Research Article

Reduction of high oleic sunflower oil to glyceryl trioleyl ether

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"High oleic" sunflower oil was converted into the respective triether using $InBr_3$ or $GaBr_3$ as catalysts and triethylsilane or 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agent in solvent-free reactions. $GaBr_3$/TMDS was found to be the most efficient reduction system enabling to carry out the reduction at room or moderately elevated temperature using stoichiometric amounts of TMDS and low amounts of the catalyst (0.005–0.01 eq. Ga/ester functionality). The conversion of the starting material was 100% yielding 80% of glyceryl trioleyl ether **2**.

1 Introduction

Glyceryl trialkyl ethers are of interest for industrial applications, e.g. in the cosmetic and lubricant area because they are characterized by lower sensitivity against hydrolysis as well as, in general, lower melting points and viscosity compared to the corresponding triglycerides [1, 2]. Williamson ether syntheses which are performed with polyols such as glycerol and, e.g. halo alkanes as starting materials are technically most demanding giving the respective ethers in low yields [1–3]. Müller [3] studied the direct trialkylation of glycerol with saturated alkyl bromides in the presence of NaOH to give the glyceryl trialkyl ethers in about 30% yield. Baumann synthesized some saturated glyceryl trialkyl ethers by alkylation of 1-glyceryl monoalkyl ethers with alkyl methansulfonates in about 40% yield [2]. Glyceryl trioleyl ether **2** was synthesized by alkylation of 2-*O*-oleyl glycerol with oleyl methanesulfonate in 96% yield [4]. Interestingly, [14]C- as well as ^{3}H-labeled glyceryl trioleyl ether [5, 6] were synthesized and used as non-hydrolizable triolein in biological studies [7, 8].

Mangold stated more than 30 years ago: "Ideally, triacylglycerols should be converted directly into trialkylglycerols" [9]. At that time the reduction of tristearin and trimyristin with $LiAlH_4$ in the presence of BF_3.etherate was claimed [10]. However, the yields of the obtained triethers were only 3.1 and

3.4%, respectively. The main products were the corresponding alcohols. Thus, it should be of great value to develop a simple and more sustainable method for a cost-efficient and competitive reduction of triglycerides to give the respective ethers in good yield and avoiding the over reduction to alcohol.

The reduction of carboxylic acid esters of monoalcohols to the corresponding ethers has been shown to be more feasible. There are described direct [11–15] as well as two-step reductions [16–18]. However, in all cases the yields are rather moderate. Recently, the metal-catalyzed reduction of carboxylic acid esters to ethers by hydrosilanes has attracted considerable interest. Sakai et al. [19, 20] reported on the $InBr_3$-catalyzed reduction by hydrosilanes to give the respective ethers in moderate to excellent isolated yields using chloroform as solvent at 60°C and 0.05 eq. of catalyst and 4 eq. of Et_3SiH, a twofold excess, as reductant. Other indium(III) compounds such as $InCl_3$ were not catalytically active. This method is of special interest because relatively mild reaction conditions can be used and functional groups such as C,C-double bonds, halo- and nitro-substituents contained in the starting material are tolerated. Methyl 10-undecenoate and methyl oleate were reduced to the respective ethers in good to moderate yields [20]. Beller and coworkers [21] described the $Fe_3(CO)_{12}$-catalyzed reduction with 1,1,3,3-tetramethyldisiloxane (TMDS) in toluene as solvent at 100°C using 0.1 eq. of catalyst and 3 eq. of TMDS, a threefold excess. All these protocols have not been applied to triglycerides with the exception of $LiAlH_4$/BF_3.etherate giving most unsatisfactory results as discussed above [11]. The synthesis of 1-*O*-monoalkylethers of glycerol by catalytic reductive alkylation of carboxylic acids and esters,

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respectively, was recently reported [22, 23]. TMDS as reductant and GaBr$_3$ and InBr$_3$, respectively, as catalyst were used for the reduction of fatty acids to alcohols [24].

We used GaBr$_3$ as catalyst using TMDS as reductant for methyl oleate and other fatty esters and obtained quantitative conversion and almost quantitative yields of the fatty ethers [25]. Moreover, we showed that also triglycerides such as tributyrin and glyceryl tri-10-undecenoate can be quantitatively reduced to give the respective glyceryl triethers in good to moderate isolated yields. The reducing agent TMDS is used in stoichiometric amounts and is polymerized to high molecular polydimethylsiloxane. The products can easily be isolated by simple distillation. Moreover, TMDS is being produced as a by-product of the silicon industry, and is an inexpensive, commercially available reductant [26].

