Acylglycerols (= Glycerides) from the Glandular Trichome Exudate on the Leaves of *Paulownia tomentosa*

by **Teigo Asai**[a]), **Noriyuki Hara**[a]), **Sawa Kobayashi**[b]), **Shiro Kohshima**[b]), and **Yoshinori Fujimoto***[a])

[a]) Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan (phone/fax: +81-3-57342241; e-mail: fujimoto.y.aa@m.titech.ac.jp)

[b]) Department of Biological Sciences, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan

Chemical investigations of the glandular trichome exudates on the leaves of *Paulownia tomentosa* (Scrophulariaceae) led to the identification of the thirty acylglycerols (= glycerides) **1**–**30**, including five known ones (**2**, **3**, **6**, **9**, and **15**) (*Fig. 1*). Spectroscopic analysis combined with GC/MS studies of the glycerides and the liberated fatty acids, in the form of trimethylsilyl ether derivatives and trimethylsilylated methyl esters, respectively, established that the constituents belonged to 1,3-di-*O*-acetyl-2-*O*-(fatty acyl)glycerols, 1-*O*-acetyl-2-*O*-(fatty acyl)-*sn*-glycerols, and 2-*O*-(fatty acyl)glycerols, wherein the fatty acyl moiety was either an eicosanoyl or an octadecanoyl group bearing OH and/or AcO groups at the 3-, 3,6-, 3,7-, 3,8-, or 3,9-positions. The 1-*O*-acetyl-2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-hydroxyeicosanoyl]-*sn*-glycerol (**12**; 20% of the total glycerides), 2-*O*-[(3*R*,8*R*)-3,8-bis(acetyloxy)eicosanoyl]glycerol (**17**; 14%), 2-*O*-[(3*R*,9*R*)-3,9-bis(acetyloxy)eicosanoyl]glycerol (**18**; 12%), and 2-*O*-[(3*R*)-3-(acetyloxy)eicosanoyl]glycerol (**10**; 12%) were relatively abundant constituents. The configurations of the stereogenic centers of the fatty acyl moieties were determined by ^{1}H-NMR analysis of the monoesters obtained from (*R*)- and (*S*)-2-(naphthalen-2-yl)-2-methoxyacetic acid ((*R*)- and (*S*)-2NMA–OH and the hydroxy-substituted fatty acid methyl esters (*Fig. 2*). The configuration at C(2) of the glycerol moiety of the 1-*O*-acetyl-2-*O*-(fatty acyl)glycerols was determined to be (2*S*) by chemical conversion of, *e.g.*, *G-2* (= **2**/**3** 1:10) to (+)-3-*O*-[*tert*-butyl)diphenylsilyl]-*sn* glycerol of known absolute configuration.

Introduction. – Glandular trichomes are micro-organs located on the surface of the leaves, stems, flowers, and fruits of plants that exude oily substances. The chemistry and physiological roles of leaf trichome exudate have been studied in a limited number of plant species such as tobacco and tomato plants (Solanaceae). It is suggested that exudate substances are related to a plant's self-protection system, *e.g.*, to antifeedants, antifungal, antibiotics, or UV protection. For example, undecan-2-one and tridecan-2-one from the glandular trichomes of wild tomato leaves show toxicity against larvae [1]. Sucrose esters, such as 6-*O*-acetyl-2,3,4-tri-*O*-hexanoyl-α-D-glucopyranosyl β-D-fructofuranoside, and glycerolipids, such as 1-*O*-acetyl-2-*O*-(18-methylnonadecanoyl)glycerol, from the leaf-surface material of tobacco plants have aphid-resistance activity and phytotoxicity [2–4]. Nevertheless, our understanding of the chemistry and functions of glandular trichome exudate remains insufficient. More systematic chemical and biological studies of exudate would give us insight into their ecological roles.

Paulownia tomentosa STEUD. (Scrophulariaceae) is an ornamental tree distributed widely throughout China, Korea, and Japan. Its stem bark has been used in Chinese herbal medicine as a component of remedies for infectious diseases such as gonorrhea and erysipelas [5]. Earlier studies of *P. tomentosa* led to the isolation of iridoids [6][7] and lignans [8][9]. We recently noticed that *P. tomentosa* develops three types of microstructures, glandular trichomes, dendric trichomes, and extrafloral nectaries (a bowl-shaped organ), on its leaves [10]. Glandular trichomes were also distributed on the surface of *P. tomentosa* immature fruit, and a variety of geranylated flavanones was recently isolated from the viscous secretion on the surface of the immature fruits [11]. This article addresses the isolation and the structure elucidation of 30 (fatty acyl)-*O*-substituted glycerols including 25 new ones (*Fig. 1*) from the glandular trichome exudates on the leaves of *P. tomentosa*.

Results and Discussion. – A preliminary study demonstrated that the TLC pattern of the oily material collected by gently pressing glass fibers on the glandular trichomes of the young-leaf surface of *P. tomentosa* was identical with that of the leaf rinse with Et_2O. The young leaves were, therefore, rinsed twice in Et_2O, and the concentrated extract was subjected to column chromatography (silica gel) to yield eight glyceride fractions: *Fractions G-1 – G-8*. ^{1}H- and ^{13}C-NMR spectroscopic analysis of the fractions indicated that they were all acylglycerols (*Table 1*). The NMR data further suggested that the fatty acyl groups were substituted with OH and/or AcO groups. GC/MS Analysis of the original Et_2O extract in the form of trimethylsilyl (Me_3Si) derivatives allowed us to suggest the structure of some major constituents. For example, the planar structure of 1-*O*-acetyl-2-*O*-[3-(acetyloxy)-6-hydroxyeicosanoyl]glycerol **12** could be deduced from the EI-MS data of the bis(trimethylsilyl) ether derivative of **12** (*vide infra*). However, the analysis had the following limitations: *1*) the Me_3Si ether derivatives of **10**, **11**, **15**, and **16** were eluted at the same retention time. *2*) positional isomers having an AcO group at C(6), C(7), C(8), or C(9) of the fatty acyl moiety, *e.g.*, the Me_3Si ether derivatives of **5**, **6**, **7**, and **8**, exhibited very similar EI-MS. Accordingly, their structures could not be assigned unequivocally on the basis of the analysis of MS data. In addition, peaks due to 1-*O*-acylglycerols arising from an acyl migration (*vide infra*) interrupted the analysis of minor peaks. More importantly, we decided to determine the structures of these glycerides including the configurations at the OH- or AcO-substituted stereogenic centers. We, therefore, undertook an analytical strategy including chemical transformations.

We first focused on the structure elucidation of the oxygenated fatty acyl moieties of *Fractions G-1 – G-8*. The acylglycerol mixture (the Et_2O extract) was saponified with LiOH in aqueous 1,2-dimethoxyethane ($(MeOCH_2)_2$), and the liberated fatty acid mixture was treated with ethereal CH_2N_2 to give fatty acid methyl esters, which showed two spots by TLC analysis, the polar broad spot being subsequently separated into four spots. The ^{1}H-NMR spectrum of the less polar, minor fraction showed signals characteristic of 3-hydroxyfatty acid methyl esters (δ 3.97 – 4.03 (*m*), 2.52 (*dd*, $J = 16.3$, 3.0 Hz), and 2.41 (*dd*, $J = 16.3$, 9.0 Hz)). GC/MS Analysis of the Me_3Si ethers derived from this fraction exhibited two peaks in a 10 : 1 ratio. The MS of the major peak showed fragment ions at *m*/*z* 341 ($[CH(OSiMe_3)C_{17}H_{35}]^+$) and 175 ($[CH(OSiMe_3)CH_2CO_2Me]^+$) due to C(2)/C(3) and C(3)/C(4) cleavages, respectively,

