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1-*O*-Alkyl (di)glycerol ethers synthesis from methyl esters and triglycerides by two pathways: catalytic reductive alkylation and transesterification/reduction†

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From available and bio-sourced methyl esters, monoglycerides or oleic sunflower refined oil, the corresponding 1-*O*-alkyl (di)glycerol ethers were obtained in both high yields and selectivity by two different pathways. With methyl esters, a reductive alkylation with (di)glycerol was realized under 50 bar hydrogen pressure in the presence of 1 mol% of Pd/C and an acid co-catalyst. A second two step procedure was evaluated from methyl esters or triolein and consisted of a first transesterification to the corresponding monoglyceride with a BaO/Al_2O_3 catalyst, then its reduction to the desired glycerol monoether with a recyclable heterogeneous catalytic system Pd/C and Amberlyst 35 under H_2 pressure. In addition, a mechanism for the reaction was also proposed.

Introduction

Glycerol is widely used in various industrial applications ranging from food, personal care and solvents[1–3] to the synthesis of alkyd resins and polyurethanes.[4] This building block is the main co-product of the vegetable oil industry, and its global output is increasing with the acceleration of oleochemical production.[5] In fact, the synthesis of fatty acid methyl esters (FAMEs), also known as "biodiesel", led to a dramatic increase of the availability of glycerol, since 11 kg of the latter is produced for every 100 kg of ester.[5,6] In order to increase the glycerol demand, it is necessary to find new large-scale applications for this polyol. For these reasons, glycerol has attracted much attention for the synthesis of various products of high industrial interest.[6–11]

Glycerol monoethers (GMEs) are eco-friendly renewable compounds. They are used in many industrial applications such as cosmetics,[12] cleaning formulations,[13,14] pharmaceuticals[15,16] or ink formulations[17] and an important number of publications mention the interesting physical and biological properties of such compounds.[18–20] Traditionally, GMEs are synthesized *via* the Williamson etherification, starting from toxic and expensive epichlorohydrin, 3-chloropropane-1,2-diol or glycidol in order to improve the selectivity towards the three hydroxyls.[19,20] The catalytic etherification of glycerol has been achieved starting from alcohols with acid catalysts,[21–23] alkenes under acidic conditions[24,25] or by telomerization reaction.[26–28] In most of these processes, glycerol monoethers have been prepared in good yields starting from activated alcohols like benzyl alcohol,[22] but a low selectivity for monoalkylated glycerol products was often observed when starting with alkenes.[24–28] From an economical point of view, the acid-catalytic route is inefficient, particularly the conversion of glycerol and the selectivity towards the corresponding GME are too low.[21–23] The best results were described by Jérôme *et al.*, with a higher yield of 45% of monopentyl glycerol ether using Amberlyst A70 at high temperature (160 °C) and with a long reaction time (96 h).[23]

More than 15 years ago, our group described an alternative and more eco-friendly method for the Williamson ether synthesis by reductive alkylation of linear alcohols and carbonyl compounds with Pd/C as a catalyst under hydrogen pressure.[29] Recently, this transformation was adapted to polyfunctional alcohols under mild conditions for the synthesis of linear 1-*O*-alkyl (di)glycerol monoethers in both high yields and selectivity. The best conditions were found to be the utilization of (di)glycerol as a solvent and a reagent, in the presence of Pd/C as a catalyst and a Brønsted acid as a co-catalyst.[30,31] Unfortunately, aldehydes are not accessible at industrial scales from renewable starting material for the moment. Consequently, more recently, we reported for the first time the catalytic reductive alkylation of readily available and/or biosourced carboxylic acids with (poly)glycerol using a recyclable catalytic system associating Pd/C and Amberlyst 35.[32,33]

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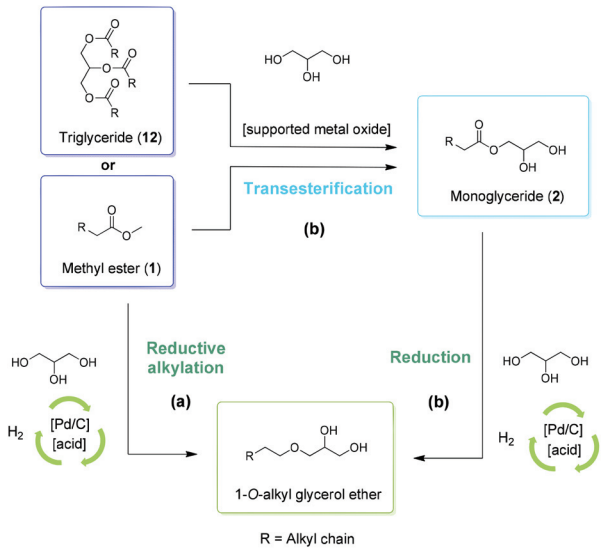
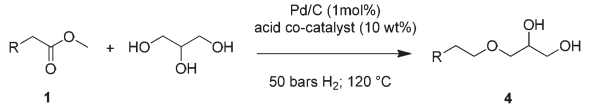


Scheme 1 Synthesis of glycerol and diglycerol monoethers (a) by reductive alkylation of glycerol or diglycerol and methyl esters **1** and (b) a two step procedure composed of a first transesterification step of triglyceride **12** or methyl ester **1** followed by a reduction of monoglyceride **2** with a recyclable catalytic system.

Based on our earlier results for the preparation of (poly)glycerol monoethers and in order to establish new and alternative eco-efficient processes for the alkylation of glycerol, the catalytic etherification with the available triglycerides **12**, methyl esters **1** and monoglycerides **2** is investigated in this report by two different pathways (Scheme 1). Interestingly, triglycerides are used as low-cost and biosourced substrates in large scale by the vegetable oil industry. In addition, methyl esters are obtained as products in the biodiesel manufacture, with a good accessibility and often a less expensive cost than the corresponding carboxylic acids.[5,6] Herein, the reductive alkylation of methyl esters with glycerol is reported (Scheme 1, path a). Besides, an efficient two step procedure for the synthesis of GMEs is also described (Scheme 1, path b). The transesterification of triolein **12** or FAMEs **1** with (di)glycerol using a mixed metal oxide as a new catalyst is followed by the reduction of the obtained monoglyceride to its corresponding glycerol monoether under H_2 pressure. A mechanistic consideration of the reaction with these substrates is also proposed.

Results and discussion

At the beginning of our study, we first prepared GMEs by reductive alkylation of methyl esters with glycerol (Scheme 2).



Scheme 2 Reductive alkylation of a methyl ester **1** with glycerol to the corresponding 1-*O*-alkylglycerol monoether **4** under optimized conditions.

