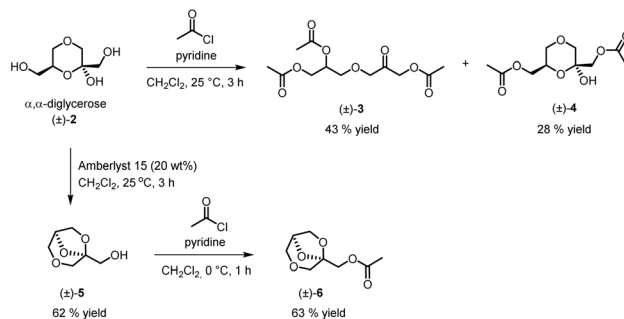

Scheme 4 Acetylation of diglycerose and derivatives.

Size-Exclusion Chromatography (SEC, see ESI†). From the SEC chromatogram, no diglycerose oligomers could be detected under these conditions, thus ruling out the formation of heavier products. Therefore, the stability of diglycerose **2** was next investigated under the previously optimized conditions (Scheme 2 and ESI†).

First, diglycerose was treated with CeBr$_3$ alone and no evident sign of degradation was detected considering that the starting material was recovered almost quantitatively (Scheme 2, A). This indicates that the catalyst does not degrade the desired product. In contrast, the use of H$_2$O$_2$ alone resulted in 85% conversion of diglycerose (Scheme 2, B). However, no product can be clearly identified on the crude reaction mixture, either by ^{1}H and ^{13}C NMR or mass spectrometry. A similar conversion was also obtained when diglycerose was treated with H$_2$O$_2$ in the presence of CeBr$_3$ (Scheme 2, C). In this case, only a bicyclic compound derived from the dehydration of diglycerose was detected and isolated with 10% yield. No other product was identified, indicating that diglycerose was mostly degraded. However, the formation of undetectable byproducts such as carboxylic acids could not be ruled out. Overall, these stability studies demonstrate that diglycerose degrades under H$_2$O$_2$/CeBr$_3$ conditions, thus explaining the moderate yield obtained. This yield actually reflects a compromise between the kinetics of formation and the kinetics of degradation of diglycerose. To confirm this hypothesis, a scale-up experiment was performed using 3 g of starting material (Scheme 3). Hence, diglycerol **1** was treated under the optimized conditions [*i.e.*, 30 wt%-H$_2$O$_2$ (3 equiv.), CeBr$_3$ (40 mol%), dioxane, 25 °C, 4 h] to give diglycerose **2** with 25% isolated yield after purification by column chromatography. This result correlates with those obtained by GC titration.

With sufficient amount of pure diglycerose **2** in hands, further reactions were investigated (Scheme 4).[36] First, acetylation with acetyl chloride was performed using **2** as a starting material. In that case, a mixture of the open-form tri-acetylated compound **3** and the cyclic-form di-acetylated compound **4** was obtained and the products were isolated with 43 and 28%, respectively. No cyclic-form tri-acetylated compound was observed, indicating that acetylation of the tertiary alcohol is more difficult under these conditions. Diglycerose **2** was then dehydrated using Amberlyst 15 as a catalyst and the bicyclic compound **5** was isolated with 62% yield. Acetylation of **5** led to the formation of the desired acetylated compound **6** with 63% isolated yield. Note that such compound could serve as an alternative biobased solvent.

The glycosylation of **2** was also studied with a range of alcohols (Scheme 5). An optimization was first carried out with benzyl alcohol in order to limit the formation of the bicyclic compound **5**, that is formed by a competitive reaction under acidic conditions (see Tables S1–S3 in the ESI† for details). Treatment of diglycerose **2** with benzyl alcohol (neat) in the presence of Amberlyst 15 gave **7** with 49% isolated yield after column chromatography. However, the formation of **5** cannot be avoided and it was obtained in 28% yield. The use of methanol led to the formation of **8** with 62% yield. Linear alcohols such as ethanol, 1-butanol, 1-pentanol and 1-heptanol were also tested and compounds **9–12** were isolated with 17–50% yield. In that case, a trend can be clearly observed: the longer the chain, the lower the yield. This trend can be explained by an increasing difference of polarity between diglycerose and the alcohol.

Scheme 3 Scale-up experiment.
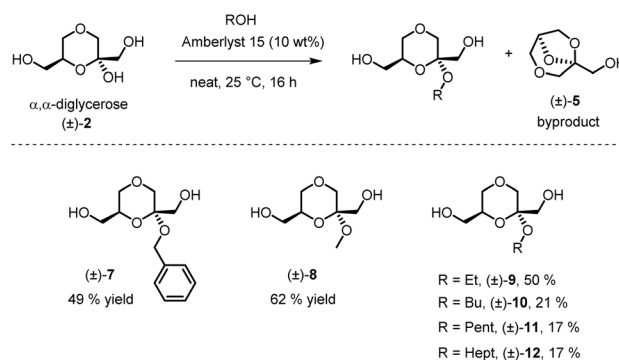
Scheme 5 Glycosylation of diglycerose with alcohols.

It was also confirmed with the use of fatty alcohols such as 1-nonanol and 1-dodecanol that did not allow forming the desired glycosylation products. Finally, branched alcohols were also considered (2-propanol, isobutanol, isoamyl alcohol) but no product was formed due to the high viscosity of the reaction mixture.

Conclusions

In conclusion, we have developed a new method for the catalytic oxidation of diglycerol to diglycerose using hydrogen peroxide as a clean oxidant and cerium bromide as a commercially available catalyst. The experimental procedure is simple as no pressurized equipment is required. The selectivity remains modest as the product was found to be unstable under the operating conditions. However, considering that the reaction can be easily scaled-up, diglycerose can be produced on the multi-gram scale. Acetylation and glycosylation of diglycerose (and its dehydration product) were also investigated in order to provide new biobased platform molecules.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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36 No attempt has been made at this stage to develop green reaction conditions and to optimize the yields. These reactions were carried out in order to investigate the reactivity of diglycerose. Moreover, these diglycerose derivatives were also prepared for characterization purposes.