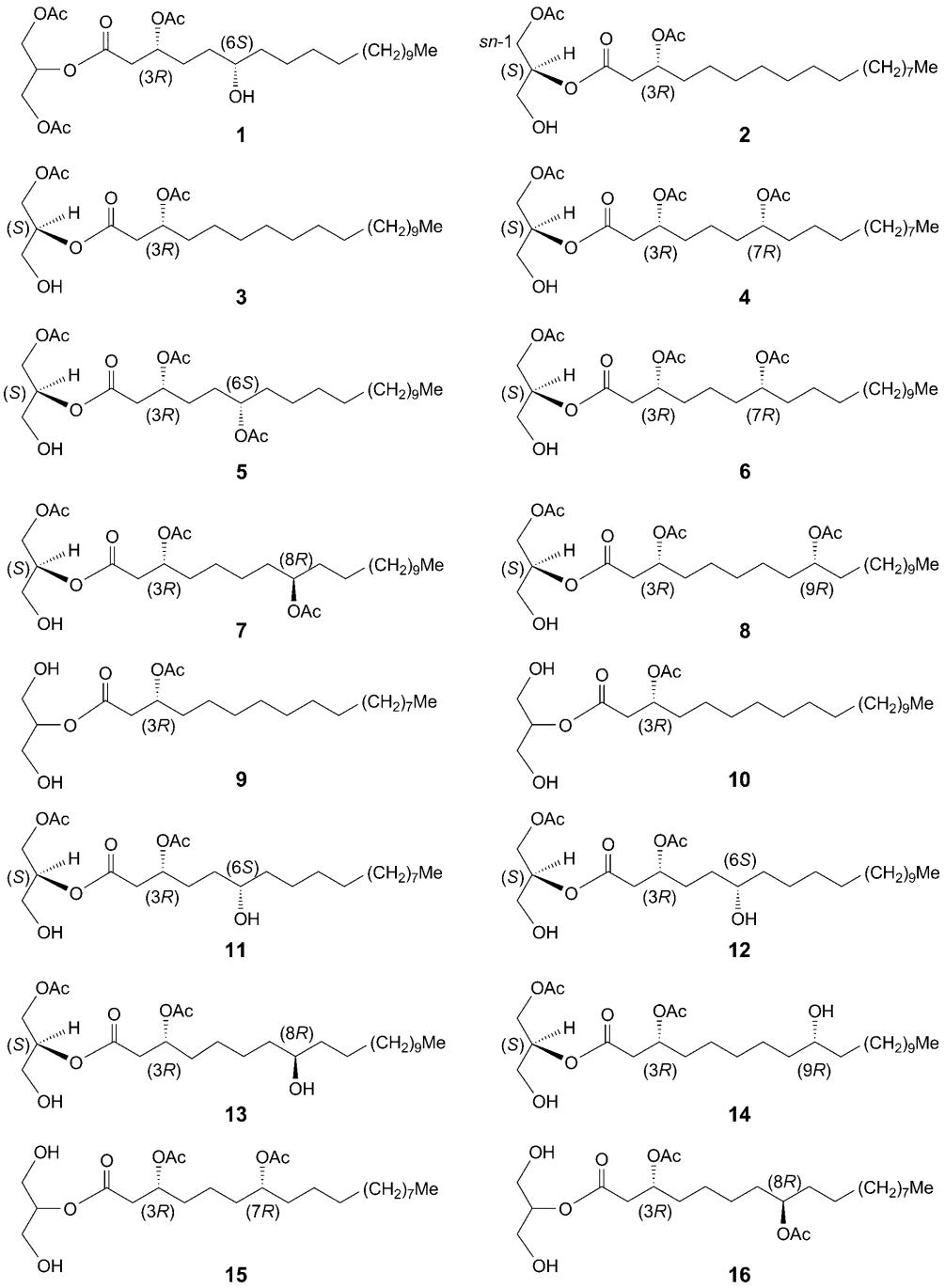


Fig. 1. *Acylglycerols characterized in glandular trichome exudate of* Paulownia tomentosa STEUD.

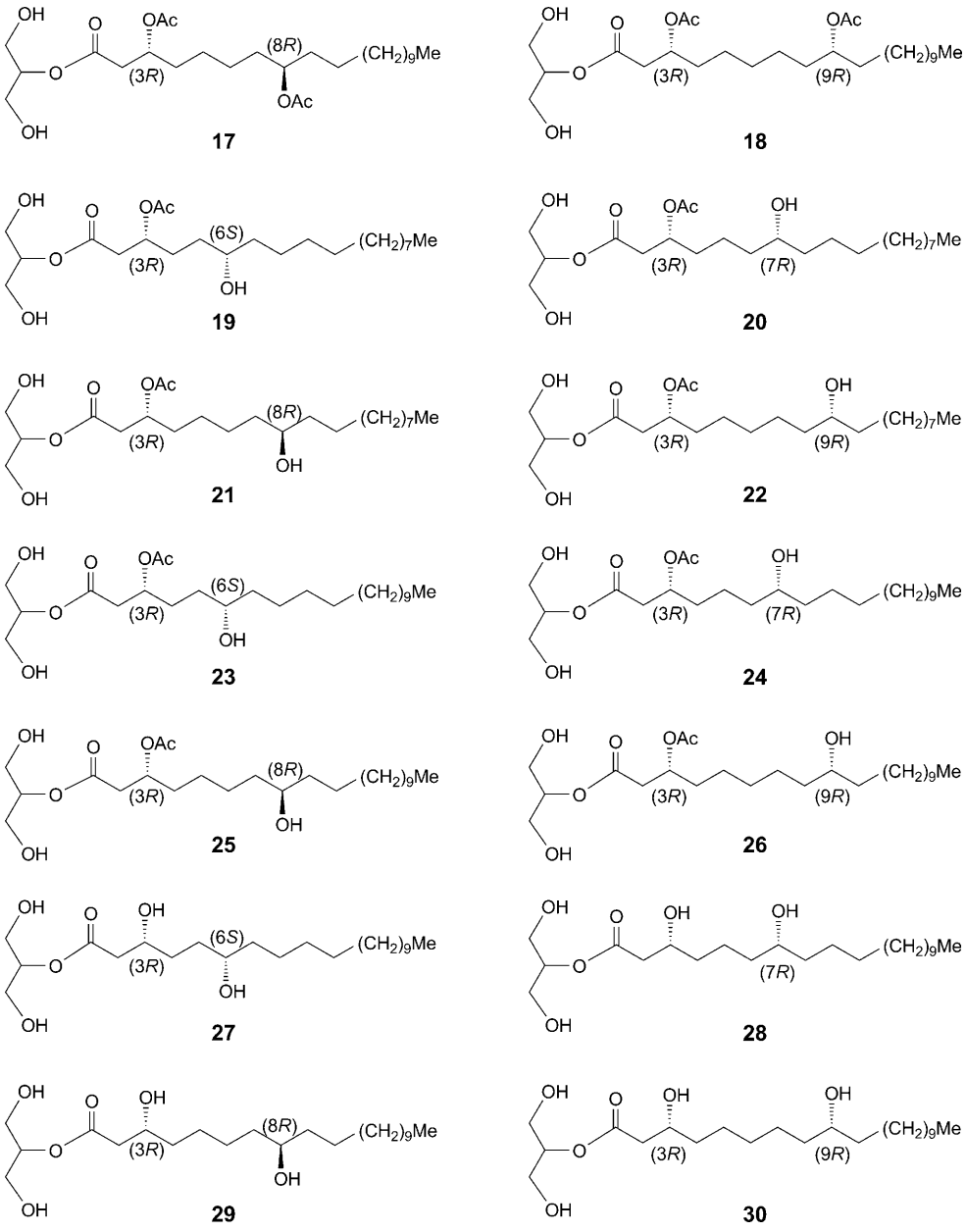


Fig. 1 (cont.)

while the minor peak exhibited the respective fragmentation ions at *m*/*z* 313 ($[CH(OSiMe_3)C_{15}H_{31}]^+$) and 175 [12]. The less polar fraction was, therefore, determined to be a 10:1 mixture of methyl 3-hydroxyeicosanoate (**31a**) and methyl 3-hydroxyoctadecanoate (**32a**) (*Fig. 2*).

Table 1. *^{1}H-NMR Data* (500 MHz, $CDCl_3$) *of* Fractions G-1 – G-8. δ in ppm, J in Hz.