Based on the conditions that we developed for the reductive alkylation of carboxylic acids with (poly)glycerol, methyl valerate **1a** was used as a model substrate.[33]

Optimization of the reaction parameters with methyl esters

As shown in Table 1, the conversion of the starting material was not complete when the optimized conditions for the reductive alkylation of carboxylic acids were applied on methyl valerate **1a** (entry 1).[33] In this first try, glycerol was used as a solvent and a reagent in a molar ratio of 1/40, 1 mol% Pd/C (5%) was used as a catalyst and 10 wt% Amberlyst 35 as a recyclable acid co-catalyst corresponding to 5 mol% H^+. The reaction was performed under 50 bar H_2 pressure and 120 °C, with a stirring speed of 800 rpm (revolutions per minute) for 16 h in a Paar steel autoclave. Under these conditions, 63% of methyl valerate **1a** were converted, with a good selectivity towards GME **4a**, detected at 50% yield (entry 1). As a consequence, the influence of the different parameters was evaluated. With 2 mol% of Pd/C, the conversion was improved, and ether **4a** was observed in 60% yield, ether **5a** in 11% and esters **2a** and **3a** in 6% yield (entry 2). By increasing the amount of Amberlyst 35 to 15 wt%, the conversion of the starting methyl valerate **1a** reached 83%, but the reaction afforded the corresponding GMEs **4a** and **5a** with a lower selectivity (entry 3).

With 4 mol% Pd/C and 30 wt% Amberlyst 35, the conversion of the starting material was complete, but the yield for the expected glycerol monoether **4a** decreased to 46%, whereas the yield for monoglycerides **2a** and **3a** increased to 47% (entry 4). In view of these results, the nature of the acid co-catalyst was changed. In order to help the addition of glycerol to the methyl ester, a more acidic ion exchange resin Amberlyst 36 was used in 10 wt% (5.5 mol% H^+). In this case, the conversion decreased to 80% and ether **4a** was observed in only 24% yield (entry 5). Amberlyst 15 is known for its efficiency in transesterification reactions.[34] In our case, when starting the reaction with 15 wt% Amberlyst 15 and 2 mol% Pd/C, the conversion of methyl valerate **1a** was not complete (81%) and the reaction afforded GMEs **4a** and **5a** in 60% yield. Monoglycerides **2a** and **3a** were obtained in this case in 21% overall yield (entry 6). By increasing the amount of Pd/C to 4 mol% as well as the Amberlyst 15 loading to 30 wt%, the conversion of the substrate was complete, but the selectivity for glycerol monoethers **4a** and **5a** remained unchanged with a 74% overall yield (entry 7). Finally, the best results were obtained when the solid acid co-catalyst was replaced by a strong Brønsted acid soluble in the medium, *i.e.* camphorsulfonic acid (CSA) (4.5 mol% H^+), with 1 mol% Pd/C (5%). Under these conditions, the reaction afforded the 1-*O*-pentylglycerol monoether **4a** in 81% yield and the 2-*O*-pentylglycerol monoether **5a** in 17% yield. The selectivity for GMEs was excellent (99%), and only traces of monoglycerides **2a** and **3a** were detected (entry 8). These results could be explained by a lower solubility of the methyl esters in the glycerol phase than the corresponding carboxylic acids.[33] Thus, the mass transfer problems were fixed with a more homogeneous medium (acid co-catalyst soluble). Besides, it was necessary to add an acid

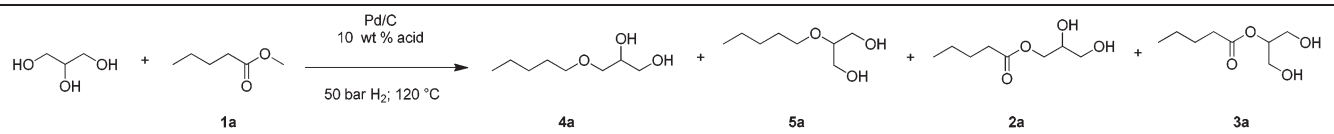
co-catalyst in the reaction medium in order to achieve a good conversion and selectivity for GMEs (entry 9). The reaction without a palladium catalyst afforded only monoglycerides **2a** and **3a** in 84% yield (entry 10). Finally, the H_2 pressure (50 bar), the molar ratio methyl valerate **1a**/glycerol (1/40) as well as the temperature (120 °C) were necessary to have a complete conversion of the starting material to the desired glycerol monoethers **4a** and **5a**. After screening Ru/C, Rh/C and Pt/C supported metals, we found that Pd/C was the most effective catalyst for the reductive alkylation reaction.

In order to evaluate the scope of the method, these last optimized conditions were used for the reductive alkylation of linear and saturated methyl esters with glycerol and diglycerol.

Reductive alkylation of methyl esters with (di)glycerol

As can be seen from the results in Table 2, these conditions were applied for the synthesis of linear, saturated 1-*O*-alkyl (di)glycerol monoethers by catalytic reductive alkylation of glycerol and diglycerol under 50 bar hydrogen pressure in the presence of 1 mol% of Pd/C, 10 wt% of CSA, starting from a

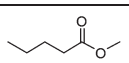
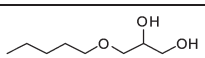
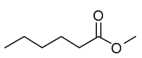
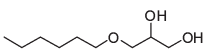
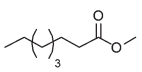
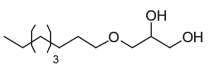
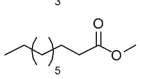
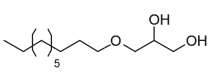
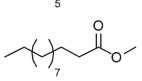
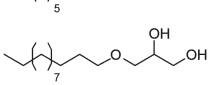
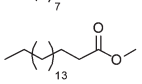
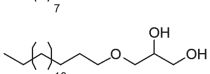
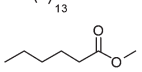
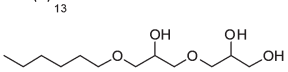
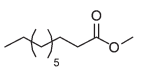
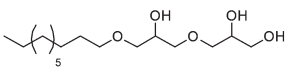
Table 1 Optimization experiments for the reductive alkylation of glycerol with methyl valerate **1a**[a]



Entry	Pd/C	Acid co-catalyst	Conversion[b] (**1a**, %)	Yield[b] (%) Ether **4a**	Ether **5a**	Esters **2a** + **3a**	Selectivity[b] (ethers/esters)
1	1 mol%	Amberlyst 35 (10 wt%)	63	50	9	4	94/6
2	2 mol%	Amberlyst 35 (10 wt%)	77	60	11	6	92/8
3	2 mol%	Amberlyst 35 (15 wt%)	83	51	10	22	73/27
4	4 mol%	Amberlyst 35 (30 wt%)	>99	46	7	47	53/47
5	1 mol%	Amberlyst 36 (10 wt%)	80	24	5	51	36/44
6	2 mol%	Amberlyst 15 (15 wt%)	81	51	9	21	74/26
7	4 mol%	Amberlyst 15 (30 wt%)	>99	62	12	26	74/26
8	1 mol%	Camphorsulfonic acid (10 wt%)	>99	81	17	1	99/1
9	1 mol%	—	26	5	<1	20	23/77
10	—	Camphorsulfonic acid (10 wt%)	85	0	0	84	0/100

[a] Experimental conditions: molar ratio methyl valerate **1a**/glycerol of 1/40, Pd/C (5%), 10 wt% acid co-catalyst, 120 °C, 50 bar H_2, stirring speed = 800 rpm, 16 h. [b] Conversions, yields and selectivity were determined by GC/MS analysis and ^{1}H NMR spectroscopy.

