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Selective catalytic oxidation of diglycerol<sup>†</sup>

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The selective oxidation of  $\alpha$ , $\alpha$ -diglycerol was studied using oxygen as a clean oxidant in the presence of a palladium/neocuproine complex. After optimization of the reaction parameters, the monooxidation product was obtained with 93% NMR yield (up to 76% isolated yield). The product was named "diglycerose" considering that it mainly exists as a cyclic hemi-ketal form.

The transformation of renewable biomass to added-value compounds is currently the subject of intense research efforts.<sup>1</sup> Biomass represents an important reservoir of polyols as it is mainly composed of starch, cellulose, hemi-cellulose, sucrose, and many more oxygenated compounds.<sup>1,2</sup> Even triglycerides, which exhibit a low oxygen content, are incorporating a polyol as a linker of fatty chains. Transesterification of triglycerides, extracted from vegetable oils, affords fatty acid methyl esters that are used as either biodiesel,<sup>3</sup> starting materials for oleochemicals<sup>4</sup> or biopolymers.<sup>5</sup> Glycerol is obtained as the main coproduct of the methanolysis of vegetable oils and is valorized along its own value chain. It could be directly used as a renewable solvent<sup>6</sup> or as a monomer for the production of biobased polyesters.<sup>7</sup> Glycerol is also an excellent platform molecule to prepare a wide range of biobased chemicals<sup>8</sup> such as acrolein,9 glyceric acid,10 1,2-propanediol,11 among others.8 Moreover, it can be transformed to glycerol carbonate,<sup>12</sup> solketal<sup>13</sup> and 1,2,3-trimethoxypropane,<sup>14</sup> that serve as biobased solvents.<sup>15</sup> Glycerol can also be used as a polar head in the preparation of renewable surfactants based on esters,<sup>16</sup> acetals<sup>17</sup> or ethers.<sup>18</sup> In contrast, the chemistry of diglycerol is comparatively under-developed.

Diglycerol is a derivative of glycerol that is formally the result of the condensation of two molecules of glycerol. It is mainly prepared by direct oligomerization of glycerol.<sup>19</sup> Diglycerol can be directly used as a monomer for the preparation of polyesters.<sup>20</sup> Moreover, it can be converted to diglycerol dicarbonate (DGDC),<sup>21</sup> that is further used as a building-block for the synthesis of polyhydroxyurethanes (PHUs).<sup>22</sup> Diglycerol-based surfactants can be also produced such as diglycerol esters,<sup>23</sup> acetals,<sup>24</sup> and ethers.<sup>18</sup> Other ether derivatives can be also prepared by dehydrogenative arylation<sup>25</sup> or permethylation<sup>26</sup> to give hydrotropes and solvents, respectively.

The selective oxidation of polyols, especially those incorporating a 1,2-diol motif, provides  $\alpha$ -hydroxyketones, that are encountered in natural products and serve as useful synthetic intermediates.<sup>27</sup> The oxidation of 1,2-diols to  $\alpha$ -hydroxyketones is a challenging task considering that many byproducts (e.g., 1,2-diketones, aldehydes, carboxylic acids) could be formed by over-oxidation and C-C cleavage. Some selective methods were first reported using stoichiometric oxidants such as dioxiranes<sup>28</sup> or Br<sub>2</sub>.<sup>29</sup> Catalytic methods were also developed based on Ru-<sup>30</sup> and Ni-catalyzed dehydrogenation.<sup>31</sup> Particularly, Waymouth et al. have reported a highly selective catalytic method for the oxidation of glycerol to dihydroxyacetone with a palladium/neocuproine complex using hydroquinone as an oxidant.<sup>32</sup> The method was further developed using oxygen (or air) and applied to erythritol<sup>33</sup> and other polyols,<sup>34</sup> and even carbohydrates.<sup>35</sup> However, to the best of our knowledge, the selective catalytic oxidation of diglycerol has never been reported.

In this context, we report here a selective catalytic method for the mono-oxidation of diglycerol using oxygen as a clean oxidant.