	G-1 (= **1**)	*G-2* (= **2/3**)	*G-3* (= **4/5/6/7/8**)	*G-4* (= **9/10**)	*G-5* (= **11/12/13/14**)	*G-6* (= **15/16/17/18**)	*G-7* (= **19/20/21/22/23/24/25/26**)	*G-8*[a]) (= **27/28/29/30**)
2 H–*sn*-C(1)	4.31 (*dd*, J = 12.0, 5.0)[b]), 4.14 (*dd*, J = 12.0, 6.0)	4.30 (*dd*, J = 12.0, 4.5), 4.23 (*dd*, J = 12.0, 6.0)	4.29 (*dd*, J = 12.0, 4.5), 4.23 (*dd*, J = 12.0, 5.5)	3.79 – 3.85 (*m*, 4 H)	4.30 (*dd*, J = 12.0, 4.5), 4.23 (*dd*, J = 12.0, 6.0)	3.80 – 3.88 (*m*, 4 H)	3.78 – 3.85 (*m*, 4 H)	3.74 – 3.80 (*m*, 4 H)
2 H–*sn*-C(3)	4.30 (*dd*, J = 12.0, 5.0)[b]) 4.14 (*dd*, J = 12.0, 6.0)	3.68 – 3.79 (*m*)	3.68 – 3.79 (*m*)		3.78 (*dd*, J = 12.5, 3.9), 3.71 (*dd*, J = 12.5, 5.4)			
H–*sn*-C(2)	5.22 – 5.28 (*m*)	5.06 – 5.10 (*m*)	5.06 – 5.10 (*m*)	4.86 – 4.91 (*m*)	5.07 – 5.11 (*m*)	4.87 – 4.91 (*m*)	4.87 – 4.91 (*m*)	4.93 – 4.97 (*m*)
H_a–C(2)	2.65 (*dd*, J = 15.5, 7.0)	2.62 (*dd*, J = 15.5, 7.5)	2.55 – 2.64 (*m*, 2 H)	2.61 (*dd*, J = 15.5, 4.5)	2.68 (*dd*, J = 15.3, 7.0)	2.55 – 2.64 (*m*, 2 H)	2.56 – 2.66 (*m*, 2 H)	2.40 – 2.60 (*m*, 2 H)
H_b–C(2)	2.58 (*dd*, J = 15.5, 5.5)	2.58 (*dd*, J = 15.5, 4.5)		2.58 (*dd*, J = 15.5, 6.0)	2.58 (*dd*, J = 15.3, 5.5)			
H–C(3)	5.22 – 5.28 (*m*)	5.19 – 5.24 (*m*)	5.19 – 5.24 (*m*)	5.27 – 5.33 (*m*)	5.20 – 5.25 (*m*)	5.27 – 5.33 (*m*)	5.28 – 5.35 (*m*)	4.01 – 4.08 (*m*)
H–C(6, 7, 8, or 9)	3.57 – 3.63 (*m*)	–	4.81 – 4.87 (*m*)	–	3.58 – 3.64 (*m*)	4.81 – 4.87 (*m*)	3.54 – 3.62 (*m*)	3.53 – 3.57 (*m*)
AcO	2.10 (*s*, 6 H), 2.07 (*s*, 3 H)	2.07 (*s*, 3 H), 2.05 (*s*, 3 H)	2.08 (*s*, 3 H), 2.04 – 2.05 (*m*, 6 H)	2.06 (*s*, 3 H)	2.08 (*s*, 3 H), 2.04 – 2.05 (*m*, 3 H)	2.04 – 2.07 (*m*, 6 H)	2.04 – 2.07 (*m*, 3 H)	

[a]) Recorded in $CDCl_3/CD_3OD$ 9 : 1. [b]) Values may be interchanged.

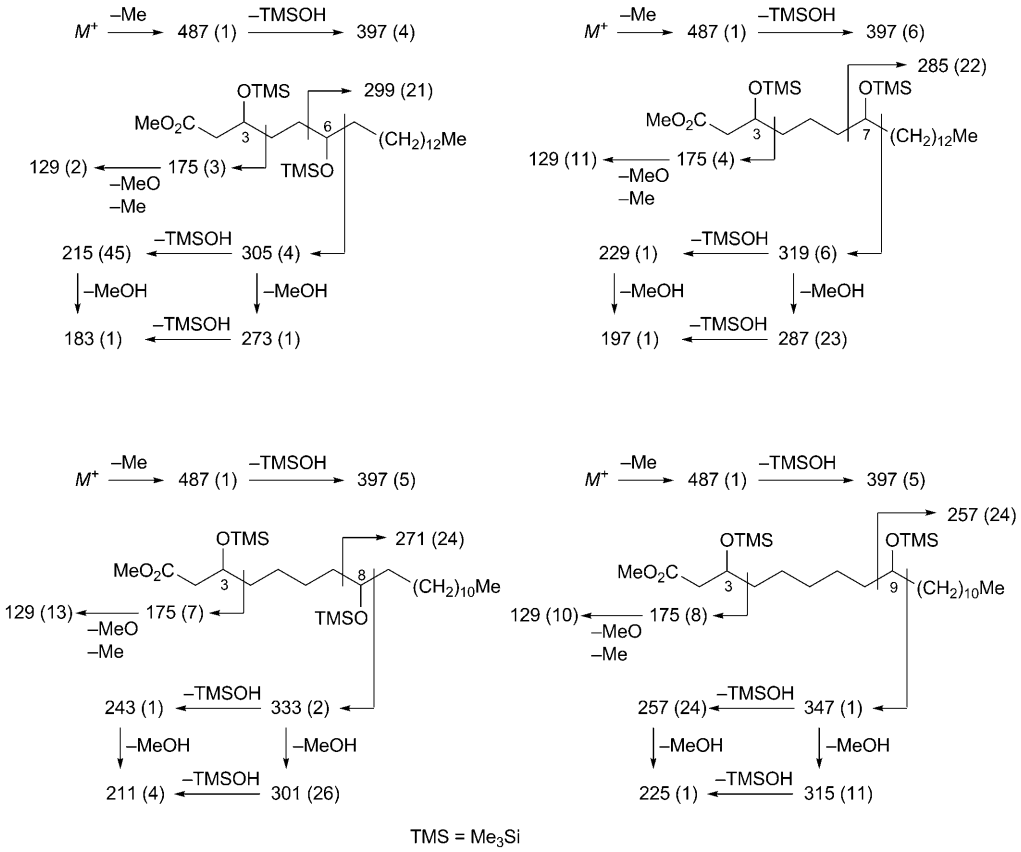
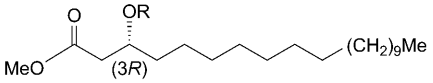


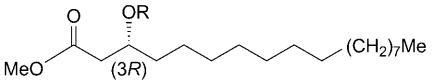
Fig. 2. *Fatty acid derivatives obtained from the glyceride fractions*

The ^{1}H-NMR spectrum of the more polar, major fraction was similar to that of the less polar fraction, except for the presence of additional OCH signals at δ 3.54–3.65 (*m*). The Me_3Si derivatives of this fraction showed eight peaks in the GC/MS in a 4:4:2:1:37:3:27:22 ratio, in the order of elution. These were determined to be the bis(trimethylsilyl) ethers of methyl 3,6-, 3,7-, 3,8-, and 3,9-dihydroxyoctadecanoates **34a**, **36a**, **38a**, and **40a** and of their respective eicosanoate homologues **33a**, **35a**, **37a**, and **39a** on the basis of diagnostic fragmentation patterns (*Fig. 3*) [13]. The fraction was further separated into four fractions (R_f values, 0.38, 0.34, 0.30, and 0.28, developed twice with hexane/AcOEt 1:1), and all separate fractions were analyzed, after conversion into Me_3Si ether derivatives, by GC/MS. The R_f 0.38 fraction was found to be a 20:1 mixture of the Me_3Si ether derivatives of **39a** and **40a**, the R_f 0.34 fraction a 13:1 mixture of those of **37a** and **38a**, the R_f 0.30 fraction a 10:1 mixture of those of **33a** and **34a**, and the R_f 0.28 fraction a 3:4 mixture of those of **35a** and **36a**.

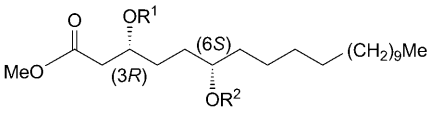
The absolute configurations at the OCH centers of the mono- and dihydroxy-substituted fatty acid methyl ester mixtures were determined by application of the 2-(naphthalen-2-yl)-2-methoxyacetic acid (=α-methoxynaphthalene-2-acetic acid;



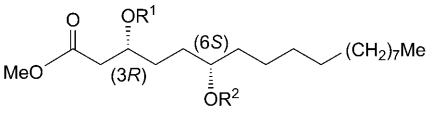
31a R = H
31b R = (*R*)-2NMA
31c R = (*S*)-2NMA



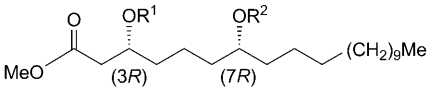
32a R = H
32b R = (*R*)-2NMA
32c R = (*S*)-2NMA



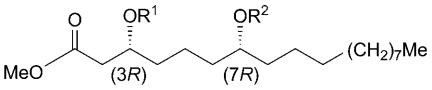
33a $R^1 = R^2 = H$
33b R^1 = (*R*)-2NMA, R^2 = H
33c R^1 = (*S*)-2NMA, R^2 = H
33d R^1 = H, R^2 = (*R*)-2NMA
33e R^1 = H, R^2 = (*S*)-2NMA