Table 2 Reductive alkylation of mono- and di-glycerol with different methyl esters **1**[a]

Entry	Methyl ester (**1**)		Alcohol/ solvent	Product		Conversion[b] (**1**, %)	Selectivity[c]	Isolated yield (1-*O*-alkylether, %)
1		**1a**	Glycerol		**4a**	>99	85/15	71
2		**1b**	Glycerol		**4b**	>99	83/17	73
3		**1c**	Glycerol		**4c**	>99	81/19	53
4		**1d**	Glycerol		**4d**	>99	80/20	43
5		**1e**	Glycerol		**4e**	>99	83/17	41
6		**1f**	Glycerol		**4f**	>99	82/18	26
7		**1b**	Diglycerol		**6b**	>99	nd[d]	62
8		**1d**	Diglycerol		**6d**	>99	nd[d]	41

[a] Experimental conditions: 1 mol% Pd/C (5%), 10 wt% CSA, 50 bar H_2 pressure, 120 °C, stirring speed = 800 rpm, 16 h. [b] Conversions were determined by GC/MS analysis and ^{1}H NMR spectroscopy. [c] Selectivity between 1-*O*-alkyl and 2-*O*-alkyl (di)glycerol ethers determined by ^{1}H NMR spectroscopy. [d] Selectivity between 1-*O*-alkyl and 2-*O*-alkyl (poly)glycerol monoethers could not be determined.

methyl ester **1** in a substrate/glycerol molar ratio of 1/40 for 16 h.

When starting from methyl valerate **1a** and methyl hexanoate **1b**, the catalytic reductive alkylation of glycerol afforded GMEs **4a** and **4b** in 71% and 73% isolated yields, respectively (entries 1 and 2). With esters bearing longer alkyl chain length like methyl octanoate **1c**, methyl decanoate **1d** and methyl dodecanoate **1e**, the desired 1-*O*-alkylmonoethers **4c**, **4d** and **4e** were isolated in moderate 53%, 43% and 41% yields (entries 3, 4 and 5). Finally, with methyl stearate **1f**, the reaction afforded the corresponding GME **4f** in 26% isolated yield (entry 6). These results could be explained by the formation of dialkylated glycerol products. Indeed, the reaction medium became biphasic in these cases.

Thus, after a first etherification, the monoalkylated product migrated into the methyl ester phase where a second alkylation occurred. As a consequence, the yields for 1-*O*-alkyl glycerol monoethers decreased, whereas the yields for dialkylated glycerol ethers increased. As observed in the case of carboxylic acids, the selectivity towards the formation of 1-*O*-alkyl glycerol monoethers **4** and 2-*O*-alkyl glycerol monoethers **5** ranged from 4/1 to 5/1, independently of the alkyl chain's length. It indicated similarities between both mechanisms as discussed further in this report. Finally, when using diglycerol as a solvent and a reagent with methyl esters **1b** and **1d**, the expected 1-*O*-alkyl diglycerol monoethers **6b** and **6d** were isolated in 62% and 41% yield, respectively, with a complete conversion of the starting FAMEs (entries 7 and 8).

Reductive alkylation of monoglycerides with (di)glycerol

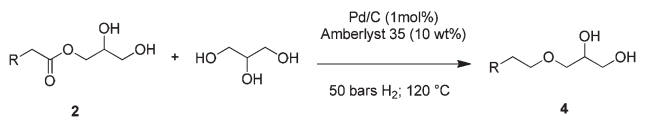
From these results, six main reasons pushed us to apply this reaction to α-monoglycerides (Scheme 3). (1) They can be an intermediate in the reductive alkylation with methyl esters or carboxylic acids; (2) they are more soluble in the glycerol phase than the corresponding methyl esters, because of the presence of the two hydroxyls, thus resolving the mass transfer problems; (3) they might afford the corresponding 1-*O*-alkylglycerol monoethers with an excellent selectivity, since a first transesterification in the glycerol phase is not necessary; (4) like methyl esters, these compounds are biosourced and/or easily available, which makes the process cheaper; (5) they represent an alternative way to form GMEs and can already be valorized as surfactants; (6) to the best of our knowledge, there is no example in the literature for the reduction of an ester function to its corresponding ether by catalytic hydrogenation.

As can be seen in Table 3, optimized conditions developed for the reductive alkylation of methyl esters were applied with α-monoglycerides, but by replacing the expensive Brønsted acid CSA by Amberlyst 35 as a co-catalyst, in order to use the same recyclable catalytic system developed for the reductive alkylation of carboxylic acids.[33] Etherification of glycerol with monoglycerides containing a short alkyl chain (glycerol pentanoate **2a** and glycerol hexanoate **2b**) afforded ethers **4a** and **4b** in 74% and 75% isolated yields, respectively (entries 1 and 2). Thus, these results demonstrated that it was possible to reduce a monoglyceride to its corresponding glycerol monoether under H_2 pressure by using this catalytic system. Interestingly, the selectivities between 1-*O*-alkylglycerol monoethers **4** and 2-*O*-alkylglycerol monoethers **5** were similar to those observed starting from carboxylic acids or methyl esters (4/1 to 5/1), even if the reactions were started with 100% of α-monoglycerides. These results suggested that monoglycerides may not be a key intermediate in the reductive alkylation of glycerol with methyl esters or carboxylic acids, but they are rather first dehydrated to form 5-membered cyclic hemi-*ortho* esters in the glycerol media before being reduced to the corresponding primary and secondary GMEs as explained further in this paper. When starting from glycerol octanoate **2c**, glycerol decanoate **2d**, glycerol dodecanoate **2e**, glycerol stearate **2f** and glycerol oleate **2g** the reaction afforded the corresponding GMEs **4c**, **4d**, **4e** and **4f** in yields of 58%, 49%, 43%, 34% and 35% respectively (entries 3–7). By increasing the alkyl chain length, the selectivity between 1-*O*-alkylglycerol monoethers **4** and 2-*O*-alkylglycerol monoethers **5** increased from 4/1 to 9/1. It is worth mentioning that the yields for GMEs were slightly better than those observed when starting with the corresponding FAMEs (Table 2). Surprisingly, the reductive alkylation of diglycerol with diglycerol hexanoate **7b** and diglycerol decanoate **7d** afforded ethers **6b** and **6d** in lower yields of 35% and 26% without a complete conversion of the substrates (Table 3, entries 8 and 9). These results may be explained by a steric hindrance of the starting ester's diglyceryl moiety.