Diglycerol is usually produced by oligomerization of glycerol, resulting in the formation of 3 main isomers.<sup>19</sup> The proportion of each isomer in commercially available diglycerol was found to be ~80% for  $\alpha,\alpha$ -isomer, ~20% for  $\alpha,\beta$ -isomer and <1% for  $\beta,\beta$ -isomer, as determined by <sup>13</sup>C NMR. The oxidation of diglycerol already offers a great challenge in term of

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regioselectivity but also in term of mono- *versus* multiple oxidations. So, in order to have a simpler model for oxidation of diglycerol, the purification of the crude starting material was carried out through the formation of  $\alpha,\alpha$ -diglycerol dicarbonate 2 (Fig. S1 in ESI<sup>†</sup>).<sup>36</sup>

The selective mono-oxidation of the  $\alpha, \alpha$ -isomer of diglycerol  $\alpha, \alpha$ -1 was performed with palladium-based catalysts using oxygen as a clean oxidant in acetonitrile/water (10:1) at 30 °C (Table 1). First, no oxidation product was obtained when using either a mixture of Pd(OAc)<sub>2</sub> and neocuproine Pd-1 or a preformed<sup>37</sup> Pd(OAc)<sub>2</sub>/neocuproine complex Pd-2 (Table 1, entries 1 and 2). In these two cases, the starting material was recovered unaltered.

These results were somewhat surprising since the same catalysts gave good results for the oxidation of glycerol **4** and the corresponding dihydroxyacetone **5** was obtained with 41 and 60% yield, respectively (Table 1, entries 1 and 2). With **Pd-3** complex, prepared following a reported method,<sup>38</sup> only trace amounts (<5%) of the mono-oxidation product of diglycerol was observed (Table 1, entry 3). Once again, the same catalyst performed very well for the oxidation of glycerol and dihydroxyacetone **5** was obtained with 90% yield (Table 1, entry 3). From these results, it is striking to see that the reported palladium-based catalysts exhibit good catalytic activities for the oxidation of glycerol while they are completely ineffective for diglycerol. We hypothesized that the poor solubility of diglycerol under the chosen reaction conditions was responsible for the poor conversion.

To solve this problem, the proportion of water was increased to promote the dissolution of diglycerol and  $CH_3CN/H_2O$  (v/v 7 : 1) was selected as solvent system for further optimization. Then, the temperature was gradually increased from 30 to 80 °C (Fig. S2 in ESI†). The best result was obtained at 70 °C with an isolated yield of 27% for the mono-oxidation product **3**, accompanied with about 11% yield of the bis-oxi-

Table 1	Oxidation of (di)glycero	ol with palladium-based catalysts <sup>a</sup>
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<sup>*a*</sup> Reaction conditions: α,α-Diglycerol or glycerol (0.45 mmol), palladium-based catalyst **Pd1-3** (10 mol%), O<sub>2</sub> (1 bar), CH<sub>3</sub>CN/H<sub>2</sub>O (v/v 10:1, 5.5 mL), 30 °C, 24 h. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR. dation product 6. Increasing the temperature to 80 °C did not improve the results. On the contrary, very low yields were obtained under these conditions. This was attributed to the catalyst deactivation with the formation of Pd(0) aggregates, *i.e.* "Pd black".<sup>38</sup>

From the <sup>1</sup>H NMR spectrum, it was found that the expected product 3 exists as an open and a cyclic form, representing 7 and 93%, respectively (Scheme 1). Indeed, compound 3 cyclizes to form a six-membered ring as a single diastereoisomer. The relative *cis* configuration between the two hydroxymethyl groups was determined by NMR analyses after derivatization (see ESI†). The formation of a seven-membered ring system has not been detected, such product being usually highly disfavored. Product 3 has been named "diglycerose" due to its structural similarities with ketoses.