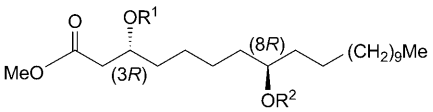
34a $R^1 = R^2 = H$
34b R^1 = (*R*)-2NMA, R^2 = H
34c R^1 = (*S*)-2NMA, R^2 = H
34d R^1 = H, R^2 = (*R*)-2NMA
34e R^1 = H, R^2 = (*S*)-2NMA



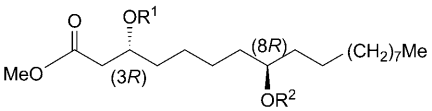
35a $R^1 = R^2 = H$
35b R^1 = (*R*)-2NMA, R^2 = H
35c R^1 = (*S*)-2NMA, R^2 = H
35d R^1 = H, R^2 = (*R*)-2NMA
35e R^1 = H, R^2 = (*S*)-2NMA



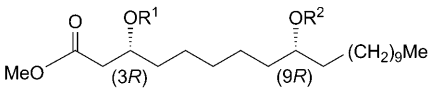
36a $R^1 = R^2 = H$
36b R^1 = (*R*)-2NMA, R^2 = H
36c R^1 = (*S*)-2NMA, R^2 = H
36d R^1 = H, R^2 = (*R*)-2NMA
36e R^1 = H, R^2 = (*S*)-2NMA



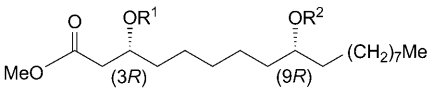
37a $R^1 = R^2 = H$
37b R^1 = (*R*)-2NMA, R^2 = H
37c R^1 = (*S*)-2NMA, R^2 = H
37d R^1 = H, R^2 = (*R*)-2NMA
37e R^1 = H, R^2 = (*S*)-2NMA



38a $R^1 = R^2 = H$
38b R^1 = (*R*)-2NMA, R^2 = H
38c R^1 = (*S*)-2NMA, R^2 = H
38d R^1 = H, R^2 = (*R*)-2NMA
38e R^1 = H, R^2 = (*S*)-2NMA



39a $R^1 = R^2 = H$
39b R^1 = (*R*)-2NMA, R^2 = H
39c R^1 = (*S*)-2NMA, R^2 = H
39d R^1 = H, R^2 = (*R*)-2NMA
39e R^1 = H, R^2 = (*S*)-2NMA



40a $R^1 = R^2 = H$
40b R^1 = (*R*)-2NMA, R^2 = H
40c R^1 = (*S*)-2NMA, R^2 = H
40d R^1 = H, R^2 = (*R*)-2NMA
40e R^1 = H, R^2 = (*S*)-2NMA

Fig. 3. *Mass fragmentation of the methyl bis[(trimethylsilyl)oxy]eicosanoates.* A fragment ion due to Me_3Si^+ (= $[TMS]^+$) was observed at *m/z* 73 as the base peak (100%) for all compounds. Relative intensities [%] are shown in parentheses. For the corresponding octadecanoate derivatives, $[M - Me]^+$, $[M - Me - Me_3SiOH]^+$, and terminal Me-containing cleavage ions were observed at 28 mass units lower than the respective ions shown above.

2NMA-OH) ester method [14][15]. Treatment of **31a**/**32a** with 1.6 equiv. of (*R*)-2NMA-OH or (*S*)-2NMA-OH in the presence of 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC·HCl), *N*,*N*-dimethylpyridin-4-amine (DMAP), and DMAP·HCl in $CHCl_3$ [16] gave the 3-*O*-(*R*)-2NMA derivatives **31b**/**32b** and the 3-*O*-(*S*)-2NMA derivatives **31c**/**32c**, respectively, in 80% yield. The negative $\Delta\delta(R-S)$ values observed for the 2 H–C(2) and methoxycarbonyl (COOMe) signals implied the (3*R*)-configuration (*Table 2*). The methyl esters **39a**/**40a** were treated with (*R*)-2NMA-OH (1.3 equiv.) under similar conditions to give an inseparable 1:1 mixture of 3-*O*-(*R*)-2NMA derivatives **39b**/**40b** and 9-*O*-(*R*)-2NMA derivatives **39d**/**40d** in 60% yield. The corresponding 3-*O*-(*S*)-2NMA derivatives **39c**/**40c** and 9-*O*-(*S*)-2NMA derivatives **39e**/**40e** were also obtained as an inseparable 1:1 mixture. The ^{1}H-NMR data of these 2NMA derivatives, which were assigned in comparison with those of **31b**/**32b** and **31c**/**32c**, are listed in *Table 2*. The $\Delta\delta(R-S)$ values for the 2 H–C(2) and COOMe signals of the 3-*O*-2NMA derivatives were negative, whereas the $\Delta\delta(R-S)$ value for H–C(9) was positive. The $\Delta\delta(R-S)$ values for H–C(3) and 2 H–C(2) of the 9-*O*-2NMA derivatives were negative. These data established the (3*R*,9*R*)-configuration for **39a**/**40a**. In the same manner, the (3*R*,8*R*)-configuration of **37a**/**38a** and the (3*R*,7*R*)-configuration of **35a**/**36a** were assigned on the basis of the ^{1}H-NMR data of their 2NMA derivatives **37b**/**38b**, **37c**/**38c**, **37d**/**38d**, and **37e**/**38e**, and **35b**/**36b**, **35c**/**36c**, **35d**/**36d**, and **35e**/**36e**, respectively (*Table 2*). The $\Delta\delta(R-S)$ values for the H–C(6), 2 H–C(2), and COOMe signals of the 3-*O*-2NMA derivatives **33b**/**34b** and **33c**/**34c** of **33a**/**34a** implied the (3*R*)-configuration. However, the $\Delta\delta(R-S)$ values for the H–C(3), 2 H–C(2), and COOMe signals of the 6-*O*-2NMA derivatives **33d**/**34d** and **33e**/**34e** were positive, in contrast to the data of the above three positional isomers. Accordingly, the C(6) configuration of the 3,6-dihydroxy-substituted fatty acid esters **33a**/**34a** was determined to be (*S*).

These initial studies on the fatty acyl moieties of a mixture of *G-1*–*G-8* provided a base line set of spectral data as well as authentic samples of the Me_3Si-substituted methyl esters for GC analysis. The separated glyceride fractions, *G-1*–*G-8*, were analyzed in an analogous manner.

Fraction G-1 (=**1**) showed a quasimolecular ion in the HR-FAB-MS at *m*/*z* 545.3680 ($[M+H]^+$), which corresponded to the molecular formula $C_{29}H_{52}O_9$. The ^{1}H-NMR spectrum showed signals of five H-atoms assignable to the glycerol moiety of a tri-*O*-acylglycerol, signals of two OCH groups at δ 3.57–3.63 (*m*) and 5.22–5.28 (*m*, spin–spin coupled to the neighboring CH_2), of a CH_2 group at δ 2.65 (*dd*, $J=15.5$, 7.0 Hz) and 2.58 (*dd*, $J=15.5$, 5.5 Hz), and of longer-chain CH_2 groups at δ 1.25 with a terminal Me *t* at δ 0.88 ($J=7.2$ Hz) assignable to a 3-(acetyloxy)-*n*-hydroxy-substituted fatty acyl moiety ($n=6$, 7, 8, or 9 from the results of the initial studies), and the signals of three Ac groups (*Table 1*). The ^{13}C-NMR spectrum showed four ester C=O groups at δ 170.5 (2×), 170.3, and 169.5. The HMBC spectrum of *G-1* exhibited a correlation from the *Me*C=O signal at δ (H) 2.10 (overlapping two Me *s*) to the signal at δ(C) 170.5 (overlapping two Ac C=O groups), which was, in turn, correlated with the glycerol OCH_2 signals at δ 4.30 and 4.31 (H_a–C(1), H_a–C(3)) and 4.14 (2 H, H_b–C(1), H_b–C(3)). The OCH_2 groups did not show any correlation to the fatty acyl C=O group at δ 169.5, whose assignment was confirmed by an HMBC correlation from CH_2(2) of the fatty acyl moiety. The chemical shifts of C(4) (δ 30.1) and C(5) (δ 32.5), assigned by

Table 2. *^{1}H-NMR Data* (500 MHz, $CDCl_3$) *of the Mono-*O-*(*R*)- and Mono-*O-*(*S*)-2NMA Derivatives of the Hydroxy-Substituted Fatty Acid Methyl Esters.* δ in ppm, *J* in Hz.

