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Lipase-mediated desymmetrization of glycerol with aromatic and aliphatic anhydrides

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Abstract—Chirazyme L-2 (*Candida antarctica*) catalyzed esterification of glycerol with aromatic and aliphatic anhydrides in 1,4-dioxane is described. All the aromatic monoacylglycerols (MAGs) were produced as (*R*)-enantiomers, while aliphatic MAGs were obtained either as racemic mixtures or the (*S*)-enantiomers. The influence of substituted aromatic rings, chain length, and presence of a conjugated double bond in the acyl donor moiety on the enantiotopic selectivity as well as the efficiency of the enzyme was studied.

1. Introduction

Monoacylglycerols (MAGs) are known as emulsifiers with antimicrobial properties, which are widely employed in the food, pharmaceutical, and cosmetic industries. In their enantiomerically pure forms, these compounds are important synthetic intermediates and building blocks with their synthesis becoming the focus of much attention over the last decade.

For the syntheses of chiral MAGs enzymatic approaches, such as the kinetic resolution of racemic glycerol derivatives or desymmetrization of the prochiral glycerol, 1,3-propanediols and their derivatives have been developed.[1–3] These methods are based upon the ability of the lipases to distinguish between enantiomeric and enantiotopic groups and usually employ an organic solvent as media. Most often, the acyl donor in these reactions is either a short-, medium-, or long-chain fatty acid or vinyl ester. The influence of the acyl donor structure on the enantioselectivity of lipases in MAGs syntheses has hardly been reported.[1,4] On the other hand, many examples in the literature show that in general the efficiency and enantioselectivity of lipases can be affected by altering the size of the acyl group or varying the substituents in aromatic ring, present in the molecule.[5–8]

Recently, we have used Chirazyme (*Candida antarctica*) for an efficient esterification of glycerol with benzoic anhydride in 1,4-dioxane.[9] (*R*)-α-MBG was obtained with high enantiomeric excesses on a large scale.[10] We also found benzoic anhydride was the better acyl donor than the vinyl and methyl esters of benzoic acid.[11]

Acid anhydrides are readily available chemicals and can be easily used as highly reactive and non-water-producing acyl donors for enzyme esterifications.[12–14] As an extension of our work we used substituted aromatic anhydrides as well as short- and medium-chain fatty acid anhydrides to accomplish the lipase-catalyzed esterification of glycerol and studied the effect of the acyl donor on the enantioselectivity of Chirazyme. Some correlations between the acyl donor structure and lipase efficiency were also observed.

2. Results and discussion

The lipase-catalyzed asymmetrization of the prochiral molecule of glycerol was accomplished via acylation to its primary hydroxyl groups, as shown in Tables 1 and 2.

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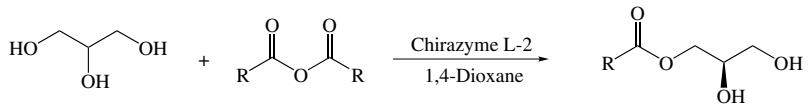
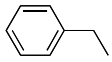
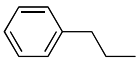
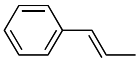
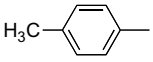
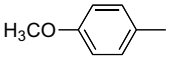
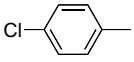
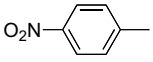
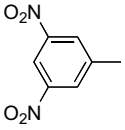
Table 1. Lipase-catalyzed esterification of glycerol with aromatic anhydrides



Compound	R	Yield (%)	Reaction time (h)	Enantiomeric excess (%)	Absolute configuration
1		16	24	14	*R*
2		65	36	21	*R*
3		1	39	100	*R*
4		23	72	63	*R*
5		1	48	29	*R*
6		15	48	14	*R*
7		17	48	66	*R*
8		21	15	74	*R*

Aromatic and aliphatic acid anhydrides were used as acyl donors. The aromatic acid anhydrides had a substituted ring at the *p*-position and either one or two methylene groups or a double bond between the aromatic and acyl parts. The aliphatic anhydrides bore straight or branched chains ranging in length from 3 to 14 carbons. Most of the acyl donors are commercially available. We synthesized myristic, cyclohexanecarboxylic, sorbic, and all the aromatic acid anhydrides from the corresponding acids or chlorides. To prepare authentic samples of MAGs, we first obtained their acetonides from the reaction of racemic or chiral 2,2-dimethyl-1,3-dioxolane-4-methanol and acyl chlorides or anhydrides. The resulting derivatives were further deprotected with Amberlyst 15 (wet).

Under the following conditions: 100 mM glycerol, 100 mM acid anhydride, 1,4-dioxane (5 mL), 15 °C, Chirazyme (25 mg) was active toward all the anhydrides. In a controlled experiment under the same conditions without an enzyme, no acylation was observed. The progress of the enzyme esterification concerning the yield and e.e. of MAGs was monitored with GC or HPLC. The e.e.'s of the MAGs were measured on chiral columns after derivatization into acetonides.[11,15] A model reaction of ketalization of two racemic MAGs, monopivaloyl glycerol, and monoheptanoylglycerol showed that using (±)-10-camphorsulfonic acid and 20% acetone dimethylacetal did not cause an asymmetric transformation.

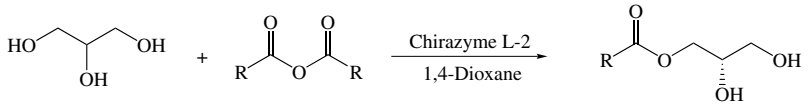
2.1. Effect of the structure of the acyl donor on enantioselectivity of Chirazyme

2.1.1. Aromatic acid anhydrides

2.1.1.1. Influence of the substituted aromatic ring present in the acid anhydrides. Chirazyme showed distinct pro-*R* selectivity in the esterification of glycerol with aromatic anhydrides (Table 1). The lipase preferred the bulkiest, 3,5-dinitrobenzoic anhydride and transformed it into **8** with an e.e. of 74%. During the reaction, this value dropped to 30%, which may be due to an acyl migration. The rest of the substituted aromatic anhydrides resulted in MAGs with lesser e.e. With respect to their *p*-substituents, they are put in order of decreasing values of e.e., as follows: $NO_2 > CH_3 > CH_3O > Cl$ (Fig. 1). Comparison of the Hammett constants and van der Waals radii of the substituents did not reveal a strong correlation between their electronic effects and size and the enantioselectivity of the enzyme.[16]