Next, various solvents were screened. The temperature was set at 50 °C to limit the formation of palladium black and the time was limited to 2 hours to avoid the formation of the bisoxidation product 6 (Table 2). First, repeating the reaction in  $CH_3CN/H_2O(7:1)$  in 2 hours gave only 5% yield (Table 1, entry 1). Protic polar solvents such as MeOH and EtOH did not lead to any conversion of the starting material. Ethereal solvents were next screened. No reaction was obtained when using CPME and 2-MeTHF while the product was formed in THF and 1,4-dioxane with 31 and 43% yield, respectively (Table 1, entries 2-5). Then, fluorinated solvents were tested as they are known to well dissolve oxygen.<sup>39</sup> (Trifluoromethyl)benzene was first used but no reaction was observed (Table 1, entry 6). Satisfyingly, when using TFE and HFIP, diglycerose 3 was obtained with 54 and 74%, respectively (Table 1, entries 7 and 8). The success of HFIP has been reported in numerous occasions<sup>40</sup> in homogeneous catalysis using transition metals,<sup>41</sup> notably in CH activation.<sup>42</sup> In our case, the use of HFIP could increase the oxygen solubility but it could also increase catalyst lifetime. Indeed, Waymouth has shown that phenol derivatives can increase the lifetime of Pd/neocuproine complexes.<sup>38</sup> So, considering that HFIP exhibits a similar  $pK_a$ (9.3) as phenol, it is likely that it also helps to prevent the catalyst degradation.

Consequently, HFIP was selected for further optimization (Table 3). Increasing the oxygen pressure to 3 and 6 bar, led to a complete conversion and diglycerose **3** was obtained with 89



Scheme 1 Mono-oxidation product of diglycerol.

**Table 2** Oxidation of  $\alpha$ , $\alpha$ -diglycerol in different solvent systems<sup>a</sup>

нс	он он	O <sub>2</sub> (1 bar) <b>Pd-3</b> (10 mol %) → Solvent, 50°C, 2h		HO OH	
α,α-1				3	
Entry	Solvent	Conv. <sup>b</sup> (%)	Yield <sup>b</sup> (%)	Selec. <sup>b</sup> (%)	Cyclic form <sup>b</sup> (%)
1	$CH_{3}CN/H_{2}O(7:1)$	5	5	99	94
2	CPME	0	0	0	_
3	2-MeTHF	0	0	0	_
4	THF	37	31	99	98
5	1,4-Dioxane	44	43	99	98
6	(Trifluoromethyl) benzene	0	0	0	_
7	TFE	71	54	99	93
8	HFIP	76	74	99	93

<sup>*a*</sup> Reaction conditions: α,α-Diglycerol (0.45 mmol), **Pd-3** (10 mol%), O<sub>2</sub> (1 bar), solvent (5.5 mL), 50 °C, 2 h. <sup>*b*</sup> Conversion, yield, selectivity and ratio of mono-oxidation product on cyclic form were determined by <sup>1</sup>H NMR using mesitylene as internal standard. CPME: cyclopentyl methyl ether, 2-MeTHF: 2-methyl tetrahydrofuran, THF: tetrahydrofuran, TFE: trifluoroethanol, HFIP: 1,1,1,3,3,3-hexafluoroisopropanol.

Table 3 Diglycerol oxidation in HFIP<sup>a</sup>



Entry	O <sub>2</sub> (bar)	Catalyst (mol%)	Time (h)	Conv. <sup>b</sup> (%)	Yield <sup>b</sup> (%)	Selec. <sup>1</sup> (%)		
1	3	10	2	95	89	98		
2	6	10	2	>99	94	98		
3	6	5	2	69	66	99		
4	3	5	2	69	63	99		
5	3	2.5	2	34	33	99		
6 <sup>c</sup>	3	2.5	2	79	75	99		
7 <sup>c</sup>	3	2.5	6	79	77	99		
8 <sup>c</sup>	3	2.5	18	>99	$93 (61)^d$	98		
9 <sup>c</sup>	3	1	18	77	74	99		
$10^c$	3	1	30	77	73	99		
$11^{c,e}$	3	2.5	18	54	51	99		
$12^{c,f}$	3	2.5	18	64	60	99		

<sup>*a*</sup> Reaction conditions: α,α-Diglycerol (0.45 mmol), **Pd-3**, O<sub>2</sub>, HFIP (5.5 mL), 50 °C unless otherwise stated. <sup>*b*</sup> Conversion, yield, selectivity and ratio of mono-oxidation product (3 *versus* 6) were determined by <sup>1</sup>H NMR using mesitylene as internal standard. <sup>*c*</sup> Styrene (2.25 mmol, 5 equiv.) was added. <sup>*d*</sup> Isolated yield in brackets. <sup>*e*</sup> Using **Pd-1**. <sup>*f*</sup> Using **Pd-2**.