Mechanism

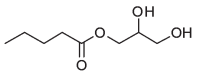
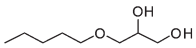
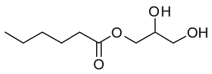
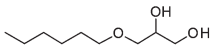
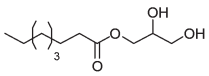
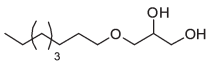
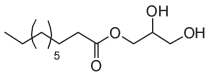
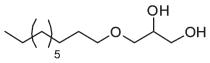
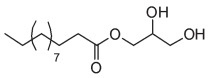
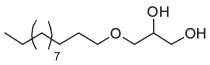
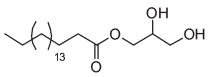
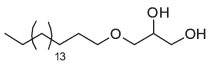
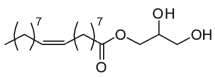
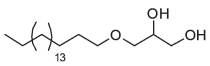
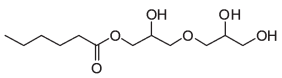
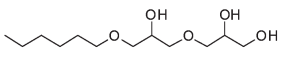
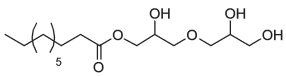
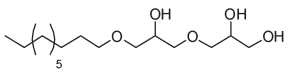
In this present study, the results confirm the mechanism proposed for the reductive alkylation of carboxylic acids, in which the key step of the reaction seems to be the formation of a complex between the Pd/C surface and a 5-membered cyclic hemi-*ortho* ester **9**.[33] The proposed mechanism of this transformation is given in Fig. 1, and explains the 4/1 to 9/1 selectivity between 1-*O*-alkylglycerol monoethers **4** and 2-*O*-alkylglycerol monoethers **5** obtained from methyl esters **1** or α-monoglycerides **2**.

In the case of methyl esters **1**, the acid co-catalyst catalyzes the addition of glycerol to the carbonyl of the substrate. As seen from the result given in Table 1, without an acid co-catalyst the reaction was not efficient enough. Monoglyceride **2** can be formed by dehydration of intermediate **8**. The formation of this glycerol ester is reversible, as indicated by the experiments performed when using monoglycerides **2** as starting material. Finally, the palladium probably promotes the selective cleavage of the primary or secondary C–O bond. In fact, a complex between a 5-membered cyclic hemi-*ortho* ester



Scheme 3 Reduction of an α-monoglyceride **2** in glycerol under optimized conditions.

Table 3 Reductive alkylation of mono- and di-glycerol with different monoglycerides **2**[a]

Entry	Substrate (**2**)		Alcohol/ solvent	Product		Conversion[b] (**2**, %)	Selectivity[c]	Isolated yield (1-*O*-alkylether, %)
1		**2a**	Glycerol		**4a**	>99	81/19	74
2		**2b**	Glycerol		**4b**	>99	86/14	75
3		**2c**	Glycerol		**4c**	>99	87/13	58
4		**2d**	Glycerol		**4d**	>99	89/11	49
5		**2e**	Glycerol		**4e**	>99	89/11	43
6		**2f**	Glycerol		**4f**	>99	89/11	34
7		**2g**	Glycerol		**4f**	>99	89/11	35
8		**7b**	Diglycerol		**6b**	73	nd[d]	35
9		**7d**	Diglycerol		**6d**	61	nd[d]	26

[a] Experimental conditions: 1 mol% Pd/C (5%), 10 wt% Amberlyst 35, 50 bar H_2 pressure, 120 °C, stirring speed = 800 rpm, 16 h. [b] Conversions were determined by GC/MS analysis and ^{1}H NMR spectroscopy. [c] Selectivity between 1-*O*-alkyl and 2-*O*-alkyl (di)glycerol ethers determined by ^{1}H NMR spectroscopy. [d] Selectivity between 1-*O*-alkyl and 2-*O*-alkyl (poly)glycerol monoethers could not be determined.

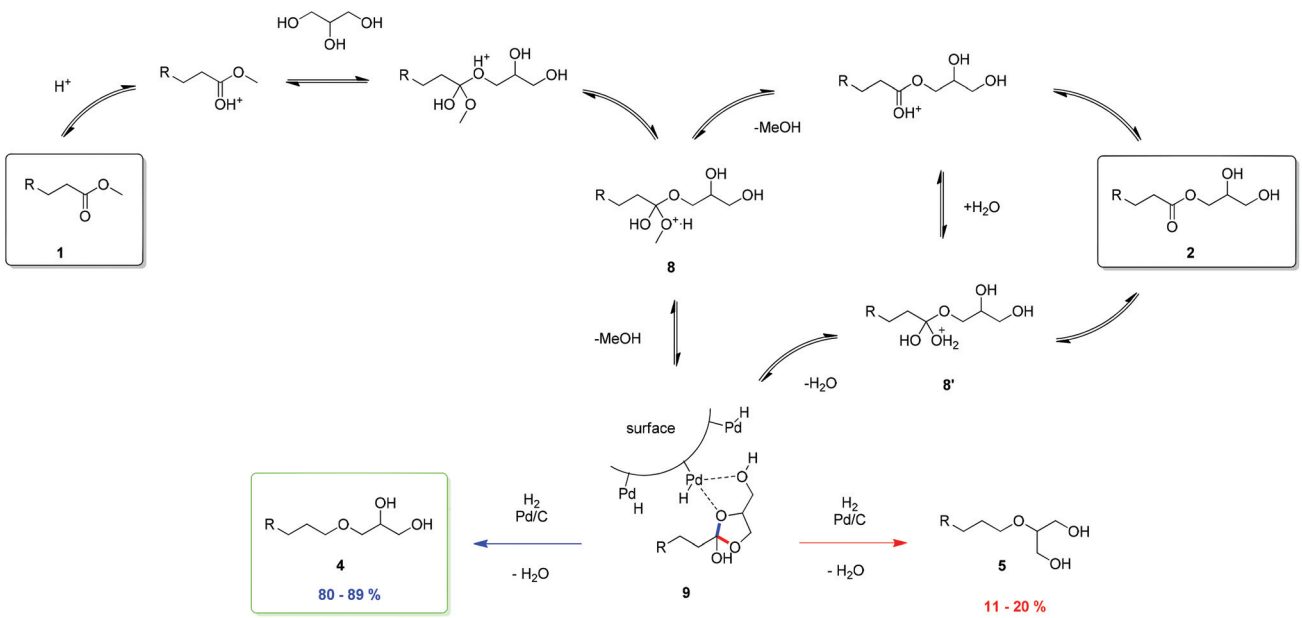


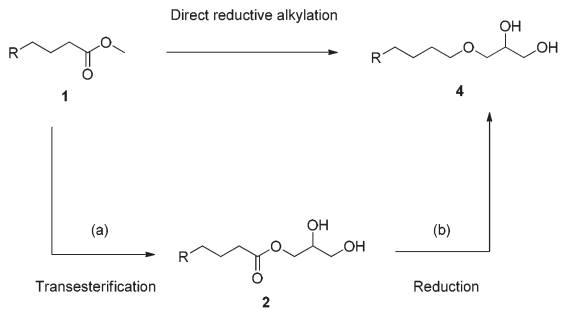
Fig. 1 Proposed mechanism for the reductive alkylation reaction of glycerol with a methyl ester **1** and an α-monoglyceride **2**.