2.1.1.2. Influence of an aliphatic chain introduced between the benzene ring and acyl function. When the acyl part of aromatic anhydrides was separated from the benzene ring with a methylene group, MAG **1** with an e.e. of 14% was obtained. Introducing a second methylene group at the same place gave an almost two-fold rise in the enantioselectivity with an e.e. of 21% for the resulting compound **2**. The presence of a double bond conjugated with both the benzene ring and acyl function, drastically increased the enantioselectivity

Table 2. Lipase-catalyzed esterification of glycerol with aliphatic acid anhydrides



Compound	R	Yield (%)	Reaction time (min)	Enantiomeric excess (%)	Absolute configuration
9	H_3C	80	180	Racemic mixture	
10	H_3C	43	120	Racemic mixture	
11	H_3C	99	540	Racemic mixture	
12	H_3C, CH_3	69	120	Racemic mixture	
13	H_3C	24	60	13	*S*
14	H_3C, CH_3	48	90	11	*S*
15	H_3C, CH_3, CH_3	47	120	29	*S*
16	H_3C	15	30	Racemic mixture	
17	H_3C	71	360	83	*S*
18	H_3C	28	90	Racemic mixture	
19	H_3C	32	240	Racemic mixture	
20	H_3C	35	180	Racemic mixture	
21	H_3C	15	240	Racemic mixture	
22	H_3C	13	240	Racemic mixture	
23		60	600	73	*S*

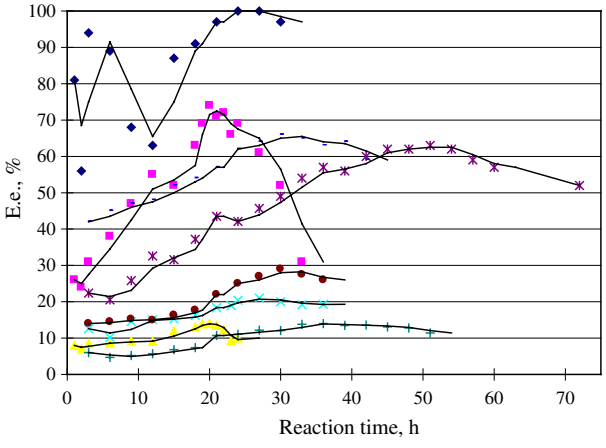


Figure 1. E.e. of MAGs, obtained from the lipase-catalyzed esterification of glycerol with aromatic anhydrides. Compounds: (▲): **1**; (X): **2**; (♦): **3**; (∗): **4**; (●): **5**; (+): **6**; (-): **7**; (■): **8**.

of the lipase. Thus, for monocinnamoyl glycerol **3**, an e.e. of 100% was achieved (Fig. 1).

2.1.2. Aliphatic acid anhydrides

2.1.2.1. Influence of the chain length. The behavior of the lipase toward the esterification of glycerol with aliphatic anhydrides was quite surprising. While the short-chain propionic, butyric, and isobutyric anhydrides yielded racemic mixtures of MAGs, the anhydrides with five carbons in each of their chains, *n*-pentanoic, *i*-pentanoic, and pivalic anhydrides gave MAGs with a preferential (*S*)-configuration (Table 1). Amongst them the highest e.e. achieved was with the bulky pivalic anhydride as a donor, although it still remained low (Fig. 2). In the enzyme literature, we found a few examples showing an increase in the e.e. of lipase-catalyzed esterifications when increasing the chain length in the acyl donor moiety.[5,8] We therefore decided to use longer aliphatic anhydrides bearing 6–14 carbons in their chains. However, instead of the expected rise in e.e. all these reactions produced racemic mixtures of MAGs. It is noteworthy to notice that the aliphatic anhydride of cyclohexanecarboxylic acid having six carbons in each ring, transformed glycerol to the (*S*)-MAG with high e.e. (Fig. 2).

2.1.2.2. Influence of conjugated double bonds present in the aliphatic chain. We supposed that the opposite

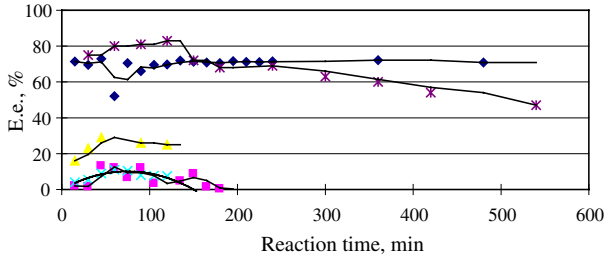


Figure 2. E.e. of MAGs, obtained from the lipase-catalyzed esterification of glycerol with aliphatic anhydrides. Compounds: (■): **13**; (X): **14**; (▲): **15**; (∗): **17**; (♦): **23**.

configurations observed for the aromatic and aliphatic MAGs were due to the OH···π or CH···π interactions between the π electrons of the aromatic anhydrides and the active site of lipase.[16] We were interested in whether inserting double bonds in the chains of aliphatic anhydrides would reverse the enantiotopic selectivity of Chirazyme and lead to aliphatic MAGs with an (*R*)-configuration. To verify this possibility, we selected crotonic and sorbic anhydrides, which are aliphatic compounds, but contain one or two double bonds in their chains, respectively. In the presence of crotonic anhydride as acyl donor, the lipase-catalyzed esterification of glycerol did not divert from the usual progress and monocrotonyl glycerol **11** was obtained as a racemic mixture. However, with sorbic anhydride as the donor, the enantioselectivity of Chirazyme was definitely pro-*S* and the highest e.e. of 83% determined for monosorboyl glycerol **17** (Table 1, Fig. 2).

2.2. Effect of the structure of the acyl donor on chirazyme efficiency

The activity of Chirazyme was not very high at 15 °C and in most cases, the yields of MAGs obtained were low to moderate. However, we found that the chemical racemization was suppressed at this temperature.[11] Additionally to avoid any racemization, we did not use a base for removing the generated acid, which also contributed to the lower yields.

The enzyme reactions of glycerol with aliphatic anhydrides completed within 4 h. It was observed that when increasing the carbon number, the yields of the MAGs decreased. The steric hindered MAGs—monoisobutyryl-, monoisopentanoyl-, and monopivaloyl glycerols were obtained in higher yields than their isomers with straight chains. Inserting a double bond, conjugated with the acyl function of aliphatic anhydrides made them react slower, but with high yield. The yield of MAG however, decreased when an additional double bond, conjugated to the first one, was introduced.