	3-*O*-(*R*)-2NMA	3-*O*-(*S*)-2NMA	$\Delta\delta(R-S)$	6-, 7-, 8-, or 9-*O*-(*R*)-2NMA	6-, 7-, 8-, or 9-*O*-(*S*)-2NMA	$\Delta\delta(R-S)$
	31b/32b	**31c/32c**				
COOMe	3.20 (*s*)	3.57 (*s*)	−0.37			
H_a−C(2)	2.49 (*dd*, *J* = 15.6, 8.0)	2.60 (*dd*, *J* = 15.5, 7.6)	−0.11			
H_b−C(2)	2.42 (*dd*, *J* = 15.6, 7.6)	2.52 (*dd*, *J* = 15.5, 5.4)	−0.10			
H−C(3)	5.24–5.30 (*m*)	5.24–5.30 (*m*)	–			
	39b/40b	**39c/40c**		**39d/40d**	**39e/40e**	
COOMe	3.22 (*s*)	3.58 (*s*)	−0.36	3.72 (*s*)	3.72 (*s*)	0.00
H_a−C(2)	2.49 (*dd*, *J* = 15.7, 8.1)	2.61 (*dd*, *J* = 15.3, 7.6)	−0.12	2.35 (*dd*, *J* = 16.4, 3.4)	2.46 (*dd*, *J* = 16.4, 3.1)	−0.11
H_b−C(2)	2.42 (*dd*, *J* = 15.7, 5.1)	2.53 (*dd*, *J* = 15.3, 5.3)	−0.11	2.23 (*dd*, *J* = 16.4, 9.0)	2.37 (*dd*, *J* = 16.4, 9.1)	−0.14
H−C(3)	5.24–5.30 (*m*)	5.24–5.30 (*m*)	–	3.72–3.80 (*m*)	3.90–3.98 (*m*)	−0.18
H−C(9)	3.48–3.54 (*m*)	3.34–3.40 (*m*)	+0.14	4.87–4.93 (*m*)	4.87–4.93 (*m*)	–
	37b/38b	**37c/38c**		**37d/38d**	**37e/38e**	
COOMe	3.23 (*s*)	3.59 (*s*)	−0.36	3.70 (*s*)	3.71 (*s*)	−0.01
H_a−C(2)	2.50 (*dd*, *J* = 15.6, 8.1)	2.61 (*dd*, *J* = 15.3, 7.6)	−0.11	2.26 (*dd*, *J* = 16.4, 3.3)	2.44 (*dd*, *J* = 16.5, 3.2)	−0.18
H_b−C(2)	2.43 (*dd*, *J* = 15.6, 5.1)	2.53 (*dd*, *J* = 15.3, 5.4)	−0.10	2.19 (*dd*, *J* = 16.4, 8.8)	2.36 (*dd*, *J* = 16.5, 9.0)	−0.17
H−C(3)	5.24–5.30 (*m*)	5.24–5.30 (*m*)	–	3.64–3.70 (*m*)	3.89–3.95 (*m*)	−0.25
H−C(8)	3.43–3.49 (*m*)	3.20–3.26 (*m*)	+0.23	4.87–4.93 (*m*)	4.87–4.93 (*m*)	–
	35b/36b	**35c/36c**		**35d/36d**	**35e/36e**	
COOMe	3.22 (*s*)	3.59 (*s*)	−0.36	3.70 (*s*)	3.71 (*s*)	−0.01
H_a−C(2)	2.50 (*dd*, *J* = 15.5, 8.4)	2.62 (*dd*, *J* = 15.6, 7.3)	−0.11	2.35–2.36 (*m*)	2.40 (*dd*, *J* = 16.6, 2.9)	−0.04
H_b−C(2)	2.44 (*dd*, *J* = 15.5, 5.1)	2.54 (*dd*, *J* = 15.6, 5.3)	−0.10	2.29–2.30 (*m*)	2.32 (*dd*, *J* = 16.6, 8.6)	−0.02
H−C(3)	5.25–5.31 (*m*)	5.25–5.31 (*m*)	–	3.47–3.53 (*m*)	3.85–3.91 (*m*)	−0.38
H−C(7)	3.41–3.47 (*m*)	3.05–3.13 (*m*)	+0.35	4.88–4.94 (*m*)	4.88–4.94 (*m*)	–
	33b/34b	**33c/34c**		**33d/34d**	**33e/34e**	
COOMe	3.25 (*s*)	3.60 (*s*)	−0.35	3.69 (*s*)	3.63 (*s*)	+0.06
H_a−C(2)	2.52 (*dd*, *J* = 15.7, 7.7)	2.64 (*dd*, *J* = 15.7, 7.8)	−0.12	2.36 (*dd*, *J* = 16.6, 3.1)	1.84–1.85 (*m*)	+0.52
H_b−C(2)	2.44 (*dd*, *J* = 15.7, 5.3)	2.54 (*dd*, *J* = 15.7, 5.7)	−0.10	2.29 (*dd*, *J* = 16.6, 8.9)	1.83–1.84 (*m*)	+0.46
H−C(3)	5.29–5.35 (*m*)	5.29–5.35 (*m*)	–	3.90–3.96 (*m*)	3.59–3.65 (*m*)	+0.31
H−C(6)	3.48–3.54 (*m*)	3.18–3.24 (*m*)	0.30	4.92–4.98 (*m*)	4.92–4.98 (*m*)	–

HMBC correlations, suggested a 3-(acetyloxy)-6-hydroxy substitution pattern. The oxygenation at C(3) and C(6) was evidenced by the fact that GC/MS analysis of the Me_3Si-substituted methyl ester derivative obtained from *G-1* showed a single peak

corresponding to the bis(trimethylsilyl) ether derivative of **33a**. Furthermore, GC/MS analysis of *G-1* in the form of the Me_3Si ether derivative displayed characteristic fragment ions at *m/z* 419 (C(6)/C(7) cleavage) and 299 ([$CH(OSiMe_3)C_{14}H_{29}$], C(5)/C(6) cleavage) (*Table 3*), which supported the OH–C(6) function in the fatty acyl moiety. *G-1* was thus determined to be 1,3-di-*O*-acetyl-2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-hydroxyeicosanoyl]glycerol (**1**). The configuration at C(3) and C(6) of the fatty acyl moiety of **1** was deduced from the data of the initial studies described above. The (6*S*)-configuration was confirmed by application of *Mosher*'s ester method to *G-1* ($\Delta\delta(S-R) = +0.06$ ppm for the H–C(3) signals of the 6-*O*-MTPA derivatives of *G-1*, and $\Delta\delta(S-R) = +0.09/+0.07$ ppm for the 2 H–C(2) signals). (MTPA = α-methoxy-α-(trifluoromethyl)phenylacetyl = 3,3,3-trifluoro-2-methoxy-2-phenylpropyl).

Fraction G-2 (**2**/**3**) displayed a quasimolecular ion in the HR-FAB-MS at *m/z* 487.3613 ([$M+H]^+$), which corresponded to the molecular formula $C_{27}H_{50}O_7$. The ^{1}H-NMR spectrum displayed signals for five H-atoms assignable to the glycerol moiety of a 1,2-di-*O*-acylglycerol, signals of a 3-(acetyloxy)-substituted fatty acyl moiety (δ 5.19–5.24 (*m*), 2.62 (*dd*, *J* = 15.5, 7.5 Hz), and 2.58 (*dd*, *J* = 15.5, 4.5 Hz)) and two *Me*C=O groups (*Table 1*). In the HMBC spectrum of *G-2*, the glycerol OCH_2 groups (δ 4.30 and 4.23) were correlated with the Ac C=O group (δ 170.9), which, in turn, was correlated with the *Me*C=O group (δ 2.07), thus indicating that the fatty acyl and Ac groups were linked to C(2) and C(1) (or C(3)), respectively, of the glycerol moiety. GC Analysis of the Me_3Si-substituted methyl ester derivatives of the fatty acid fraction obtained from *G-2* showed two peaks in a 10:1 ratio, corresponding to the Me_3Si ether derivatives of **31a** and **32a**. The molecules had another stereogenic center at C(2) of the glycerol moiety, and the configuration was determined to be (*S*) by converting *G-2* to a compound with known absolute configuration, (+)-3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol [17]. The configurational homogeneity (100% ee) at C(2) of the glycerol moiety of *G-2* was further confirmed by ^{1}H-NMR analysis of the corresponding bis-*O*-(*S*)-MTPA derivatives in comparison with the data of 1,2-bis-*O*-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol and 2,3-bis-*O*-(*S*)-MTPA derivative of 1-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol, which were prepared from the 3-*O*- and 1-*O*-silylated *sn*-glycerol, respectively. Hence, *G-2* was established to be a 10:1 mixture of 1-*O*-acetyl-2-*O*-[(3*R*)-3-(acetyloxy)eicosanoyl]-*sn*-glycerol (**3**) and 1-*O*-acetyl-2-*O*-[(3*R*)-3-(acetyloxy)octadecanoyl]-*sn*-glycerol (**2**).