9 and Pd/C could be formed after dehydration of **8** or **8′**. Because of the assistance from the free hydroxyl that coordinates the palladium surface, the cleavage of the secondary C–O bond is easier than the primary one. Finally, the 1-*O*-alkylglycerol monoether **4** is obtained by hydrogenolysis of **9**. According to this mechanism, the selectivity between the

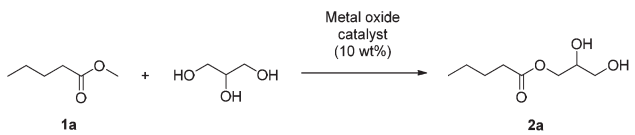
1-*O*-alkylglycerol monoether **4** and the 2-*O*-alkylglycerol monoether **5** ranging from 4/1 to 9/1 is explained.

Catalytic synthesis of primary glycerol mono-esters

Monoglycerides may represent an alternative route to glycerol monoethers starting from methyl esters after a first transesterification step. As a consequence, it was interesting to develop an alternative two step procedure, in which the intermediate monoglyceride **2** was obtained by transesterification of a methyl ester **1** in glycerol and then reduced to its corresponding glycerol monoether (Scheme 4). The synthesis of primary monoglycerides is well described in the literature.[7] The transesterification reaction of methyl esters with glycerol catalyzed by heterogeneous catalysts in the absence of a solvent presents environmental and practical advantages.[35–41] In addition, when using methyl esters as substrates instead of carboxylic acids, no autocatalytic reaction occurs, thus making more efficient the control of the selectivity between primary and secondary esters by the catalyst. Some metal oxides are known for their efficiency in the transesterification of fatty methyl esters with glycerol, like MgO based catalysts.[7,35,37–41] As expected, the most basic metal oxides were generally the most active catalysts in these examples. In order to improve the yield as well as the selectivity for α-monoglycerides **2**, several metal oxide catalysts, which can be removed from the medium by filtration, were evaluated for the transesterification reaction (Scheme 5). All the experiments were performed with methyl valerate **1a**, in order to have good solubility in glycerol. The molar ratio substrate/glycerol was defined at 1/20, to be close to the reductive alkylation optimized conditions. The reaction was performed with 10 wt% of catalyst at 120 °C for 16 h. All the results are summarized in Table 4.



Scheme 4 Two step procedure for the synthesis of glycerol monoethers **4**, starting from a methyl ester **1**, including (a) a first transesterification step followed by (b) a reduction of monoglyceride **2**.



Scheme 5 Transesterification of methyl valerate **1a** with glycerol, catalyzed by a metal oxide catalyst.

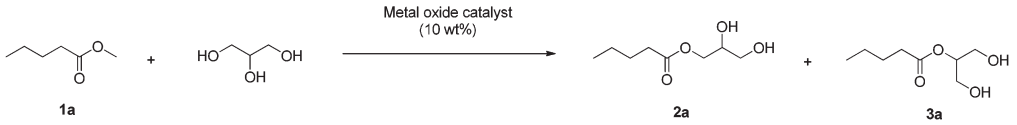
The transesterification reaction was first performed with La_2O_3 and a supported La_2O_3/Al_2O_3 catalyst with a higher surface area. In both cases, the conversion of the starting methyl valerate **1a** was low, and the expected α-monoglyceride **2a** was obtained in 39% and 33% yield, respectively (entries 1 and 2). With CeO_2, the conversion was very low (entry 3). This result was already observed in the literature.[35] With praseodymium oxide, the yield for product **2a** increased to 60% (entry 4). Experiments were performed with hydroxyapatite, Amberlyst 15 and magnesium oxides. In the case of hydroxyapatite, only traces of monoglyceride **2a** were observed (entry 5). With Amberlyst 15, the conversion was around 74%, and ester **2a** was obtained in 69% yield (entry 6). Next, two reactions with magnesium oxides with high surface areas of 230 $m^2\ g^{-1}$ and 600 $m^2\ g^{-1}$ were performed. In fact, Barrault *et al.* have shown that the increase of the catalytic activity of MgO was linked to the specific area.[35] In our case, the reaction afforded the corresponding glycerol ester **2a** in high 88% and 84% yields, respectively (entries 7 and 8). With barium oxide, the conversion of ester **1a** was almost complete, and 91% of glycerol ester **2a** was obtained (entry 9). This result can be explained by the presence of stronger basic sites on BaO than MgO due to a lower electronegativity of barium (0.89) than magnesium (1.31). Finally, the best result was obtained with barium oxide on a basic γ-alumina [BaO (22%); Al_2O_3 (78%)]. The conversion of the starting material **1a** was complete, with an excellent regioselectivity towards the α-monoglyceride **2a**, obtained in 98% yield (entry 10). This mixed metal oxide, generally known for the treatment of NO_x when combined with a noble metal,[42] showed excellent results for the heterogeneous catalytic transesterification of methyl valerate **1a** with glycerol. The effect of the basic sites from both oxides BaO and Al_2O_3 may play an important role in the conversion and the regioselectivity of the reaction. The characterization of the catalyst is in progress in order to understand its high efficiency.

In view of these results, the reaction conditions were optimized with the mixed metal oxide BaO/Al_2O_3.

Effect of the reaction parameters on the transesterification reaction

The influences of the temperature, the molar ratio methyl valerate **1a**/glycerol and the catalyst loading were evaluated in order to determine the best conditions for a solvent free transesterification reaction (Table 5). At 80 °C, the conversion of methyl ester **1a** was low and the corresponding monoglyceride was obtained in 26% yield (entry 1). When the temperature was increased to 100 °C, the conversion of the substrate was complete, and the expected α-monoglyceride **2a** was detected in 99% yield (entry 2), as observed at 120 °C (entry 3). The molar ratio methyl valerate **1a**/glycerol was an important parameter for the selectivity between monoglycerides and diglycerides. By concentrating the reaction medium in a molar ratio methyl ester **1a**/glycerol of 1/10, the conversion slightly decreased to 88%, but the selectivity for the desired ester **2a** remained unchanged (entry 4). At higher concentrations of 1/5 and 1/2, monoester **2a** was obtained in 73% and 36% yields

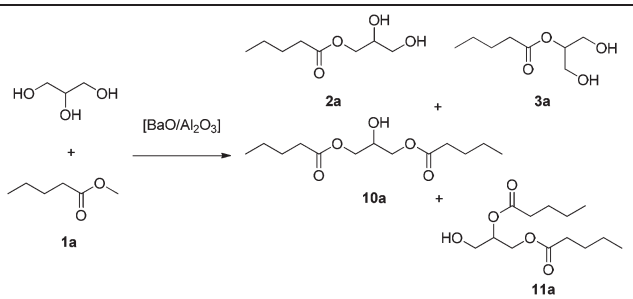
Table 4 Catalyst screening for the transesterification reaction of methyl valerate **1a** with glycerol[a]



Entry	Basic catalyst (10 wt%)	Surface area ($m^2\ g^{-1}$)	Conversion[b] (**1a**, %)	Yield[b] (%) Primary monoglyceride **2a**	Yield[b] (%) Secondary monoglyceride **3a**	Selectivity[b] **2a**/**3a**
1	La_2O_3	70	42	39	3	93/7
2	La_2O_3 (4%)/Al_2O_3 (96%)	190	35	33	2	94/6
3	CeO_2	113	3	3	0	100/0
4	Pr_6O_{11}	3.3	63	60	3	95/5
5	Hydroxyapatite	9	1	1	0	—
6	Amberlyst 15 dry	45	74	69	5	93/7
7	MgO(I)	230	90	88	2	98/2
8	MgO(II)	600	86	84	2	97/3
9	BaO	—	99	91	8	92/8
10	BaO (22%)/Al_2O_3 (78%)	103	>99	98	2	98/2

[a] Experimental conditions: molar ratio methyl valerate/glycerol of 1/20, catalyst (10 wt%), 120 °C, 16 h. [b] Conversions, yields and selectivity were determined by GC/MS analysis and ^{1}H NMR spectroscopy.