In comparison with aliphatic anhydrides, the aromatic acyl donors esterified glycerol much slower (Tables 1 and 2, Fig. 3). Electronic effects were observed to influence the reactivity of the carboxylic group connected with the substituted aromatic ring. Thus, for having in their molecule a strong electron donating substituent

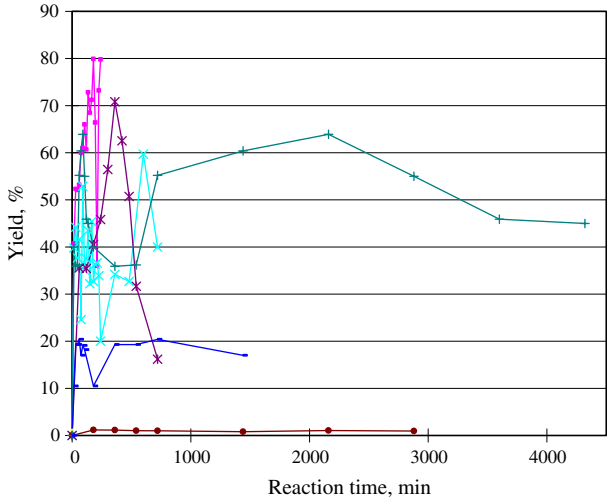


Figure 3. Time course of the lipase-catalyzed reaction of glycerol with some aromatic and aliphatic anhydrides. Compounds: (+): **2**; (●): **3**; (-): **8**; (■): **9**; (∗): **17**; (X): **23**.

or a conjugated double bond, *p*-metoxybenzoic and cinnamic anhydrides gave the lowest yields of MAGs.

3. Conclusions

Chirazyme showed distinct pro-*R* selectivity toward the esterification of glycerol with aromatic anhydrides and pro-*S* or no selectivity when the acyl donors were aliphatic anhydrides. The introduction of a conjugated double bond in the acid donor moiety drastically increased the enantiotopic selectivity of the enzyme. Steric and electronic effects of the acid anhydride moieties were found to affect the efficiency of Chirazyme.

4. Experimental

4.1. Analytical methods

^{1}H and ^{13}C NMR spectra were recorded on JEOL LA-400 and JEOL EX-270 spectrometers for solutions in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard and *J* values are given in hertz (Hz). HPLC analyses were carried out on Waters LC Module 1 equipped with UV/VIS spectrophotometer and Hitachi, equipped with UV detector L-400, intelligent pump L-6200 using ODS-80Ts column (Tosoh), Nova-Pak® C18 column (Waters) and chiral columns Chiralcel OJ (Daicel). Gas chromatograms were recorded on a Shimadzu GC-14B and Shimadzu GC-2010 using packed PEG 20 m column (GLScience) and chiral columns α-DEX 120 (Supelco) 0.25 × 30 m and WCOT fused silia (Varian) 0.25, 0.25 × 25 m. Melting points were determined on Mettler FP5 and are uncorrected. All chemical reactions were qualitatively monitored by thin layer chromatography using Merck silica gel plates Kieselgel 60 F_{254} (Kanto Chem.). The spots were visualized under UV, iodine or by spraying with molibdate–sulfate solution containing 85% H_3PO_4.

4.2. Materials

An immobilized lipase from *Candida antarctica* (Chirazyme L-2 lyo. c.f.) was provided by Roche Diagnostics. Monocaprin, monostearin, and monopalmitin were purchased from Tokyo Kasei. Cyclohexanecarboxylic, myristic, hydrocinnamic, *p*-methoxybenzoic, and *p*-chlorobenzoic anhydrides were synthesized from the corresponding acids or acid chlorides in pyridine.[17] Both sorbic and cinnamic acid anhydrides were obtained by reaction of carboxylic acids with triphosgene.[18] Phenylacetic anhydride was synthesized by reaction between phenylacetic acid and ethyl ethynyl ether.[19] *p*-Methylbenzoic, *p*-nitrobenzoic and 3,5-dinitrobenzoic anhydrides were obtained from the corresponding acyl chlorides and $NaHCO_3$ using phase-transfer catalyst in CH_3CN.[20] Amberlyst 15J (wet) was from Organo. All other chemicals were from commercial sources and used without further purification.

4.3. General procedure for enzymatic acylation of glycerol

To a solution of glycerol (100 mM) and acid anhydride (100 mM) in 1,4-dioxane (5 mL) was added CHIRAZYME L-2 lyo. c.f. (25 mg). The reaction mixture was magnetically stirred at 15 °C. The enzymatic esterification of glycerol with aliphatic and aromatic acid anhydrides was monitored with GC and HPLC, respectively, after periodically withdrawing of aliquots from the reaction mixtures. The enantiomeric purity of the obtained MAGs was determined after their derivatization into acetonides and GC or HPLC with chiral columns used. The authentic samples of MAGs were synthesized by chemical means as stated below in Section 4.4 and characterized on the basis of their spectral data. Samples of chiral MAGs were prepared from commercial (*R*)- and (*S*)-2,2-dimethyl-1,3-dioxolane-4-methanols prior to use.

The following conditions for determination of the e.e. of the monoacylglycerols after their derivatization into acetonides were used.

1. For the aromatic MAGs: **1**, GC (α-DEX 120) with temperature gradient 100–220 °C; **2**, **4**, **5**, **6**, and **7**: HPLC (Chiralcel OJ), eluent *n*-hexane:*i*-propanol 95: 5 (v/v) at 254 nm with the flow rates as follows, compounds **4** and **6**, 0.3 mL/min; **2**, 0.4 mL/min; **5**, 0.5 mL/min; **7**, 0.75 mL/min; **3**, eluent *n*-hexane:*i*-propanol 83:17 (v/v), 0.5 mL/min and **8**, eluent *n*-hexane:*i*-propanol 70:30 (v/v), 0.9 mL/min.
2. For the short-chain aliphatic MAGs: GC (α-DEX 120) under isocratic temperatures as follows: **9**, **12**, and **15**, 90 °C; **10**, **13** and **14**, 100 °C.
3. For the medium-chain aliphatic MAGs with GC (WCOT fused silia): **16**, with temperature gradient 100–130 °C, 5°/min; **18**, 140 °C; **19**, 150 °C and **20**, 160 °C; **21**, 170 °C; **22**, with temperature gradient 150–180 °C, 5°/min.
4. For **11**, HPLC (Chiralcel OJ), eluent *n*-hexane:*i*-propanol 70:30 (v/v), 0.75 mL/min and **17**, eluent *n*-hexane:*i*-propanol 95:5 (v/v), 0.9 mL/min.
5. For **23**, HPLC (Chiralcel OJ-RH), eluent 40% CH_3CN: 10 mM H_3PO_4, flow rate 0.4 mL/min.