under 3 or 6 bar of oxygen. Under these conditions, compound 3 was obtained with 66 and 63% yield (Table 3, entries 3 and 4). Further decreasing the catalyst loading to 2.5 mol%, only gave 33% yield (Table 3, entry 5). Recently, it was shown that additives such as phenol or styrene have a beneficial impact on the catalyst activity and lifetime.<sup>38</sup> In our case, in the presence of styrene (5 equiv.) with 2.5 mol% catalyst loading, the vield increased to 75% (Table 3, entry 6). Increasing the reaction time to 18 hours allowed to reach full conversion and 3 was obtained with 93% yield (Table 3, entries 7 and 8). Further decreasing the catalyst loading to 1 mol% did not allow to reach high yield, even with extended reaction time (Table 3, entries 9 and 10). Finally, the oxidation of diglycerol was repeated using catalytic systems Pd-1 and Pd-2 under the optimized conditions. In that case, diglycerose 3 was only formed with 51 and 60% yield, respectively (Table 3, entries 11 and 12). These experiments show that all catalytic systems are active under the optimized conditions, which are found to be crucial for the success of this reaction. The trend between the three different catalytic systems is the same than the one observed for the oxidation of glycerol (Table 1), with Pd-3 complex being the most active catalyst. The superiority of this cationic palladium(II) complex in the oxidation of alcohols has been previously attributed to the presence of both the acetate and triflate ions.<sup>43</sup> While the non-coordinating triflate ion generates an open coordination site that allows fast initial rates,<sup>44</sup> the acetate ion acts as an internal base that facilitates the intramolecular deprotonation.45

A scale-up reaction was performed on a 10-fold scale under optimized conditions and diglycerose **3** was obtained with 76% isolated yield (Scheme 2).

The oxidation method was found to be efficient and selective on  $\alpha, \alpha$ -diglycerol. Therefore it could also be applied to  $\alpha,\beta$ -diglycerol. However,  $\alpha,\beta$ -diglycerol recovered from the filtrate after hydrolysis of diglycerol dicarbonate was not pure enough. Consequently, it was prepared in three steps from solketal following a reported procedure (see ESI<sup>†</sup> for details).<sup>46</sup> Selective oxidation of  $\alpha,\beta$ -diglycerol was also carried out under the optimized conditions. In that case, the mono-oxidation product 7 was only obtained with 4% yield and bicylic ketal 8 formed by dehydration of 7 - was obtained with 76% yield (Scheme 3). Satisfyingly, reducing the  $O_2$  pressure to 1 bar gave 7 with 51% isolated yield.  $\alpha,\beta$ -Diglycerose 7 also exists as a cyclic hemi-ketal (no open formed detected) and was obtained with a dr of 88:12. In the major diastereoisomer, the hydroxymethyl groups adopt a relative trans configuration (determined by NMR, see ESI<sup>†</sup>).

and 94% yield, respectively (Table 3, entries 1 and 2). Satisfyingly, the selectivity for the mono-oxidation product remained high (around 98%), highlighting the high selectivity of the catalytic system. Considering that palladium is an expensive metal, the amount of catalyst should be reduced. The reaction was first carried out with 5 mol% of catalyst



**Scheme 2** Scale-up reaction for  $\alpha$ , $\alpha$ -diglycerol.

**Scheme 3** Scale-up reaction for  $\alpha$ , $\beta$ -diglycerol.

The difference of reactivity between  $\alpha, \alpha$ - and  $\alpha, \beta$ -diglycerol led us to investigate their oxidation rates under the optimized conditions. The oxidation was first performed under 1 bar of  $O_2$  for convenience in sampling the reaction mixture. The reaction progress for each diglycerol isomer is plotted in Fig. 1. From these experiments, it is clear that  $\alpha, \alpha$ -diglycerol  $\alpha, \alpha$ -1 is more easily oxidized than  $\alpha, \beta$ -diglycerol  $\alpha, \beta$ -1, with their conversion reaching 59 and 39% after 24 hours, respectively. Interestingly, an initiation period of about 2 hours was observed for both isomers. When the reaction was performed under 3 bar of oxygen, the conversion of  $\alpha, \alpha$ -1 reached 92% after 24 hours and no initiation period was observed.