Table 5 Influence of the temperature, the molar ratio and the catalyst loading on the transesterification reaction of methyl valerate **1a** with glycerol[a]



Entry	T (°C)	Molar ratio **1a**/glycerol	Catalyst (wt%)	Conv.[b] (**1a**, %)	Yield[b] (%) Ester **2a** (%)	Yield[b] (%) Diesters (**10a** + **11a**, %)
1	80	1/20	10	26	26	0
2	100	1/20	10	>99	>99	0
3	120	1/20	10	>99	>99	0
4	120	1/10	10	88	88	0
5	120	1/5	10	93	73	13
6	120	1/2	10	52	36	12
7	120	1/20	5	>99	>99	0
8	120	1/20	2.5	>99	>99	0
9	120	1/20	1	57	57	0
10	120	1/20	0	0	0	0

[a] Reaction time = 16 h. [b] Conversions and yields were determined by ^{1}H NMR spectroscopy.

whereas diesters **10a** and **11a** were obtained in 13% and 12% yields (entries 5 and 6). In addition, the conversion of the starting material decreased to 93% and 52%, respectively. The ratio 1/20 was kept and the amount of BaO/Al_2O_3 was considered. By decreasing the quantity of the catalyst to 5 wt% and 2.5 wt%, the reaction afforded monoglyceride **2a** in quantitative yield (entries 7 and 8). However, by decreasing the amount to 1 wt%, the conversion dropped to 57% (entry 9). Finally, without catalyst BaO/Al_2O_3, no conversion was observed, confirming that no autocatalytic reaction occurred (entry 10).

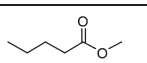
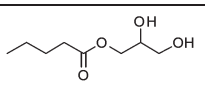
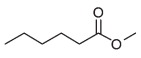
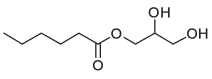
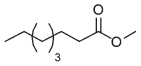
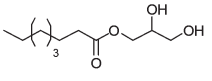
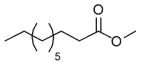
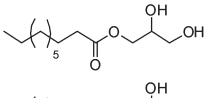
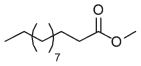
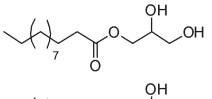
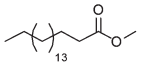
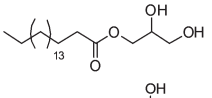
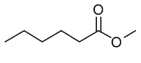
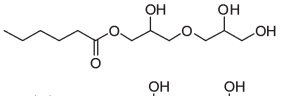
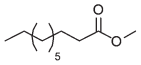
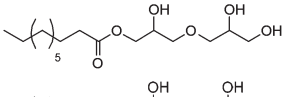
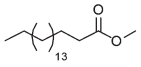
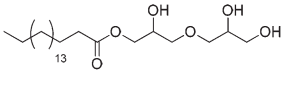
Thus, the optimized conditions were found to be a reaction temperature higher than 100 °C, a molar ratio methyl ester/glycerol of 1/20 and a small amount of mixed metal oxide BaO/Al_2O_3 catalyst (2.5–5 wt%) without any solvent.

Transesterification of methyl esters with glycerol

The optimized conditions were then applied to different FAMEs with various alkyl chain lengths. The reactions were performed with a molar ratio methyl ester/glycerol of 1/20, with 5 wt% of BaO/Al_2O_3 and for 16 h. The reaction temperature was increased with the alkyl chain length, in order to improve the conversion after 16 h, as shown in Table 6.

The transesterification of methyl valerate **1a** and methyl hexanoate **1b** with glycerol afforded the corresponding monoglycerides **2a** and **2b** in quantitative isolated yields (entries 1 and 2). This methodology was then applied to methyl esters with longer alkyl chains at higher temperatures in order to increase the solubility of glycerol in the FAME phase. Reaction with methyl octanoate **1c** afforded glycerol ester **2c** in 96% isolated yield (entry 3). In this case, 3% of diglycerides were obtained. With methyl decanoate **1d**, the conversion decreased slightly to 91%, and the selectivity for the expected monoglyceride **2d** was lower. Indeed, compound **2d** was isolated in 79% yield, and 12% of diglycerides were obtained (entry 4). When methyl dodecanoate **1e** was used as a substrate, the conversion decreased to 88%, and ester **2e** was obtained in 71% isolated yield (entry 5). In this example, the amount of diglycerides increased to 17%. Finally, with methyl stearate **1f** the reaction temperature had to be increased to 200 °C and the

Table 6 Transesterification of methyl esters **1** with glycerol or diglycerol[a]

Entry	Substrate (**1**)		Alcohol/solvent	Temp. (°C)	Product		Conv.[b] (**1**, %)	Isolated yield (%) α-Monoglyceride	Isolated yield (%) Diesters
1		**1a**	Glycerol	100		**2a**	>99	99	0
2		**1b**	Glycerol	120		**2b**	>99	99	0
3		**1c**	Glycerol	140		**2c**	99	96	3
4		**1d**	Glycerol	160		**2d**	91	79	12
5		**1e**	Glycerol	180		**2e**	88	71	17
6[c]		**1f**	Glycerol	200		**2f**	94	55	45
7		**1b**	Diglycerol	130		**7b**	>99	83	17
8		**1d**	Diglycerol	160		**7d**	79	54	25
9[c]		**1f**	Diglycerol	200		**7f**	96	53	47

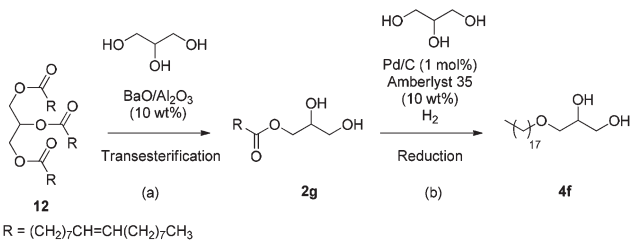
[a] Experimental conditions: molar ratio methyl ester/glycerol of 1/20, BaO/Al_2O_3 (5 wt%), 120 °C, 16 h. [b] Conversions were determined by GC/MS analysis and ^1H NMR spectroscopy. [c] Reaction time = 36 h.

corresponding monoester **2f** was isolated in 55% yield (entry 6). This fall of conversion and growth of diglyceride yields were explained by a lower solubility of the substrates with longer alkyl chains in the glycerol phase, leading to a consecutive reaction to form diglycerides. The reaction was finally performed with diglycerol as a reagent and a solvent, in order to synthesize diglycerol monoesters. Transesterification of methyl hexanoate **1b** with diglycerol afforded the corresponding diglycerol ester **7b** in 83% isolated yield (entry 7). Similarly, reaction of methyl decanoate **1d** with diglycerol afforded ester **7d** in 54% isolated yield (entry 8). Reaction with methyl stearate **1f** at 200 °C gave monoester **7f** in 53% isolated yield (entry 9).