4.4. Chemical synthesis of MAGs

4.4.1. Synthesis of (*RS*)-1,2-isopropylidene derivatives

4.4.1.1. General procedure for synthesis of (*RS*)-1,2-isopropylidene derivatives from the corresponding acyl-chlorides or anhydrides. Acyl chloride (10 mmol) or acid anhydride (11 mmol) was added to a solution of 2,2-dimethyl-1,3-dioxolane-4-methanol (10 mmol) in pyridine (10 mL) and stirred for 24 h at rt. After evaporation of the solvent, the residue was partitioned between water (10 mL) and EtOAc (30 mL). The organic layer was successively washed with 5% $CuSO_4 \cdot 5H_2O$ (3×50 mL), saturated $NaHCO_3$ aq (3×50 mL) and saturated NaCl aq (50 mL), dried over Na_2SO_4 and then evaporated. All the products were further purified by column chromatography over silica gel with eluent *n*-hexane:EtOAc. The yields obtained were over 90%.

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl phenylacetate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.36–7.27 (m, 5H), 4.34–4.28 (m, 1H), 4.18 (dd, 1H, $J = 4.6, 11.5$), 4.13 (dd, 1H, $J = 5.6, 11.5$), 4.03 (dd, 1H, $J = 6.4, 8.3$), 3.70 (dd, 1H, $J = 6.1, 8.3$), 3.67 (s, 2H), 1.41 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 173.0, 135.2, 129.6, 129.3, 128.6, 128.4, 127.3, 73.5, 66.2, 64.3, 41.1, 30.1, 28.3, 25.4; R_t 28.61 (*S*), 28.83 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl hydrocinnamate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.31–7.27 (m, 2H), 7.22–7.19 (m, 3H), 4.27 (m, 1H), 4.15 (dd, 1H, $J = 4.6, 11.5$), 4.09 (dd, 1H, $J = 5.8, 11.5$), 4.03 (dd, 1H, $J = 6.4, 8.4$), 3.68 (dd, 1H, $J = 6.2, 8.4$), 2.96 (t, 2H, $J = 7.6$), 2.68 (t, 2H, $J = 7.6$), 1.42 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 172.6, 140.3, 128.5, 128.3, 127.9, 127.7, 126.3, 109.8, 73.5, 66.7, 66.3, 35.6, 30.8, 26.7, 24.4; R_t 27.3 (*S*), 29.2 (*R*).

Dimethyl-1,3-dioxolane-4-yl)methyl cinnamate, white crystals, mp 44.2 °C; ^{1}H NMR ($CDCl_3$): δ 7.71 (d, 1H, $J = 15.9$), 7.51–7.37 (m, 5H), 6.47 (d, 2H, $J = 15.9$), 4.44–4.36 (m, 1H), 4.31 (dd, 1H, $J = 4.6, 11.3$), 4.22 (dd, 1H, $J = 5.9, 11.6$), 4.12 (dd, 1H, $J = 6.5, 8.4$), 3.80 (dd, 1H, $J = 5.9, 8.1$), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.5, 145.3, 134.2, 130.3, 128.8, 128.0, 117.4, 109.8, 74.9, 73.8, 66.4, 27.3, 26.8; R_t 11.08 (*R*), 12.50 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *p*-methylbenzoate, white crystals, mp 46.9 °C; ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 2H, $J = 8.1$), 7.24 (d, 2H, $J = 8.1$), 4.45 (m, 1H), 4.38 (dd, 1H, $J = 4.9, 11.1$), 4.35 (dd, 1H, $J = 5.6, 10.9$), 4.15 (dd, 1H, $J = 6.5, 8.5$), 3.88 (dd, 1H, $J = 6.0, 8.4$), 2.41 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.4, 143.8, 129.7, 129.4, 129.1, 128.9, 127.0, 109.8, 73.7, 69.4, 64.8, 26.7, 25.4, 21.6; R_t 22.3 (*S*), 25.2 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *p*-methoxybenzoate, white crystals, mp 39.8 °C; ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 2H, $J = 9.0$), 6.92 (d, 2H, $J = 9.0$), 4.45 (m,