We applied the protocol of Sakai et al. [20] to "high oleic" sunflower oil **1** and observed an almost complete conversion of the triglyceride after a reaction time of 1 h. The yield of glyceryl trioleylether **2** was about 42% after liquid chromatography [27]. Moreover, we applied the system GaBr$_3$/ TMDS on triester **1** obtaining quantitative conversion and high yield of triether **2**.

Herein, we report the full experimental details of this work using InBr$_3$ and GaBr$_3$ as catalyst and Et$_3$SiH and TMDS as reductant.

2 Materials and methods

General: "High oleic" (HO-) sunflower oil (91.2% oleic acid, 3.0% palmitic acid, 2.8% linoleic acid, 1.9% stearic acid) **1** was purchased from T + T Oleochemie GmbH, Germany. InBr$_3$, GaBr$_3$, triethylsilane and TMDS were obtained from Aldrich. HO sunflower oil was dried over molecular sieve and treated with silica gel to remove polar impurities. All the other chemicals were used as obtained.

Analytical Equipment: ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a Bruker DRX 500 spectrometer at 300 K using residual non-deuterated solvent (^{1}H NMR) or CDCl$_3$ (^{13}C NMR) as internal standards. Mass spectra were recorded on a Finnigan LCQ (Thermo Finnigan, San José, CA, USA) quadrupole ion trap mass spectrometer equipped with a standard electrospray ion source, which was used with a stainless steel metal capillary (110 mm id, 240 mm od, 120.5 mm of length, Metal Needle Kit, Thermo Finnigan). "Kugelrohr" distillation apparatus was purchased from Büchi Labortechnik AG, Flawil, Switzerland.

TLC was performed on silica gel TLC cards (silica gel, layer thickness 0.20 mm, Merck). Compounds were visualized by 2 N sulfuric acid/heat. Silica gel 60 (70–230 mesh, Merck) was used for column chromatography. For the ESI– MS experiments the spots of the products were directly extracted from the TLC layer using an apparatus and method developed by Luftmann [28] and transferred online to the ESI mass spectrometer.

All products were unambiguously identified by ^{1}H and ^{13}C NMR and partially by TLC–ESI-MS.

2.1 Reduction of HO sunflower oil

2.1.1 Reduction with InBr$_3$/triethylsilane

a. A mixture of HO-sunflower oil **1** (0.89 g, 1.0 mmol) and InBr$_3$ (53 mg, 0.15 mmol) was degassed in a two-necked round bottom flask and then flushed with nitrogen (3 cycles). After dropwise addition of triethylsilane (1.92 mL, 12 mmol) the sample was heated in nitrogen atmosphere to 60°C. Some gas formation, which stopped after few minutes was observed and a yellow solid precipitated. The reaction was followed by TLC (petroleum ether/diethyl ether 8:1). After 1.5 h HO-sunflower oil was completely transformed. After additional 1.5 h the mixture was cooled to RT, 10 mL of water and of dichloromethane, respectively, were added, and stirred at RT over night. The layers were separated in a separating funnel and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtrated and the solvent was removed in vacuo.

The TLC of the residue (1.45 g) showed at least six products. The mixture was analyzed by TLC–MS (ESI-MS): glyceryl trioleylether **2** (ESI-pos: $m/z = 865$ (M + Na$^+$), glyceryl monooleyl ether dioleate **3** (ESI-pos: $m/z = 893$ (M + Na$^+$), glyceryl dioleyl ether monooleate **4** (ESI-pos: $m/z = 1735$ ($2 \times 856 +$ Na$^+$), glyceryl mono-triethylsilyl dioleylether **5** (ESI-pos: $m/z = 729$ (M + Na$^+$), oleyl alcohol **6** and oleyl triethylsilyl ether **7a** were identified.