Fraction G-3 (= **4**/**5**/**6**/**7**/**8**) seemed to be a mixture of compounds having the molecular formulae $C_{29}H_{52}O_9$ and $C_{27}H_{48}O_9$, based on quasimolecular ions at *m/z* 545.3652 and 517.3392 ([$M+H]^+$) in the HR-FAB-MS. The ^{1}H-NMR spectrum of *G-3* showed four signals (5 H) assignable to the glycerol moiety of a 1,2-di-*O*-acylglycerol, signals of two OCH groups at δ 5.19–5.24 (*m*) and 4.81–4.87 (*m*) and of a CH_2 group at δ 2.55–2.64 (spin–spin coupled to the OCH at δ 5.19–5.24 (*m*)), and of three MeC=O groups at δ 2.08 (*s*) and 2.04–2.05 (*m*, 6 H, *Table 1*). These data indicated that the acyl moiety contained two AcO groups at C(3) and at C(6), C(7), C(8), or C(9). A rather complex pattern of the CH_2(2) and MeC=O signals in the fatty acyl moiety suggested that the fatty acyl moiety could be a mixture in terms of the position of the unsettled AcO group. HMBCs revealed that the fatty-acyl and Ac groups were linked to C(2) and C(1) (or C(3)), respectively, of the glycerol moiety. GC Analysis of the Me_3Si-substituted methyl esters derived from *G-3* showed five peaks in a

28:6:6:26:34 ratio, eluting in that order. These peaks were identified as the bis(trimethylsilyl) ether derivatives of **36a**, **33a**, **35a**, **37a**, and **39a**, in that order, by direct comparison with authentic samples. The C(2) configuration of the glycerol moiety of *G-3* was determined to be (*S*) in the same manner as described for *G-2*. Accordingly, *G-3* was elucidated to be a 28:6:6:26:34 mixture of 1-*O*-acetyl-2-*O*-[(3*R*,7*R*)-3,7-bis(acetyloxy)octadecanoyl]-*sn*-glycerol (**4**), 1-*O*-acetyl-2-*O*-[(3*R*,6*S*)-3,6-bis(acetyloxy)eicosanoyl]-*sn*-glycerol (**5**), 1-*O*-acetyl-2-*O*-[(3*R*,7*R*)-3,7-bis(acetyloxy)eicosanoyl]-*sn*-glycerol (**6**), 1-*O*-acetyl-2-*O*-[(3*R*,8*R*)-3,8-bis(acetyloxy)eicosanoyl]-*sn*-glycerol (**7**) and 1-*O*-acetyl-2-*O*-[(3*R*,9*R*)-3,9-bis(acetyloxy)eicosanoyl]-*sn*-glycerol (**8**).

Fraction G-4 (= **9**/**10**) was difficult to separate from *G-5* by column chromatography (silica gel). The structure elucidation was, therefore, carried out with a 1:1 mixture of *G-4* and *G-5*. The molecular formula of *G-4* was deduced as $C_{25}H_{48}O_6$ on the basis of a quasimolecular ion at *m*/*z* 445.3574 ($[M+H]^+$) in the HR-FAB-MS. The ^{1}H-NMR spectrum of the sample showed, in addition to the signals of *G-5*, the signals of five H-atoms assignable to the glycerol moiety of a 2-*O*-acylglycerol and signals of a 3-(acetyloxy)-substituted fatty-acyl moiety (δ 2.58 (*dd*, $J = 15.5$, 6.0 Hz), 2.61 (*dd*, $J = 15.5$, 4.5 Hz), and 5.27–5.33 (*m*); *Table 1*). Acetylation of the sample gave two separable products in a *ca.* 1:1 ratio. The less polar and the more polar products were assigned to the diacetate derivatives of *G-4* (*m*/*z* 529 $[M+H]^+$) and *G-5* (*m*/*z* 587 $[M+H]^+$), respectively, on the basis of FAB-MS and ^{1}H-NMR data. The ^{1}H-NMR spectrum of the less polar acetylation product (from *G-4*) showed signals assignable to the glycerol moiety of a tri-*O*-acylglycerol, in addition to signals due to a 3-(acetyloxy)-substituted fatty acyl moiety (δ 5.22–5.28 (*m*), 2.62 (*dd*, $J = 15.4$, 7.5 Hz), and 2.57 (*dd*, $J = 15.4$, 10.0 Hz)). The downfield shifts of the CH_2(1) and CH_2(3) H-atoms of the glycerol moiety, compared to those of *G-4*, implied that the acetylation took place at these positions. The triacetate was hydrolyzed, and the resulting acid was converted to the methyl ester. GC Analysis of the corresponding Me_3Si-substituted methyl ester showed two peaks corresponding to the Me_3Si ether derivatives of **31a** and **32a** in a 10:1 ratio. Hence, *G-4* was determined to be a 10:1 mixture of 2-*O*-[(3*R*)-3-(acetyloxy)eicosanoyl]glycerol (**10**) and 2-*O*-[(3*R*)-3-(acetyloxy)octadecanoyl]glycerol (**9**).

Fraction G-5 (= **11**/**12**/**13**/**14**) showed a quasimolecular-ion peak in the HR-FAB-MS at *m*/*z* 503.3586 ($[M+H]^+$), which corresponded to the molecular formula $C_{27}H_{50}O_8$. The ^{1}H-NMR spectrum of *G-5* resembled that of *G-3* but exhibited only two MeC=O signals, and an OCH signal assignable to H–C(6), H–C(7), H–C(8), or H–C(9) resonated upfield at δ 3.58–3.64 (*m*) compared to that of *G-3*. The spectral data suggested that *G-5* could consist of 1-*O*-acetyl-2-*O*-[3-(acetyloxy)-*n*-hydroxyfatty acyl]glycerols ($n = 6–9$). The 1-*O*-acetyl-2-*O*-(fatty acyl) substitution was evidenced by HMBCs as described for *G-2*. GC Analysis of the Me_3Si-substituted methyl ester derivative of the fatty acid fraction obtained from *G-5* showed four peaks in a 15:70:8:7 ratio, eluting in that order, which were identified as the bis(trimethylsilyl) ether derivatives of **34a**, **33a**, **37a**, and **39a**, respectively, by direct comparison with authentic samples. The configuration at C(2) of the glycerol moiety of *G-5* was determined to be (*S*) in the same manner as described for *G-2*. *G-5* was, therefore, determined to be a 15:70:8:7 mixture of 1-*O*-acetyl-2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-

Table 3. *GC/MS Data of the Trimethylsilyl Derivatives of Glycerides* **1**–**30**[a]).