1H), 4.37 (dd, 1H, $J = 4.8, 11.6$), 4.34 (dd, 1H, $J = 5.5, 11.6$), 4.14 (dd, 1H, $J = 6.4, 8.5$), 3.87 (dd, 1H, $J = 5.9, 8.5$), 3.86 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.1, 163.5, 131.7, 129.6, 122.2, 113.6, 109.8, 73.8, 68.5, 66.4, 64.7, 55.4, 26.7, 25.4; R_t 25.9 (*S*), 31.8 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *p*-chlorobenzoate, white crystals, mp 49.8 °C; ^{1}H NMR ($CDCl_3$): δ 7.99 (d, 2H, $J = 6.6$), 7.42 (d, 2H, $J = 8.4$), 4.46 (t, 1H, $J = 5.7$), 4.40 (dd, 1H, $J = 4.5, 11.4$), 4.35 (dd, 1H, $J = 5.4, 11.5$), 4.15 (dd, 1H, $J = 6.5, 8.4$), 3.87 (dd, 1H, $J = 5.9, 8.5$), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 165.5, 139.6, 131.1, 128.8, 128.2, 109.9, 73.6, 66.3, 65.3, 26.7, 25.3; R_t 22.4 (*S*), 25.8 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *p*-nitrobenzoate, white crystals, mp 57.4 °C; ^{1}H NMR ($CDCl_3$): δ 8.30 (d, 2H, $J = 8.5$), 8.24 (d, 2H, $J = 8.8$), 4.52–4.45 (m, 2H), 4.40 (dd, 1H, $J = 6.7, 12.6$), 4.17 (dd, 1H, $J = 6.5, 10.3$), 3.88 (dd, 1H, $J = 5.5, 8.7$), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 164.5, 150.7, 135.1, 130.8, 123.6, 110.1, 73.4, 66.2, 66.0, 26.7, 25.2; R_t 24.2 (*S*), 27.8 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl 3,5-dinitrobenzoate, white crystals, mp 74.8 °C; ^{1}H NMR ($CDCl_3$): δ 9.24–9.18 (m, 3H), 4.50–4.46 (m, 3H), 4.22–4.16 (m, 1H), 3.90–3.85 (m, 1H), 1.48 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.2, 148.6, 133.4, 129.4, 122.5, 110.2, 73.2, 67.0, 66.1, 26.8, 25.3; R_t 23.08 (*S*), 27.06 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *n*-propanoate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.34–4.30 (m, 1H), 4.18 (dd, 1H, $J = 4.5, 15.5$), 4.12–4.07 (m, 2H), 3.75 (dd, 1H, $J = 6.2, 8.4$), 2.38 (q, 2H, $J = 7.6$), 1.44 (s, 3H), 1.37 (s, 3H), 1.15 (t, 3H, $J = 7.6$); ^{13}C NMR ($CDCl_3$): δ 174.2, 109.8, 73.6, 66.2, 64.6, 27.3, 26.6, 25.3, 9.0; R_t 24.50 (*S*), 25.00 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *n*-butanoate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.39–4.29 (m, 1H), 4.17 (dd, 1H, $J = 4.9, 11.5$), 4.12–4.06 (m, 2H), 3.75 (dd, 1H, $J = 6.1, 8.3$), 2.34 (t, 2H, $J = 6.8$), 1.67 (6th, 2H, $J = 7.6$), 1.44 (s, 3H), 1.37 (s, 3H), 0.95 (t, 3H, $J = 7.3$); ^{13}C NMR ($CDCl_3$): δ 173.4, 109.8, 73.6, 66.2, 64.4, 35.9, 26.6, 25.3, 18.3, 13.5; R_t 27.30 (*S*), 27.70 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl crotonate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.08–6.95 (m, 1H), 5.88 (dq, 1H, $J = 15.4, 1.6$), 4.39–4.29 (m, 1H), 4.22 (dd, 1H, $J = 4.6, 11.6$), 4.14 (dd, 1H, $J = 5.7, 11.1$), 4.09 (dd, 1H, $J = 6.2, 8.4$), 3.76 (dd, 1H, $J = 5.9, 8.4$), 1.89 (dd, 1H, $J = 1.9, 6.8$), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.0, 145.3, 122.1, 109.8, 73.7, 66.4, 64.5, 26.8, 25.5, 18.1; R_t 5.14 (*S*), 5.56 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl isobutanoate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.35–4.29 (m, 1H), 4.18–4.06 (m, 3H), 3.76 (dd, 1H, $J = 6.3, 8.4$), 2.65–2.55 (m, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 1.18 (d, 6H, $J = 6.8$); ^{13}C NMR ($CDCl_3$): δ 176.9, 109.7, 73.6, 66.3, 64.3, 33.9, 26.6, 25.3, 18.9, 18.7; R_t 27.90 (*S*), 28.50 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl *n*-pentanoate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.35–4.29 (m, 1H), 4.16 (dd, 1H, $J = 4.8, 11.6$), 4.11–4.06 (m, 2H), 3.74 (dd, 1H, $J = 6.2, 8.4$), 2.35 (t, 2H, $J = 7.3$), 1.69–1.58 (m, 2H), 1.44 (s, 3H), 1.39–1.31 (m, 2H), 1.37 (s, 3H), 0.92 (t, 3H, $J = 7.3$); ^{13}C NMR ($CDCl_3$): δ 173.6, 110.8, 73.6, 66.3, 64.5, 33.8, 26.9, 26.7, 25.4, 22.2, 13.7; R_t 30.40 (*S*), 30.82 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl isopentanoate, col- orless oil; ^{1}H NMR ($CDCl_3$): δ 4.39–4.29 (m, 1H), 4.17 (dd, 1H, $J = 4.9, 11.5$), 4.12–4.06 (m, 2H), 3.75 (dd, 1H, $J = 6.1, 8.3$), 2.24 (d, 2H, $J = 6.8$), 2.14–2.08 (m, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 0.96 (d, 6H, $J = 6.6$); ^{13}C NMR ($CDCl_3$): δ 172.9, 110.8, 73.6, 66.3, 64.4, 43.1, 26.7, 26.7, 25.6, 25.4, 22.3; R_t 34.01 (*R*), 34.49 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl pivalate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.30 (t, 1H, $J = 5.7$), 4.13 (dd, 1H, $J = 5.0, 11.5$), 4.11 (dd, 1H, $J = 5.0, 6.5$), 4.07 (dd, 1H, $J = 6.4, 8.3$), 3.73 (dd, 1H, $J = 6.1, 8.3$), 1.44 (s, 3H), 1.33 (s, 3H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 178.2, 109.6, 73.6, 66.3, 64.1, 38.8, 27.1, 26.6, 25.4; R_t 27.67 (S), 28.31 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl caproate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.35–4.29 (m, 1H), 4.17 (dd, 1H, $J = 4.9, 11.7$), 4.11 (d, 1H, $J = 5.4$), 4.07 (dd, 1H, $J = 1.9, 5.8$), 3.74 (dd, 1H, $J = 6.3, 8.5$), 2.35 (t, 2H, $J = 7.6$), 1.67–1.60 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35–1.28 (m, 4H), 0.90 (t, 3H, $J = 7.1$); ^{13}C NMR ($CDCl_3$): δ 173.6, 109.8, 73.6, 66.3, 64.5, 34.0, 31.2, 26.6, 25.4, 24.5, 22.3, 13.9; R_t 25.15 (*R*), 25.50 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl sorbate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.33–7.29 (m, 1H), 6.20–6.14 (m, 2H), 5.81 (d, 1H, $J = 15.3$), 4.40–4.32 (m, 1H), 4.24 (dd, 1H, $J = 4.6, 11.5$), 4.15 (dd, 1H, $J = 5.1, 11.6$), 4.08 (d, 1H, $J = 6.6$), 3.77 (dd, 1H, $J = 6.1, 8.2$), 1.86 (d, 3H, $J = 4.9$), 1.44 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 166.9, 145.7, 139.8, 129.6, 118.1, 109.8, 73.7, 66.4, 64.6, 26.8, 25.5, 18.8; R_t 5.78 (*S*), 6.12 (*R*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl heptanoate, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.33–4.31 (m, 1H), 4.18–4.15 (m, 1H), 4.11–4.06 (m, 2H), 3.76–3.72 (m, 1H), 2.34 (t, 2H, $J = 5.8$), 1.63–1.60 (m, 2H), 1.43 (s, 3H), 1.37 (s, 3H), 1.29 (s, 6H), 0.90–0.84 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 173.5, 109.7, 73.6, 66.2, 64.4, 34.0, 31.3, 28.7, 26.6, 25.3, 24.8, 22.4, 13.9; R_t 19.69 (*R*), 19.96 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl caprylate, white crystals, mp 27.4 °C; ^{1}H NMR ($CDCl_3$): δ 4.35–4.28 (m, 1H), 4.17 (dd, 1H, $J = 4.6, 11.5$), 4.10 (d, 1H, $J = 5.8$), 4.07 (dd, 1H, $J = 2.2, 5.8$), 3.74 (dd, 1H, $J = 6.1, 8.6$), 2.34 (t, 2H, $J = 7.3$), 1.70–1.60 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.29 (s, 8H), 0.88 (t, 3H, $J = 6.6$); ^{13}C NMR ($CDCl_3$): δ 173.7, 109.8, 73.6, 66.3, 64.5, 34.1, 31.6, 29.0, 28.9, 26.7, 25.4, 24.9, 22.6, 14.0; R_t 20.12 (*R*), 20.33 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl laurate, white crystals, mp 32.5 °C; ^{1}H NMR ($CDCl_3$): δ 4.35–4.28 (m, 1H), 4.17 (dd, 1H, J = 4.6, 11.5), 4.11 (d, 1H, J = 5.6), 4.07 (dd, 1H, J = 2.2, 5.6), 3.74 (dd, 1H, J = 6.1, 8.6), 2.34 (t, 2H, J = 7.6), 1.67–1.59 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.26 (s, 16H), 0.88 (t, 3H, J = 6.6); ^{13}C NMR ($CDCl_3$): δ 173.7, 109.8, 73.6, 66.3, 64.5, 34.1, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 26.7, 25.4, 24.9, 22.7, 14.1; R_t 42.94 (*R*), 43.39 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl myristate, white crystals, mp 44.7 °C; ^{1}H NMR ($CDCl_3$): δ 4.35–4.29 (m, 1H), 4.17 (dd, 1H, J = 4.6, 11.5), 4.11 (d, 1H, J = 5.6), 4.07 (dd, 1H, J = 2.0, 5.8), 3.74 (dd, 1H, J = 6.3, 8.5), 2.34 (t, 2H, J = 7.6), 1.64–1.59 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.26 (s, 20H), 0.88 (t, 3H, J = 6.6); ^{13}C NMR ($CDCl_3$): δ 173.7, 109.8, 73.6, 66.3, 64.5, 34.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.7, 25.4, 24.9, 22.7, 14.1; R_t 42.29 (*R*), 43.45 (*S*).