b. The reaction described in a) was carried out with triglyceride **1** (20 g, 22.47 mmol), InBr$_3$ (0.238 g, 0.67 mmol) and triethylsilane (43.2 mL, 269.7 mmol). The reaction mixture was stirred over night at 60°C to give after 16 h complete conversion of triglyceride **1** (TLC). The obtained product mixture was comparable to that described above. The sample was cooled to RT, excess of Et$_3$SiH was removed in vacuo and the residue was dissolved in petroleum ether (45 mL). The precipitated solid was removed by filtration and the solvent was evaporated to give a residue of 31 g. It was subjected to "Kugelrohr" distillation (65–180°C, 5×10^{-3} mbar) to remove hexaethyldisiloxane, oleyl alcohol und oleyl triethylsilyl ether and to give a residue of 18.3 g. An aliquot of 8.05 g (44 weight %) was purified by column chromatography (silica gel 60, petroleum ether/diethyl ether = 9:1) to obtain 4.1 g of isolated product that contained, as shown by ^{1}H NMR, approximately 12% of protons derived from triethylsilyl species. Thus, the yield of **2** was calculated to be 42%. Additionally, 1.1 g (12%) of glyceryl monooleylether-1,3-dioleate **3** was

isolated. The yields of **2** and **3** were calculated assuming 100% glyceryl trioleate. Products **2** and **3** were identified by ^1H and ^{13}C NMR spectroscopy.

Glyceryl trioleyl ether **2**: ^1H NMR (500.1 MHz, CDCl$_3$): $\delta = 5.35$ (dt, $\mathcal{J} = 10.9$, 5.5 Hz, CH=CH, 6 H), 3.49 (m, OCH and 5× OCH$_2$, 11 H), 2.01 (6× dt, $\mathcal{J} = 6.9$, 6.9 Hz, CH$_2$CH=CH, 12 H), 1.57 (3× tt, $\mathcal{J} = 7.5$, 6.7, 6.6 Hz, OCH$_2$CH_2, 6 H), 1.28 (m, CH$_2$), 0.89 (3× t, $\mathcal{J} = 7.0$ Hz, CH$_3$, 9 H) ppm.
^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 129.9$ and 129.8, 77.9 (OCH), 71.6 (2× OCH$_2$), 70.8 (2× OCH$_2$), 70.6 (OCH$_2$), 31.9 (OCH$_2$CH$_2$), 30.1, 29.8=29.1, 27.2, 26.1, 22.7 (3× CH$_2$CH$_3$), 14.1 (3× CH$_3$) ppm [4].

Glyceryl monooleylether-1,3-dioleate **3**. Characteristic signals are given: ^1H NMR (500.1 MHz, CDCl$_3$): $\delta = 5.35$ (dt, $\mathcal{J} = 10.9$, 5.5 Hz, CH=CH, 6 H), 3.49 (m, OCH and 5× OCH$_2$, 11 H), 2.01 (6× dt, $\mathcal{J} = 6.9$, 6.9 Hz, CH$_2$CH=CH, 12 H), 1.57 (3× tt, $\mathcal{J} = 7.5$, 6.7, 6.6 Hz, OCH$_2$CH_2, 6 H), 1.28 (m, CH$_2$), 0.89 (3× t, $\mathcal{J} = 7.0$ Hz, CH$_3$, 9 H) ppm.
^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 173.3$ and 173.0 (C=O), 130.0, 129.9, 129.8, and 129.7, 71.7, 70.1, 69.0, 62.7, 34.3, 34.1, 31.9 (OCH$_2$CH_2) ppm.

2.1.2 Reduction with InBr$_3$/1,1,3,3-tetramethyldisiloxane

A mixture of triglyceride **1** (0.89 g, 1.0 mmol) and InBr$_3$ (53 mg, 0.15 mmol) was degassed in a 2-necked round bottom flask and then flushed with nitrogen (three freeze–thaw cycles). After dropwise addition of TMDS (1.07 mL, 804 mg, 6 mmol) the colorless mixture changed to a cloudy yellow-orange liquid. The sample was heated in nitrogen atmosphere to 60°C. The reaction was followed by TLC (petroleum ether/diethyl ether 8:1) showing after 30 min complete transformation of triester **1**.

The mixture was cooled to RT, 5 mL of diethyl ether were added and the sample was filtered over silica gel using diethyl ether (100 mL) as eluent. After evaporation of the solvent the residue (1.28 g) was subjected to column choromatography (petroleum ether/diethyl ether = 8:1) giving 410 mg (49%) of pure glyceryl trioleyl ether **2**. Moreover, 190 mg (0.3 mmol, 10%) of oleylsilylether **7b** containing on average five units of dimethyl siloxane groups was isolated. Additionally, oleyl alcohol **6** was formed as minor product.