Glyceride	t_R [min]	Rel. abundance [%]	Fragmentation ions *m/z* (rel. [%])[c])
9	7.2	1.2	545 (2, $[M-Me]^+$), 485 (6, $[M-Me-AcOH]^+$), 429 (5), 339 (13), 265 (18), 218 (50), 129 (63), 103 (21), 73 (100)
3	8.3	tr.[b])	515 (2, $[M-Me]^+$), 455 (14, $[M-Me-AcOH]^+$), 440 (3), 397 (3), 380 (4), 325 (1), 293 (66), 189 (72), 129 (45), 73 (100)
19	9.3	0.8	633 (1, $[M-Me]^+$), 573 (8, $[M-Me-AcOH]^+$), 509 (8), *479* (2), 469 (11), 412 (7), 340 (12), *271* (35), 236 (68), 218 (51), 129 (52), 103 (22), 73 (100)
20	9.6	1.1	633 (3, $[M-Me]^+$), 573 (7, $[M-Me-AcOH]^+$), 509 (7), *493* (2), 469 (11), 412 (8), 340 (13), *257* (36), 236 (68), 218 (62), 129 (48), 103 (22), 73 (100)
21	9.8	0.6	633 (3, $[M-Me]^+$), 573 (9, $[M-Me-AcOH]^+$), 509 (4), *507* (3), 469 (12), 412 (7), 340 (14), *243* (37), 236 (64), 218 (56), 129 (44), 103 (18), 73 (100)
22	10.0	tr.[b])	633 (4, $[M-Me]^+$), 573 (6, $[M-Me-AcOH]^+$), *521* (3), 509 (5), 469 (10), 412 (6), 340 (11), *229* (41), 236 (70), 218 (67), 129 (64), 103 (21), 73 (100)
10	11.0	11.8	573 (3, $[M-Me]^+$), 513 (7, $[M-Me-AcOH]^+$), 457 (5), 367 (13), 293 (18), 218 (60), 129 (68), 103 (26), 73 (100)
11	11.0	2.0	603 (6, $[M-Me]^+$), 543 (10, $[M-Me-AcOH]^+$), 471 (5), *449* (11), 413 (7), *389* (16), 353 (12), *271* (71), 189 (64), 129 (66), 73 (100)
15	11.0	2.4	603 (3, $[M-Me]^+$), 543 (11, $[M-Me-AcOH]^+$), 513 (7), 457 (6), 368 (12), 291 (18), 236 (28), 229 (14), 218 (72), 129 (66), 103 (18), 73 (100)
16	11.0	3.5	603 (3, $[M-Me]^+$), 543 (11, $[M-Me-AcOH]^+$), 513 (7), 457 (6), 368 (12), 291 (18), 236 (28), 229 (14), 218 (72), 129 (66), 103 (18), 73 (100)
27	12.0	1.6	691 (1, $[M-Me]^+$), 603 (1), *509* (2), 471 (1), 451 (4), 419 (3), 339 (5), *299* (9), 273 (12), 219 (12), 218 (12), 147 (9), 103 (21), 129 (12), 73 (100)
28	12.3	tr.[b])	691 (2, $[M-Me]^+$), 603 (2), *523* (1), 471 (1), 451 (5), 429 (1), 339 (3), 287 (11), *285* (8), 219 (8), 218 (8), 147 (8), 103 (22), 129 (18), 73 (100)
29	12.6	1.8	691 (1, $[M-Me]^+$), 603 (2), *537* (3), 471 (1), 451 (1), 429 (2), 339 (1), 301 (8), *271* (13), 219 (8), 218 (8), 147 (9), 103 (24), 129 (15), 73 (100)
30	12.9	0.9	691 (1, $[M-Me]^+$), 603 (2), *551* (3), 471 (7), 451 (3), 429 (2), 339 (1), 315 (3), *257* (14), 219 (9), 218 (9), 147 (12), 103 (21), 129 (13), 73 (100)
2	13.1	2.7	543 (4, $[M-Me]^+$), 483 (16, $[M-Me-AcOH]^+$), 468 (4), 425 (6), 408 (8), 353 (1), 293 (61), 189 (72), 129 (48), 73 (100)
4	13.1	1.2	573 (2, $[M-Me]^+$), 513 (12, $[M-Me-AcOH]^+$), 453 (14), 337 (20), 263 (22), 189 (72), 129 (50), 73 (100)
23	14.3	4.4	661 (3, $[M-Me]^+$), 601 (5, $[M-Me-AcOH]^+$), 537 (6), 497 (11), *479* (4), 440 (12), 368 (11), *299* (32), 236 (64), 218 (53), 129 (52), 103 (18), 73 (100)

Table 3 (cont.)

Glyceride	t_R [min]	Rel. abundance [%]	Fragmentation ions *m/z* (rel. [%])[c])
24	14.7	0.6	661 (3, $[M-Me]^+$), 601 (6, $[M-Me-AcOH]^+$), 537 (6), 497 (13), *493* (3), 440 (12), 368 (11), *285* (32), 236 (62), 218 (54), 129 (50), 103 (22), 73 (100)
25	14.9	2.9	661 (3, $[M-Me]^+$), 601 (7, $[M-Me-AcOH]^+$), 537 (8), *507* (3), 497 (12), 440 (13), 368 (14), *271* (32), 236 (58), 218 (44), 129 (47), 103 (21), 73 (100)
26	15.2	3.0	661 (5, $[M-Me]^+$), 601 (7, $[M-Me-AcOH]^+$), 537 (8), *521* (4), 497 (12), 440 (13), 368 (12), *257* (30), 236 (60), 218 (54), 129 (52), 103 (19), 73 (100)
12	16.5	19.8	631 (7, $[M-Me]^+$), 571 (11, $[M-Me-AcOH]^+$), 499 (6), *449* (11), 441 (6), *389* (24), 381 (14), *299* (52), 189 (46), 129 (48), 73 (100)
13	16.9	1.5	631 (7, $[M-Me]^+$), 571 (10, $[M-Me-AcOH]^+$), 499 (7), *477* (12), 441 (6), *417* (12), 381 (14), *271* (46), 189 (52), 129 (60), 73 (100)
14	17.3	1.5	631 (8, $[M-Me]^+$), 571 (12, $[M-Me-AcOH]^+$), 499 (6), *491* (9), 441 (6), *431* (7), 381 (15), *257* (45), 189 (50), 129 (62), 73 (100)
17	17.4	14.3	631 (3, $[M-Me]^+$), 571 (11, $[M-Me-AcOH]^+$), 511 (7), 368 (13), 291 (25), 257 (24), 236 (26), 218 (66), 129 (66), 103 (18), 73 (100)
18	17.5	12.4	631 (4, $[M-Me]^+$), 571 (11, $[M-Me-AcOH]^+$), 511 (7), 368 (14), 291 (26), 257 (14), 236 (24), 218 (60), 129 (60), 103 (20), 73 (100)
1	18.6	2.3	601 (1, $[M-Me]^+$), 541 (3, $[M-Me-AcOH]^+$), 481 (2), 441 (3), *419* (7), 381 (8), *359* (18), *299* (41), 227 (47), 159 (62), 73 (100)
5	19.0	tr.[b])	601 (4, $[M-Me]^+$), 541 (12, $[M-Me-AcOH]^+$), 481 (6), 365 (16), 291 (26), 189 (51), 129 (62), 73 (100)
6	19.6	tr.[b])	601 (4, $[M-Me]^+$), 541 (9, $[M-Me-AcOH]^+$), 481 (3), 365 (11), 291 (20), 189 (40), 129 (58), 73 (100)
7	20.2	1.9	601 (3, $[M-Me]^+$), 541 (14, $[M-Me-AcOH]^+$), 481 (6), 365 (14), 291 (27), 189 (44), 129 (60), 73 (100)
8	20.4	2.1	601 (3, $[M-Me]^+$), 541 (14, $[M-Me-AcOH]^+$), 481 (7), 365 (16), 291 (24), 189 (50), 129 (64), 73 (100)

[a]) Retention times (t_R) and relative-abundance values [%] are from GC analysis of the Me_3Si derivatives of **1**–**30**. For GC conditions, see *Exper. Part.* [b]) Traces (tr.), *i.e.*, less than 0.5%. The MS data for minor Me_3Si derivatives were adopted from the GC/MS data of the separated glyceride fractions. [c]) *m/z* of fragment ions in italics were diagnostic for the assignment of the position of the silylated OH group at C(6), C(7), C(8), or C(9).

hydroxyoctadecanoyl]-*sn*-glycerol (**11**), 1-*O*-acetyl-2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-hydroxyeicosanoyl]-*sn*-glycerol (**12**), 1-*O*-acetyl-2-*O*-[(3*R*,8*R*)-3-(acetyloxy)-8-hydroxyeicosanoyl]-*sn*-glycerol (**13**), and 1-*O*-acetyl-2-*O*-[(3*R*,9*R*)-3-(acetyloxy)-9-hydroxyeicosanoyl]-*sn*-glycerol (**14**). GC/MS Analysis of *G-5* in the form of the Me_3Si derivatives supported these structures including the positions of OH substitution

(*Table 3*). For example, the bis(trimethylsilyl) ether derivative of **12** displayed an ion at *m/z* 631 ($[M-Me]^+$) as well as fragment ions at *m/z* 449 and 299 ($[CH(OSiMe_3)C_{14}H_{29}]^+$) (*Tabl 3*), arising from the cleavage at C(6)/C(7) and C(5)/C(6), respectively, confirming the 6-OH substitution in the fatty acyl moiety.

Fraction G-6 (=**15**/**16**/**17**/**18**) seemed to be a mixture of compounds having the molecular formulae $C_{27}H_{50}O_8$ and $C_{25}H_{46}O_8$, based on quasimolecular-ion peaks at *m/z* 503.3627 and 475.3256 ($[M+H]^+$) in the HR-FAB-MS. The ^{1}H-NMR spectrum of *G-6* showed signals of five H-atoms assignable to the glycerol moiety of a 2-*O*-(fatty acyl)glycerol and signals of a CH_2 group at δ 2.55–2.64 (*m*), of two OCH groups at δ 5.27–5.33 (*m*) and 4.81–4.87 (*m*) assignable to a bis(acetyloxy)-substituted fatty acyl moiety, and of two MeC=O groups at δ 2.04–2.07 (*Table 1*). GC Analysis of the Me_3Si-substituted methyl ester of the fatty acid fraction obtained from *G-6* showed four peaks corresponding to the bis(trimethylsilyl) ether derivatives of **36a**, **38a**, **37a**, and **39a** in a 8:12:42:38 ratio and in that elution order. Hence, *G-6* was determined to be a mixture of 2-*O*-[(3*R*,7*R*)-3,7-bis(acetyloxy)octadecanoyl]glycerol (**15**), 2-*O*-[(3*R*,8*R*)-3,8-bis(acetyloxy)octadecanoyl]glycerol (**16**), 2-*O*-[(3*R*,8*R*)-3,8-bis(acetyloxy)eicosanoyl]glycerol (**17**), and 2-*O*-[(3*R*,9*R*)-3,9-bis(acetyloxy)eicosanoyl]glycerol (**18**).