(2,2-Dimethyl-1,3-dioxolane-4-yl)methyl cyclohexancarbonyl glycerol, colorless oil: ^{1}H NMR (DMSO) δ 4.25–4.20 (m, 1H), 4.07 (dd, 1H, J = 4.2, 11.7), 3.98 (dd, 2H, J = 4.1, 11.2), 3.64 (t, 1H, J = 6.3), 1.82–1.78 (m, 2H), 1.66–1.63 (m, 2H), 1.58–1.55 (m, 1H), 1.38–1.35 (m, 2H), 1.31 (s, 3H), 1.25 (s, 3H), 1.24–1.16 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 176.1, 103.5, 73.2, 68.7, 64.2, 42.3, 29.0, 28.9, 27.1, 26.9, 26.4, 24.6, 24.2; R_t 4.49 (*R*), 4.98 (*S*).

4.4.1.2. Ketalization of monocaprin[21] (2,2-Dimethyl-1,3-dioxolane-4-yl)methyl caprate, colorless oil: ^{1}H NMR δ 4.35–4.29 (m, 1H), 4.17 (dd, 1H, J = 4.6, 11.5), 4.11 (d, 1H, J = 5.8), 4.07 (dd, 1H, J = 2.2, 5.4), 3.74 (dd, 1H, J = 6.1, 8.3), 2.33 (t, 2H, J = 7.6), 1.67–1.59 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.26 (s, 12H), 0.88 (t, 3H, J = 6.6); ^{13}C NMR ($CDCl_3$) δ 173.6, 109.8, 73.6, 66.3, 64.5, 34.1, 31.8, 29.4, 29.2, 29.1, 26.6, 25.4, 24.8, 22.6, 14.1; R_t 29.78 (*R*), 30.16 (*S*); EIMS 271 $[M-15]^+$ (100.0), 228 (3.4), 227 (1.3), 199 (1.2), 185 (3.2), 171 (7.1), 155 (17.2), 129 (6.9), 116 (11.7), 101 (27.9), 85 (6.9), 57 (10.5), 55 (10.1), 43 (26.7), 41 (19.6); HREIMS *m/z* 271.1880 $[M-15]^+$ (calcd for $C_{15}H_{27}O_4$ 271.3792).

4.4.2. Deprotection of the isopropylidene derivatives.[22] 1-*O*-(Phenylacetyl)glycerol **1**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.36–7.27 (m, 5H), 4.23 (dd, 1H, J = 4.4, 11.5), 4.17 (dd, 1H, J = 6.1, 11.7), 3.93–3.89 (m, 1H), 3.71–3.67 (m, 1H), 3.68 (s, 2H), 3.57–3.52 (m, 1H), 2.39 (t, 1H, J = 4.6), 1.94 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 173.3, 140.2, 129.2, 128.7, 126.3, 70.0, 65.3, 62.4, 41.8, 35.7, 30.9.

1-*O*-(Hydrocinnamoyl)glycerol **2**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.32–7.20 (m, 5H), 4.18 (dd, 1H, J = 4.6, 11.7), 4.13 (dd, 1H, J = 6.2,11.6), 3.88–3.83 (m, 1H), 3.61 (dd, 1H, J = 4.0, 11.6), 3.50 (dd, 1H, J = 5.7, 11.6), 2.97 (t, 2H, J = 7.6), 2.70 (t, 2H, J = 7.7), 2.47 (br s, 1H), 1.69 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 173.3, 140.2, 128.6, 128.3, 126.4, 65.3, 63.2, 35.7, 30.9; EIMS 224 $[M]^+$ (46.3), 206 (7.7), 193 (10.3), 150 (7.9), 133 (25.6), 105 (51.9), 104 (100.0), 91 (52.7), 77 (11.6), 65 (4.4), 43 (4.1); HREIMS *m/z* 224.1034 $[M]^+$ (calcd for $C_{12}H_{16}O_4$ 224.2584).

1-*O*-(Cinnamoyl)glycerol **3**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.71 (d, 1H, J = 16.2), 7.54–7.51 (m, 2H), 7.41–7.38 (m, 3H), 6.47 (d, 1H, J = 15.9), 4.35 (dd, 1H, J = 4.3, 11.6), 4.29 (dd, 1H, J = 5.7, 11.3), 4.07–4.00 (m, 1H), 3.75 (dd, 1H, J = 3.5, 11.6), 3.66 (dd, 1H, 5.7, 11.3), 2.80 (br s, 1H). 2.36 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 167.2, 145.8, 133.9, 130.5, 128.8, 128.1, 117.1, 70.3, 65.4, 63.3.