2.1.3 Reduction with GaBr$_3$/1,1,3,3-tetramethyldisiloxane

a. A mixture of HO-sunflower oil **1** (10 g, 11.3 mmol) and GaBr$_3$ (60.0 mg, 0.19 mmol, 1.72%) was degassed in a 2-necked round bottom flask, flushed with nitrogen (two freeze–thaw cycles) and cooled in an ice bath to −5°C. After dropwise addition of TMDS (18.0 mL,

101.6 mmol) the ice bath was removed and some formation of gas was observed. The sample was stirred at RT over night to give complete conversion of triglyceride **1** (TLC: petroleum ether/diethyl ether 9:1). After addition of 100 mL of toluene and 70 mL of aqueous NaOH (2 M) the sample was stirred again over night, and then washed until neutral and dried over Na$_2$SO$_4$. After filtration the solvent was evaporated in vacuo. ^1H and ^{13}C NMR spectra of the residue showed that about 80% of **2** and about 20% of glyceryl dioleylether **5b** was formed. The residue (15.7 g) was subjected to column chromatography (3 columns) using petroleum ether/diethyl ether = 9.5:0.5 as eluent to give a total of 4.7 g (50%) of pure triether **2**.

b. A mixture of HO-sunflower oil **1** (1.77 g, 2 mmol) and GaBr$_3$ (19 mg, 0.06 mmol, 1%) was reacted with TMDS (1.08 mL, 3.05 mmol) as above. After 20 h of reaction time **1** as well as the intermediates **3** and **4**, formed during the reaction, were completely converted. ^1H and ^{13}C NMR of the reaction mixture showed a yield of **2** of about 80% and about 20% of minor product **5b** and 7% of oleyl alcohol **7b**.

c. A mixture of HO-sunflower oil **1** (10 g, 11.3 mmol) and GaBr$_3$ (105.0 mg, 0.34 mmol, 3.0%) was degassed in a 2-necked round bottom flask, flushed with nitrogen (two freeze–thaw cycles) and cooled in an ice bath to −5°C. After dropwise addition of TMDS (6.6 mL, 37.0 mmol) the ice bath was removed and a formation of gas was observed. The sample was stirred at RT until the formation of gas had stopped (10 min) and was then stirred at 60°C (4 h) to give complete conversion of triglyceride **1** as well as of the intermediates **3** and **4**. Some oleyl alcohol **6** and silylated oleyl alcohol **7b** was detected as minor products by TLC (petroleum ether/diethyl ether 9:1). ^1H and ^{13}C NMR of the reaction mixture showed a yield of about 80% of **2**, 7% of **7b** and 20% of **5b**. An aliquot of 25% of the reaction mixture was extracted with acetone. Polydimethylsiloxane was completely separated giving 2.1 g (93%) of a mixture of about 80% of **3**, 20% of **5b**, and 7% of **7b**.

3 Results and discussion

We modified the protocol of Sakai used for the reduction of methyl oleate [20] and applied it for the reduction of HO-sunflower oil **1**. It was shown that the InBr$_3$-catalyzed reduction of triglyceride **1** could be performed without any solvent. The reaction mixture (**1**:triethysilane:InBr$_3$ = 1:12:0,15) having a ratio of hydride to ester functions of 4:1 was stirred at 60°C and followed by TLC. After a reaction time of 1.5 h triglyceride **1** was completely converted. The TLC-card showed at least six new compounds, which were analyzed by TLC–MS (ESI-MS). The main product was
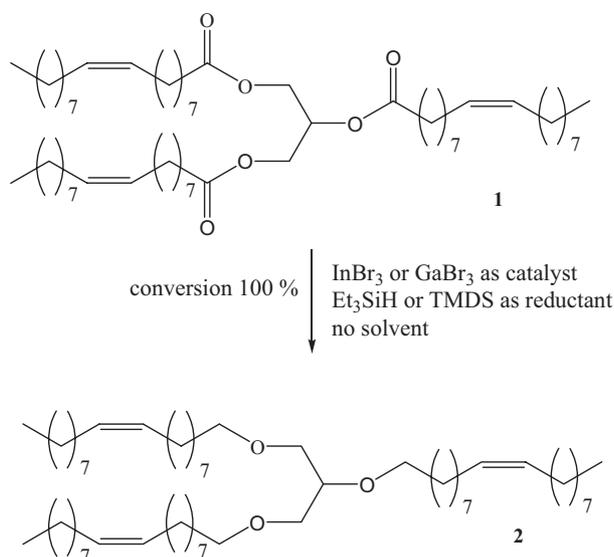
Scheme 1. Reduction of HO-sunflower oil **1** by Et₃SiH or TMDS catalyzed by InBr₃ and GaBr₃, respectively.