This result demonstrates that increasing the oxygen pressure has a positive outcome on the overall rate of the reaction. Indeed, increasing the pressure of oxygen increases its concentration in HFIP. Considering that oxygen is necessary to re-oxidize Pd(0) to Pd(I) and therefore to complete the catalytic cycle, increasing its concentration allows reaching higher turnover frequencies.

To further understand the formation of the dehydration products, pure  $\alpha$ , $\alpha$ -diglycerose **3** and  $\alpha$ , $\beta$ -diglycerose **7** were treated under acidic conditions (Fig. 2). After 1 hour at 30 °C, the conversion of **3** and **7** reached 6 and 32%, respectively, while the yield of **9** and **8** reached 4 and 27%, respectively.

These results demonstrate that the dehydration of  $\alpha$ , $\beta$ -diglycerose 7 to 8 is easier than those of  $\alpha$ , $\alpha$ -diglycerose 3 to 9. They could explain why a high proportion of 8 was



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Fig. 2 Dehydration of  $\alpha, \alpha$ -diglycerose 3 and  $\alpha, \beta$ -diglycerose 7. Reaction conditions:  $\alpha, \alpha$ - or  $\alpha, \beta$ -diglycerose 3 or 7 (0.45 mmol), A15 (10 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 30 °C, 2 hours. The conversions and yields were determined by GC after derivatization, using methyl oleate as an internal standard.

formed when the reaction was conducted at 50 °C under 3 bar of oxygen from  $\alpha$ , $\beta$ -diglycerol, while almost no dehydration product **9** was detected when  $\alpha$ , $\alpha$ -diglycerol was reacted under the same conditions. To probe the synthetic utility of diglycerose, some chemical transformations were next investigated (Scheme 4).

First,  $\alpha,\alpha$ -diglycerose **3** was treated with Amberlyst 15 for 4 hours to give bicyclic ketal **9** with 48% isolated yield (Scheme 4, a). Then, benzoylation of  $\alpha,\alpha$ -diglycerose **3** was performed using benzoyl chloride and provided the per-benzoylated products with 74% combined yield (Scheme 4, b). In that case, cyclic and linear products **10** and **11** can be separated and were isolated with 65 and 9% yield, respectively. Some traces (3%) of bis-benzoylated diglycerose **12** were also isolated. In order to further confirm the structure of cyclic diglycerose, per-benzoylation was also carried out using 4-bromobenzoyl chloride (Scheme 4, c). Cyclic and linear products **13** and **14** were obtained with 45 and 6% isolated yields, respectively. Despite our efforts to obtain suitable crystals, no X-Ray



Fig. 1 Reaction progress of the oxidation of  $\alpha, \alpha$ -diglycerol ( $\alpha, \alpha$ -1) and  $\alpha, \beta$ -diglycerol ( $\alpha, \beta$ -1). Reaction conditions:  $\alpha, \alpha$ - or  $\alpha, \beta$ -diglycerol (0.45 mmol), Pd-3 (2.5 mol%), O<sub>2</sub> (1 or 3 bar), HFIP (5.5 mL), 50 °C. The conversions and yields were determined by GC after derivatization, using methyl oleate as an internal standard.



Scheme 4 Chemical transformations of  $\alpha, \alpha$ -diglycerose.

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structure can be obtained for **13**. Thereby, the structure of compound **13** was determined by 1D and 2D NMR analyses and the relative *cis*-configuration was assigned though a NOESY experiment (see ESI<sup>†</sup>).

### Conclusions

In conclusion, we have developed the selective catalytic oxidation of diglycerol using a palladium/neocuproine complex and oxygen as a clean oxidant. After optimization of the reaction parameters on  $\alpha, \alpha$ -diglycerol, the mono-oxidation product was obtained with high selectivity (99%) and high yield (93%). The product was isolated with up to 76% yield and was found to mainly exist as a cyclic hemi-ketal form. Given its structural similarities with ketoses, this original "ketose-like" compound has been named "diglycerose". The conditions were also applied to  $\alpha,\beta$ -diglycerol and the corresponding hemi-ketal was obtained with 51% yield. Finally,  $\alpha,\alpha$ -diglycerol was used as a platform molecule for benzoylation and dehydration reactions.

## Conflicts of interest

There are no conflicts to declare.

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