1-*O*-(*p*-Methylbenzoyl)glycerol **4**, white crystals, mp 67.8 °C; ^{1}H NMR ($CDCl_3$): δ 7.94 (d, 2H, J = 8.0), 7.23 (d, 2H, J = 8.0), 4.40 (dd, 1H, J = 5.2, 11.6), 4.38 (dd, 1H, J = 5.8, 11.7), 4.09–4.03 (m, 1H), 3.76 (dd, 1H, J = 3.8, 11.6), 3.68 (dd, 1H, J = 5.9, 11.7), 3.22 (br s, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 167.1, 144.1, 129.7, 129.2, 126.0, 70.4, 65.5, 63.4, 21.6.

1-*O*-(*p*-Methoxybenzoyl)glycerol **5**, white crystals, mp 50.0 °C; ^{1}H NMR ($CDCl_3$): δ 8.01 (d, 2H, J = 9.0), 6.96 (d, 2H, J = 9.0), 4.43 (dd, 1H, J = 4.9, 11.7), 4.39 (dd, 1H, J = 6.0, 11.6), 4.08–4.04 (m, 1H), 3.87 (s, 3H), 3.78–3.74 (m, 1H), 3.71–3.67 (m, 1H), 2.67 (d, 1H, J = 5.4), 2.20 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 166.9, 163.8, 131.9, 121.9, 113.8, 70.5, 65.6, 63.4, 55.5.

1-*O*-(*p*-Chlorobenzoyl)glycerol **6**, white crystals, mp 86.3 °C; ^{1}H NMR ($CDCl_3$): δ 7.98 (d, 2H, J = 8.3), 7.41 (d, 2H, J = 8.6), 4.41 (dd, 1H, J = 5.9, 11.7), 4.08 (t, 1H, J = 6.0), 3.78 (dd, 2H, J = 3.9, 11.5), 3.69 (dd, 1H, J = 5.9, 11.5), 2.75 (br s, 1H), 2.31 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 166.1, 139.9, 128.8, 128.0, 70.3, 65.9, 63.4.

1-*O*-(*p*-Nitrobenzoyl)glycerol **7**, white crystals, mp 106.2 °C; ^{1}H NMR (DMSO-d_6): δ 8.35 (d, 2H, J = 9.0), 8.22 (d, 2H, J = 8.8), 5.09 (d, 1H, J = 5.4), 4.74 (t, 1H, J = 5.7), 4.36 (dd, 1H, J = 3.8, 11.1), 4.22 (dd, 1H, J = 3.8, 11.1), 3.86 (dd, 1H, J = 5.4), 3.46 (dd, 1H, J = 5.4, 11.0), 3.42 (dd, 1H, J = 6.3, 11.0); ^{13}C NMR (DMSO-d_6): δ 164.9, 150.6, 135.1, 130.8, 123.5, 70.0, 66.5, 63.3.

1-*O*-(3,5-Dinitrobenzoyl)glycerol **8**, white crystals, mp 118.8 °C; ^{1}H NMR (DMSO-d_6): δ 9.06–8.97 (m, 3H), 5.26 (d, 1H, J = 5.4), 4.82 (t, 1H, J = 5.4), 4.46 (dd, 1H, J = 3.2, 11.3), 4.29 (dd, 1H, J = 6.2, 11.3), 3.85–3.79 (m, 1H); ^{13}C NMR (DMSO-d_6): δ 162.5, 148.2, 132.6, 128.8, 122.5, 69.0, 68.1, 62.4.

1-*O*-(Propionyl)glycerol **9**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22 (dd, 1H, J = 4.4, 11.7), 4.16 (dd, 1H, J = 6.1, 11.7), 3.96–3.93 (m, 1H), 3.74–3.68 (m, 1H), 3.64–3.58 (m, 1H), 2.46 (br s, 1H), 2.42–2.36 (m, 2H), 2.00 (br s, 1H), 1.16 (t, 3H, J = 7.6); ^{13}C NMR ($CDCl_3$): δ 172.3, 70.1, 65.3, 65.2, 20.8, 9.1.

1-*O*-(Butyryl)glycerol **10**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22 (dd, 1H, J = 4.6, 11.5), 4.16 (dd, 1H, J = 6.1, 11.7), 3.97–3.91 (m, 1H), 3.73–3.67 (m, 1H), 3.63–3.58 (m, 1H), 2.55 (br s, 1H), 2.35 (t, 2H,

J = 7.6), 2.12 (br s, 1H), 1.70–1.63 (m, 2H), 0.96 (t, 3H, J = 7.3); ^{13}C NMR ($CDCl_3$): δ 172.3, 72.1, 65.3, 65.2, 30.8, 19.8, 13.1.

1-*O*-(Crotonyl)glycerol **11**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.08–6.99 (m, 1H), 5.88 (d, 1H, J = 1.6, 15.7), 4.27 (dd, 1H, J = 4.9, 11.6), 4.21 (dd, 1H, J = 5.9, 11.9), 3.97–3.86 (m, 1H), 3.71 (dd, 1H, J = 4.3, 11.3), 3.61 (dd, 1H, J = 5.7, 11.6), 2.57 (br s, 1H), 2.13 (br s, 1H), 1.91 (dd, 3H, J = 1.6, 6.8); ^{13}C NMR ($CDCl_3$): δ 166.8, 146.1, 122.0, 70.3, 65.1, 63.3, 18.2.

1-*O*-(Isobutyryl)glycerol **12**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22 (dd, 1H, J = 4.6, 11.5), 4.16 (dd, 1H, J = 5.9, 11.5), 3.97–3.91 (m, 1H), 3.73–3.67 (m, 1H), 3.63–3.57 (m, 1H), 2.66–2.56 (m, 1H), 2.48 (br s, 1H), 2.05 (br s, 1H), 1.19 (d, 6H, J = 7.0); ^{13}C NMR ($CDCl_3$): δ 172.3, 72.1, 65.3, 65.2, 30.8, 19.8, 19.5.

1-*O*-(Pentanoyl)glycerol **13**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.21 (dd, 1H, J = 4.6, 11.5), 4.15 (dd, 1H, J = 6.1, 11.5), 3.97–3.90 (m, 1H), 3.73–3.67 (m, 1H), 3.64–3.57 (m, 1H), 2.72–2.67 (m, 1H), 2.36 (t, 2H, J = 7.6), 2.31–2.24 (m, 1H), 1.66–1.59 (m, 2H), 1.40–1.31 (m, 2H), 0.92 (t, 3H, J = 7.3); ^{13}C NMR ($CDCl_3$): δ 173.4, 70.2, 65.1, 63.3, 33.8, 26.9, 22.2, 13.6.