All (di)glycerol monoesters were isolated before being used as substrates in a reductive alkylation reaction with glycerol under optimized conditions, as shown in Table 3.

Transesterification tests of high oleic sunflower refined oil with glycerol

The preparation of monoglycerides by direct transesterification of oleic sunflower oil in the presence of heterogeneous basic catalysts like MgO and MgO/Al_2O_3 was also reported in the literature.[43,44] It was then interesting to test the mixed metal oxide catalyst BaO/Al_2O_3 in the glycerolysis of oleic refined oil **12** (≥90% of triolein), in order to obtain the corresponding monoester **2g** that will be reduced in a second step to GME **4f**



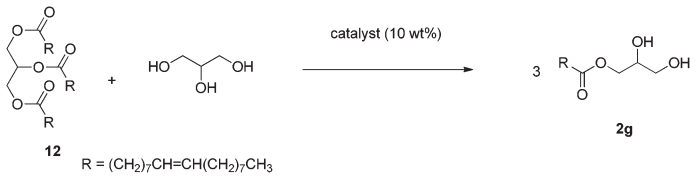
Scheme 6 Two step procedure for the synthesis of 1-*O*-alkylglycerol monoether **4f**, starting from triolein **12**, consisted of (a) a first transesterification step followed by (b) a reduction of monoglyceride **2g**.

by catalytic hydrogenation with Pd/C and Amberlyst 35 (Scheme 6).

The glycerolysis of triolein with glycerol to form monoolein with BaO/Al_2O_3 was first performed at 120 °C without any solvent in a sealed tube, using a molar ratio oleic oil/glycerol of 1/20 and 10 wt% of catalyst. The results are shown in Table 7.

Under these conditions, the conversion of triglyceride **12** was only around 5% after 24 h (entry 1). When using methyl-THF as a co-solvent, the conversion of the substrate increased slightly to 10% and the reaction gave the corresponding α-monoglyceride **2g** in 7% yield (entry 2). With a soluble

Table 7 Transesterification of refined triolein with glycerol and diglycerol[a]

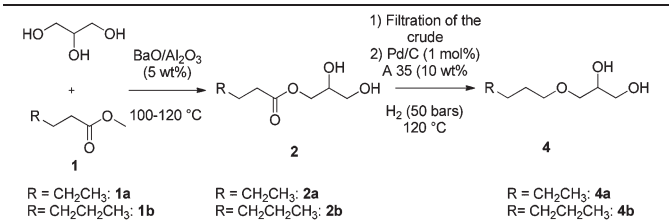


Entry	Alcohol/solvent	Co-solvent	Temp. (°C)	Catalyst	Conversion[b] (**10**, %)	Isolated yields (%) α-Monoester	Diesters
1	Glycerol	—	120	BaO (22%)/Al_2O_3 (78%)	<5	4	1
2	Glycerol	Methyl THF (15 eq.)	120	BaO (22%)/Al_2O_3 (78%)	10	7	3
3	Glycerol	—	200	K_2CO_3	95	68	25
4	Glycerol	—	200	CaO	90	66	24
5[c]	Glycerol	—	200	BaO (22%)/Al_2O_3 (78%)	>99	51	49
6[c]	Glycerol	1,2,3-TMP (15 eq.)	200	BaO (22%)/Al_2O_3 (78%)	>99	88	12
7[c]	Diglycerol	—	200	BaO (22%)/Al_2O_3 (78%)	>99	41	50
8[c]	Diglycerol	1,2,3-TMP (15 eq.)	200	BaO (22%)/Al_2O_3 (78%)	>99	63	22

[a] Experimental conditions: molar ratio oleic sunflower oil/glycerol of 1/20, catalyst (10 wt%), 24 h. [b] Conversions were determined by ^{1}H NMR spectroscopy. [c] Reaction time = 48 h.

catalyst K_2CO_3 and at higher temperature (200 °C), the conversion of triolein reached 95%, and 68% of the corresponding monoester **2g** was isolated, in agreement with literature data concerning soluble base catalysts[45] (entry 3). With 10 wt% CaO, previously calcinated for 3 h at 600 °C, the transesterification reaction afforded monoglyceride **2g** in 66% isolated yield (entry 4). In this case, the catalyst was slightly soluble in the medium. Finally, with BaO/Al_2O_3, the conversion was complete after 48 h at 200 °C, and 51% of monoolein **2g** could be isolated (entry 5). When 1,2,3-trimethoxypropane (1,2,3-TMP) as a co-solvent was added in 15 equivalents, monoolein (**2g**) was isolated in 88% yield (entry 6). This solvent allowed better solubility of the oleic refined oil **12** in the glycerol phase, and its high boiling point allowed us to perform the reaction in a sealed reactor at higher temperature (200 °C). In addition, 1,2,3-TMP was recycled after the reaction by evaporation of the crude under reduced pressure. Finally, with diglycerol as a solvent and a reactant, the corresponding monoester of diglycerol **7g** was isolated in 41% yield (entry 7). By performing the same reaction in 1,2,3-trimethoxypropane, the desired monoester of diglycerol **7g** was isolated in 63% yield (entry 8).

Table 8 Transesterification[a] of methyl esters **1a** and **1b** with glycerol followed by reduction under H_2 [b] with no intermediate purification

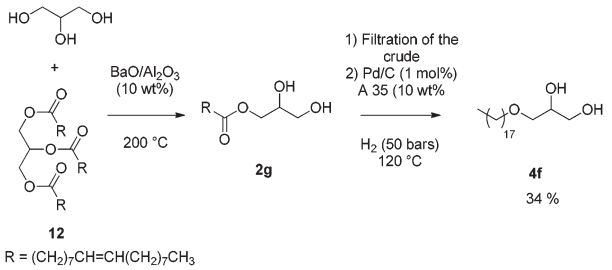


Entry	Transesterification[a] Conversion[c] (**1**, %)	Yield[c] (**2**, %)	Reduction[b] Conversion[c] (**2**, %)	Yield[c] (**4**, %)	Overall isolated yield (**4**, %)
1	>99 (**1a**)	99 (**2a**)	>99 (**2a**)	82 (**4a**)	81 (**4a**)
2	>99 (**1b**)	98 (**2b**)	>99 (**2b**)	82 (**4b**)	80 (**4b**)

[a] Experimental conditions: molar ratio methyl valerate/glycerol of 1/40, BaO/Al_2O_3 (5 wt%), 100 °C, 16 h. [b] Experimental conditions: crude monoglyceride **2** + glycerol, 1 mol% Pd/C (5%), 10 wt% Amberlyst 35, 50 bar H_2 pressure, 120 °C, 16 h. [c] Conversions and yields were determined by GC/MS analysis and ^{1}H NMR spectroscopy.