identified as glyceryl trioleyl ether **2** (Scheme 1). Further products were glyceryl monooleyl ether dioleate **3**, glyceryl dioleyl ether monooleate **4**, and glyceryl triethylsilyl dioleyl ether **5a** as well as oleylalkohol **6** and oleyltriethylsilylether **7a** (Scheme 2).

The formation of these products can easily be explained due to stepwise reduction of triglyceride **1** via glyceryl ethers **3** and **4** to give the desired product **2**. The over reduction of the acid component of **1** occurs to give alcohol **6**, which undergoes partially silylation to **7a**. Silylated dioleylglyceride **5a** was formed as coupled product to alcohol **6**.

We performed the reaction in a scale of 20 mmol of substrate **1** using the same ratio of reductant and catalyst as above. After stirring the reaction mixture over night (16 h) at 60°C the intermediates **3** and **4** were still present in the reaction mixture. Thus, even in the presence of a twofold excess of Et₃SiH the reduction to triether **2** could not be performed quantitatively. The work up turned out to be quite troublesome. Excess of Et₃SiH was removed in vacuo and hexaethyldisiloxane, oleylalkohol und oleyltriethylsilylether were separated from the reaction mixture by "Kugelrohr" distillation. Column chromatography of the residue to separate the side products and the silyl compounds gave 42% of glyceryl trioleyl ether **2**, which was identified by ¹H and ¹³C NMR spectroscopy. Unfortunately, it was not possible to separate completely the silyl compounds. Additionally, 12% of glyceryl monooleylether-1,3-dioleate **3** was isolated.

We substituted triethylsilane by TMDS and observed a much faster reduction. The solvent-free reduction of **1** with InBr₃ and TMDS as reducing system (**1**:TMDS: InBr₃ = 1:6:0.15) having a ratio of hydride to ester functions of 4:1
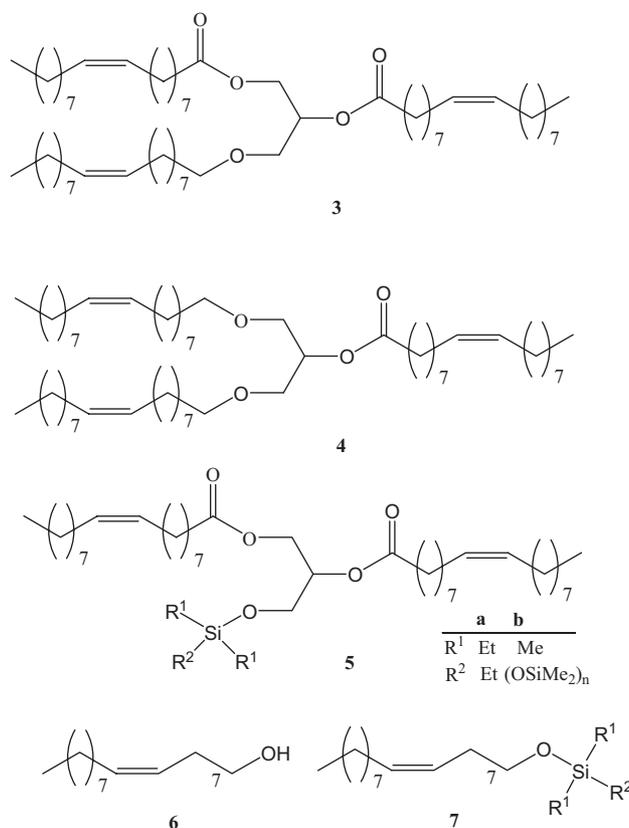
Scheme 2. Intermediate products **3** and **4** and side products of the reduction of HO sunflower oil.

resulted in quantitative conversion of triester **1** already after 30 min at 60°C. In contrast to Et₃SiH as reductant TLC as well as ¹H and ¹³C NMR spectra of the reaction mixture did not show remaining intermediate reduction products **3** and **4**. However, some overreduction to oleylalcohol could be observed. The separation of triether **2** was performed by column chromatography giving pure compound **2** in an isolated yield of 49%. Ten percent of oleylsilyl ether **7b** containing on average five units of silyl groups was additionally isolated.