1-*O*-(Isopentanoyl)glycerol **14**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22 (dd, 1H, J = 4.4, 11.5), 4.16 (dd, 1H, J = 6.1, 11.4), 3.97–3.91 (m, 1H), 3.73–3.68 (m, 1H), 3.64–3.59 (m, 1H), 2.63–2.60 (m, 1H), 2.24 (d, 2H, J = 7.1), 2.15–2.06 (m, 2H), 0.97 (d, 6H, J = 6.6); ^{13}C NMR ($CDCl_3$): δ 172.4, 70.4, 65.1, 63.3, 40.8, 23.6, 22.2, 22.0.

1-*O*-(Pivaloyl)glycerol **15**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22 (dd, 1H, J = 4.6, 11.7), 4.16 (dd, 1H, J = 5.9, 11.7), 3.97–3.91 (m, 1H), 3.73–3.67 (m, 1H), 3.63–3.57 (m, 1H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 172.5, 72.1, 65.1, 63.3, 39.5, 22.5, 22.4, 22.2.

1-*O*-(Caproyl)glycerol **16**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.21 (dd, 1H, J = 4.6, 11.4), 4.15 (dd, 1H, J = 6.1, 11.7), 3.97–3.90 (m, 1H), 3.73–3.68 (m, 1H), 3.63–3.57 (m, 1H), 2.67 (br s, 1H), 2.35 (t, 2H, J = 7.8), 2.25 (br s, 1H), 1.71–1.60 (m, 2H), 1.36–1.29 (m, 4H), 0.90 (t, 3H, J = 7.0); ^{13}C NMR ($CDCl_3$): δ 174.6, 70.2, 65.1, 63.3, 34.1, 31.2, 24.5, 22.2, 13.8.

1-*O*-(Sorboyl)glycerol **17**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.33–7.28 (m, 1H), 6.21–6.18 (m, 2H), 5.80 (d, 1H, J = 15.1), 4.32 (dd, 1H, J = 4.7, 11.5), 4.27 (dd, 1H, J = 5.6, 11.5), 4.05–3.97 (m, 1H), 3.75 (dd, 1H, J = 3.5, 11.6), 3.68 (dd, 1H, 5.7, 11.5), 2.65 (br s, 1H), 2.21 (br s, 1H), 1.87 (d, 3H, J = 4.3); ^{13}C NMR ($CDCl_3$): δ 165.5, 146.2, 140.4, 129.5, 117.8, 70.4, 65.2, 63.3, 18.8.

1-*O*-(Heptanoyl)glycerol **18**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.22–4.11 (m, 2H), 3.95–3.91 (m, 1H), 3.71–3.67 (m, 1H), 3.62–3.57 (m, 1H), 2.51 (br s, 1H), 2.35 (t, 2H, J = 7.6), 1.98 (br s, 1H), 1.65–1.59 (m, 2H), 1.30 (s, 6H), 0.89 (t, 3H, J = 7.1); ^{13}C NMR ($CDCl_3$): δ 174.4, 70.2, 65.1, 63.3, 34.1, 31.3, 28.7, 24.8, 22.4, 13.9.

1-*O*-(Capryloyl)glycerol **19**, white crystals, mp 35.6 °C; ^{1}H NMR ($CDCl_3$): δ 4.21 (dd, 1H, J = 4.6, 11.7), 4.14 (dd, 1H, J = 6.1, 11.7), 3.97–3.90 (m, 1H), 3.73–3.68 (m, 1H), 3.63–3.58 (m, 1H), 2.57 (br s, 1H), 2.36 (t, 2H, J = 7.6), 2.13 (br s, 1H), 1.65–1.60 (m, 2H), 1.30–1.28 (m, 8H), 0.88 (t, 3H, J = 7.1); ^{13}C NMR ($CDCl_3$): δ 174.4, 70.2, 65.1, 63.3, 34.1, 31.6, 29.0, 28.8, 24.8, 22.5, 13.9.

1-*O*-(Lauroyl)glycerol **21**, white crystals, mp 47.4 °C; ^{1}H NMR ($CDCl_3$): δ 4.21 (dd, 1H, J = 4.6, 11.7), 4.14 (dd, 1H, J = 6.1, 10.0), 3.97–3.90 (m, 1H), 3.63 (d, 1H, J = 11.2), 3.60 (dd, 1H, J = 5.6, 11.2), 2.63 (br s, 1H), 2.35 (t, 2H, J = 7.8), 2.21 (br s, 1H), 1.68–1.59 (m, 2H), 1.26 (s, 16H), 0.88 (t, 3H, J = 6.6); ^{13}C NMR ($CDCl_3$): δ 174.4, 70.2, 65.1, 63.3, 34.1, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 22.6, 14.1.

1-*O*-(Myristoyl)glycerol **22**, white crystals, mp 56.2 °C; ^{1}H NMR ($CDCl_3$): δ 4.21 (dd, 1H, J = 4.6, 11.7), 4.15 (dd, 1H, J = 6.1, 11.7), 3.96–3.93 (m, 1H), 3.71–3.69 (m, 1H), 3.61–3.59 (m, 1H), 2.48 (br s, 1H), 2.35 (t, 2H, J = 7.6), 2.04 (br s, 1H), 1.63 (t, 2H, J = 7.3), 1.26 (s, 20H), 0.88 (t, 3H, J = 6.6); ^{13}C NMR ($CDCl_3$): δ 172.6, 70.2, 65.1, 63.3, 34.1, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 24.9, 22.6, 14.1.

1-*O*-(Cyclohexanecarbonyl)glycerol **23**, colorless oil; ^{1}H NMR ($CDCl_3$): δ 4.18 (dd, 1H, J = 5.1, 11.5), 4.14 (dd, 1H, J = 5.6, 11.5), 3.95–3.88 (m, 1H), 3.72–3.65 (m, 1H), 3.63–3.55 (m, 1H), 3.08 (br s, 1H), 2.73 (br s, 1H), 2.39–2.31 (m, 1H), 1.93–1.89 (m, 2H), 1.80–1.72 (m, 2H), 1.68–1.62 (m, 1H), 1.49–1.37 (m, 2H), 1.33–1.20 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 173.4, 70.2, 65.1, 63.3, 33.8, 26.9, 22.2, 13.6.

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