Transesterification and reductive alkylation with no intermediate purification

In order to have a process as cheap and environmentally friendly as possible and considering the best conditions found for the transesterification reaction as well as the reductive alkylation reaction with methyl valerate **1a**, a short procedure for the synthesis of the desired 1-*O*-pentylglycerol ether **4a** in two steps with no intermediate purification of monoglyceride **2a** was realized. After a first transesterification step catalyzed by 5 wt% of BaO/Al_2O_3, a molar ratio methyl valerate **1a**/glycerol of 1/40, at 100 °C for 16 h, the medium was filtered off on a Millipore filter. The crude was then engaged in a steel autoclave, and the reductive alkylation was performed by adding 1 mol% Pd/C (5%), 10 wt% Amberlyst 35, under 50 bar H_2 pressure for 16 h. After the reaction, the glycerol monoether **4a** was obtained in 81% overall yield after the two steps (Table 8, entry 1). This result can be compared to the direct etherification of methyl valerate **1a** under the same conditions, in which the corresponding ether was detected in 50% yield (Table 1, entry 1). This result was similar to those observed when using the CSA as a co-catalyst in the direct etherification reaction of methyl valerate **1a** with glycerol, in which the



Scheme 7 Transesterification of triolein **12** with glycerol followed by reduction under H_2 pressure with no intermediate purification.

1-*O*-pentylglycerol ether **4a** was obtained in 81% yield (Table 1, entry 8). The same methodology was performed with methyl hexanoate **1b**: after the transesterification step followed by the reductive alkylation, the 1-*O*-hexylglycerol monoether **4b** was obtained in 80% yield after the two steps (Table 8, entry 2). Finally, the two step procedure with no intermediate purification was applied on sunflower oleic refined oil **12** (Scheme 7). The best conditions found for the transesterification of the starting triglyceride without a co-solvent (Table 7, entry 5) and the reductive alkylation of monoolein **2g** (Table 3, entry 7) were used in that case. The corresponding 1-*O*-stearylglycerol monoether **4f** was isolated in 34% overall yield after the two steps.

Thus, the process in two steps could be very interesting from both environmental and industrial points of view, with the use of two heterogeneous catalytic systems.

Conclusion

Two new pathways for an easy, cheap and environmentally friendly route to glycerol monoethers were reported in this paper. The direct etherification of glycerol with methyl esters and α-monoglycerides was performed under mild conditions, without any solvent, a small amount of Pd/C catalyst and a strong Brønsted acid as a co-catalyst in the case of methyl esters and an acid ion exchange resin Amberlyst 35 as a co-catalyst in the case of α-monoglycerides. With methyl esters, an alternative procedure in two steps was developed: a transesterification step with glycerol catalyzed by a small amount of a mixed metal oxide BaO/Al_2O_3 followed by the reduction of the corresponding α-monoglyceride under optimized conditions. The same procedure was successfully applied when oleic sunflower refined oil was used as a substrate.

A mechanistic consideration of the reductive alkylation reaction with methyl esters and the catalytic reduction under H_2 pressure with monoglycerides was proposed. The results led us to conclude that the key point in both mechanisms was the formation of a heterogeneous complex between the Pd/C surface and a 5-membered cyclic hemi-*ortho* ester, which explained the selectivity towards the 1-*O*-alkylglycerol ether. The catalytic reduction of α-monoglycerides is then certainly the first example of an ester function reduction to its corresponding ether under H_2 pressure.

To the best of our knowledge, with the reductive alkylation of carboxylic acids and glycerol that we reported recently, this is the first catalytic route describing the straightforward direct etherification of glycerol with these substrates. These two processes open an alternative route at industrial scales for the production of bio-based surfactants.

Experimental

General

All reagents were used as received from the chemical company. Glycerol, 99%, *Reagentplus®* was purchased from Sigma-Aldrich, diglycerol 80% from TCI, Pd/C (5%) on activated carbon, reduced and dried (Escat 1431) from Strem Chemicals. Oleic sunflower refined oil (≥90%) was provided by our industrial partner and was used without further purification. Amberlyst 15 dry, Amberlyst 36 dry, Amberlyst 35 dry were bought from Rohm and Haas and the methyl esters were supplied by Acros, Sigma-Aldrich, Alfa Aesar and TCI. The BaO/Al_2O_3 catalyst was prepared by an incipient-wetness impregnation method.[46] Reductive alkylation reactions were performed in a 300 ml steel Parr autoclave equipped with a mechanical stirrer.

General procedure for reductive alkylation of glycerol with a methyl ester or a monoglyceride using H_2 as a reducing agent

Glycerol (713 mmol, 40 eq.) and methyl ester or α-monoglyceride (17.6 mmol, 1 eq.) were mixed in a 300 ml steel autoclave at room temperature. CSA or Amberlyst 35 (10 wt%) and Pd/C (1 mol% Pd) were then added. The autoclave was first flushed with argon then with hydrogen four times. The solution was stirred (800 rpm) at 120 °C under 50 bar hydrogen for 16 h. The reaction mixture was then dissolved in absolute ethanol and filtered (Millipore Durapore filter 0.01 μm). The solvents were concentrated under reduced pressure and the organic products were extracted four times with dichloromethane or toluene. The crude products were finally purified by silica column chromatography (eluent: cyclohexane–ethyl acetate = 4 : 1 ∼ 1 : 0 for short alkyl chain lengths; cyclohexane–ethyl acetate = 9 : 1 ∼ 1 : 2 for long alkyl chain length).

General procedure for transesterification of glycerol with methyl ester or triolein

Glycerol (350 mmol, 20 eq.) and methyl ester (17.5 mmol, 1 eq.) were added in a round bottom flask under an inert atmosphere (argon). The mixture was heated to temperature and the mixed metal oxide BaO/Al_2O_3 was added (5 wt%). After 16 h, the reaction mixture was diluted in a minimum of absolute ethanol and filtered off (Millipore Durapore filter 0.01 μm). The solvents were concentrated under reduced pressure and the organic products were extracted three times with dichloromethane or toluene. The crude was finally purified by silica column chromatography to afford the desired monoglyceride (eluent: cyclohexane–ethyl acetate = 4 : 1 ∼ 1 : 0 for short alkyl chain length; cyclohexane–ethyl acetate = 5 : 1 ∼ 1 : 2 for long alkyl chain length).

For the transesterification reactions of triolein with glycerol and diglycerol, the reaction was performed in sealed tubes, under an inert atmosphere of argon. Monoolein **2g** was purified by column chromatography (silica gel; eluent: cyclohexane–ethyl acetate = 5 : 1 ~ 1 : 2) and for the monoester of diglycerol **7g**, eluent was dichloromethane–methanol 99/1 ~ 9/1.

All the product characterizations (^{1}H NMR, ^{13}C NMR, IR, HRMS) are disclosed in the ESI.†

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