Eventually, we applied the GaBr₃/TMDS system to the reduction of triglyceride **1**. The great advantage was that only small amounts of GaBr₃ of 0.5–1 mol% per ester functionality were necessary to reduce triglycerides to triethers [25]. Initially, we used a ratio of hydride to ester function of 6:1, a threefold excess of hydride. Complete conversion of **1** was observed after 1 h reacting **1**, TMDS and GaBr₃ in a ratio of 1:9:0.17 at RT. However, some intermediate products **3** and **4** comparable to the reaction performed with InBr₃/Et₃SiH (Scheme 2) were shown on the TLC card. After stirring the sample over night the intermediate products disappeared in favor of the formation of triether **2**. Most importantly, only about 7% of overreduction to oleyl alcohol occurred, less than

using InBr$_3$ as catalyst, giving about 20% of glyceryl dioleyl ether **5b** as shown by ^{13}C NMR spectroscopy. Pure triether **2** was obtained after column chromatography in 50% yield.

In our studies on the reduction of methyl oleate, we observed no or, if any, traces of reduction to the alcohol [25]. We performed some experiments with modifications of the protocol to get information if and how this side reaction could be reduced or possibly completely eliminated. We used only stoichiometric amounts of the reductant (**1**:TMDS:GaBr$_3$ = 1:3.1:0.03), having a ratio of hydride to ester functions of 2:1, and observed at RT after 20 h of reaction time complete conversion of triglyceride **1**. ^{13}C NMR spectroscopy of the final reaction mixture showed again about 7% of over reduction.

Performing the reaction at 60°C and using stoichiometric amounts of the reductand (**1**:TMDS:GaBr$_3$ = 1:3.1:0.03) complete conversion of **1** and of the reduction intermediates **3** and **4** was reached after 4 h. Again about 7% of over reduction was shown by ^{13}C NMR spectroscopy.

Another problem was the separation of the product from polydimethylsiloxane formed as coupled product. We have been shown that distillable ethers such as methyl oleyl ether or glyceryl tributyl ether can be separated easily by "Kugelrohr" distillation [25]. Unfortunately, the boiling point of **2** is too high for this procedure. Müller [3] purified the glyceryl triethers by molecular distillation. Unfortunately, we have no access to this technique, which would certainly allow the separation. However, we found that acetone could be used to separate easily by extraction product **2**, which is poorly soluble in acetone, from polydimethylsiloxane, which is readily soluble in acetone. This procedure allowed obtaining a mixture containing 80% of product **2** and 20% of by-product **5b** in 93% yield.

It may be mentioned that using triethyl silane as well as TMDS as reductant and InBr$_3$ as well as GaBr$_3$ as catalyst neither isomerisation nor partial reduction of the *cis*-configured oleyl double bond was observed. In contrast, reduction of methyl oleate with TMDS/GaBr$_3$ showed a minor isomerization of the *cis*-configured double bond of about 5% [25].

4 Conclusions

GaBr$_3$/TMDS was found to be the optimal system for the reduction of HO-sunflower oil **1** to triether **2**. The catalyst GaBr$_3$ was used in small amounts of 0.5–1 mol% calculated to one ester functionality to be reduced and the reducing agent TMDS in stoichiometric amounts. The reaction was carried out at room or moderately elevated temperature of 60°C without using any solvent. Hundred percent conversion of the substrate was obtained after short reaction time. In contrast to InBr$_3$ as catalyst and triethylsilan or TMDS as reductant only minor over reduction to oleylalcohol was observed. However, further studies will be necessary to

suppress completely the over reduction. The separation of triether **2** from the coupled product polydimethylsiloxane was performed by extraction of the latter with acetone. At this stage the described method using GaBr$_3$/TMDS for the conversion of triglycerides to glyceryl triethers is certainly the most efficient and most sustainable reaction protocol for the synthesis of glyceryl triethers making eventually the latter easily available, also in an industrial scale [27].

The authors have declared no conflict of interest.

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