Fraction G-7 (=**19**/**20**/**21**/**22**/**23**/**24**/**25**/**26**) appeared to be a mixture of compounds having the molecular formulae $C_{25}H_{48}O_7$ and $C_{23}H_{44}O_7$, based on quasimolecular-ion peaks at *m/z* 461.3453 and 433.3202 ($[M+H]^+$) in the HR-FAB-MS. The ^{1}H-NMR spectrum of *G-7* resembled that of *G-6*, except for the loss of one MeC=O signal and the concomitant upfield shift ($\rightarrow\delta$ 3.54–3.62 (*m*)) of one OCH signal (H–C(6, 7, 8, or 9), which resonated at δ 4.81–4.87 (*m*) in *G-6* (*Table 1*). These data indicated that *G-7* was a 6-, 7-, 8-, or 9-*O*-deacetyl derivative of *G-6*. GC Analysis of the Me_3Si-substituted methyl esters of the fatty acid fraction obtained from *G-7* showed eight peaks of the bis(trimethylsilyl) ether derivatives of **34a**, **36a**, **38a**, **40a**, **33a**, **35a**, **37a**, and **39a**, in a 10:8:6:7:21:3:22:23 ratio. *G-7* was, therefore, determined to be a mixture of 2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-hydroxyoctadecanoyl]glycerol) (**19**), 2-*O*-[(3*R*,7*R*)-3-(acetyloxy)-7-hydroxyoctadecanoyl]glycerol (**20**), 2-*O*-[(3*R*,8*R*)-3-(acetyloxy)-8-hydroxyoctadecanoyl]glycerol (**21**), 2-*O*-[(3*R*,9*R*)-3-(acetyloxy)-9-hydroxyoctadecanoyl]glycerol (**22**), 2-*O*-[(3*R*,6*S*)-3-(acetyloxy)-6-hydroxyeicosanoyl]glycerol (**23**), 2-*O*-[(3*R*,7*R*)-3-(acetyloxy)-7-hydroxyeicosanoyl]glycerol (**24**), 2-*O*-[(3*R*,8*R*)-3-(acetyloxy)-8-hydroxyeicosanoyl]glycerol (**25**), and 2-*O*-[(3*R*,9*R*)-3-(acetyloxy)-9-hydroxyeicosanoyl]glycerol (**26**). GC/MS Analysis of *G-7* in the form of the Me_3Si derivatives confirmed the presence of the eight glycerides in *G-7* (*Table 3*).

Fraction G-8 (=**27**/**28**/**29**/**30**) showed a quasimolecular-ion peak in the HR-FAB-MS at *m/z* 419.3413 ($[M+H]^+$), which corresponded to the molecular formula $C_{23}H_{46}O_6$. The ^{1}H-NMR spectrum revealed that *G-8* was a 3:1 mixture of 2-*O*-(fatty acyl)glycerol and 1-*O*-(fatty acyl)glycerol (*vide infra*) on the basis of the ^{1}H-NMR data of the glycerol moieties (*Table 1*). The OCH signals at δ 4.01–4.08 (*m*) and 3.53–3.57 (*m*) further indicated that the fatty acyl moiety was substituted with two OH groups at C(3) and at C(6), C(7), C(8), or C(9). GC Analysis of the Me_3Si-substituted methyl ester derivative of the fatty acid fraction obtained from *G-8* showed four peaks corresponding to the bis(trimethylsilyl) ether derivatives of **33a**, **35a**, **37a**, and **39a** in a 40:8:36:16 ratio. *G-8* was, therefore, determined to be a mixture of 2-*O*-[(3*R*,6*S*)-3,6-dihydroxyeicosanoyl]glycerol (**27**), 2-*O*-[(3*R*,7*R*)-3,7-dihydroxyeicosanoyl]glycerol

(**28**), 2-*O*-[(3*R*,8*R*)-3,8-dihydroxyeicosanoyl]glycerol (**29**), and 2-*O*-[(3*R*,9*R*)-3,9-dihydroxyeicosanoyl]glycerol (**30**). GC/MS Analysis of *G-8* in the form of the Me_3Si derivatives displayed four peaks corresponding to the tetrakis(trimethylsilyl) ether derivatives of **27**–**30** (*Table 3*) in an expected ratio, in addition to four extra peaks due to the tetrakis(trimethylsilyl) ethers of the respective 1-*O*-(fatty acyl)glycerols.

The 2-*O*-acylglycerols are known to be isomerizable to 1-*O*-acylglycerols *via* acyl migration during extraction and separation [18][19]. Because of this migratory aptitude, *G-4* was not subjected to an extensive purification. However, a carefully controlled isolation and separation procedure (*i.e.*, the use of Et_2O for washing, concentration at room temperature, and chromatography over neutral silica gel in a minimum amount of time) allowed us to obtain *G-6* and *G-7* which were accompanied by negligible amounts (>5%) of the corresponding 1-*O*-acylglycerols. *G-8* was obtained as a 3:1 mixture of 2- and 1-*O*-acylglycerols even under the controlled conditions. It can be presumed that the rearranged 1-*O*-acylglycerols found in *G-8* were artifacts, since they were an (2*R*)/(2*S*) mixture with regard to the glycerol C(2) stereogenic center.

Conclusion. – The glandular trichome exudates on the leaves of *P. tomentosa* were found to contain *O*-(fatty acyl)glycerols exclusively, and the twenty-five new *O*-(fatty acyl)glycerols **1**, **4**, **5**, **6**, **7**, **8**, **10**–**14**, and **16**–**30** were characterized along with the five known ones **2**, **3**, **6**, **9**, and **15** [12][20]. Among these, compounds **12** (20%), **17** (14%), **18** (12%), and **10** (12%) were relatively abundant. The glycerides were classified into three structure types, 1,3-di-*O*-acetyl-2-*O*-(fatty acyl)glycerols, 1-*O*-acetyl-2-*O*-(fatty acyl)-*sn*-glycerols, and 2-*O*-(fatty acyl)glycerols. The fatty acyl moiety was an eicosanoyl or octadecanoyl group, which possessed a 3-hydroxy, substituent, 3,6-, 3,7-, 3,8-, or 3,9-dihydroxy substituents, and/or the corresponding (acetyloxy) or bis(acetyloxy) moiety. Interestingly, the absolute configuration at the OH- or AcO-substituted C(6) center of the fatty acyl moiety was (*S*), whereas the other four centers, C(3), C(7), C(8), and C(9), had all (*R*)-configuration. These *O*-acylglycerols were found to be localized in the glandular trichome exudates, and were not detected in the interior of the leaves. Putative precursors, 3-hydroxy- and 3,*n*-dihydroxy-substituted fatty acids could be detected in neither the glandular trichome exudate nor the leaf extract of *P. tomentosa*. Recently, closely related glycerides have been characterized in the floral oils of Orchidaceae and Scrophulariaceae plants [12][19][21]. In addition, 3-(acetyloxy)-, 5-(acetyloxy)-, 7-(acetyloxy)-3-hydroxy-, 9-(acetyloxy)-3-hydroxy-, and 9-(acetyloxy)-5-hydroxy-substituted fatty acids were characterized as constituents of these plants' floral oils [13][22]. These fatty acid derivatives were oxygenated at odd-numbered C-atoms, suggesting a polyketide-type origin of the O-function [13]. However, the C(6)- and C(8)-oxygenated derivatives found in the present study suggest the presence of an alternative biosynthetic pathway, such as a direct hydroxylation, rather than the polyketide-type one. It seems likely that the C(3) O-function, commonly observed in the fatty acyl moieties of the *P. tomentosa* glandular trichome acylglycerols, is introduced *via* a C_2 elongation of the precursor fatty acid [23]. The present study demonstrated the similarity in the chemical compositions between glandular trichome exudates and floral oils, which suggests an evolutional relationship between glandular trichomes and elaiophores.

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Experimental Part

1. *General.* For reactions with 1–2 mg of starting materials, yields were calculated from the integration of appropriate ^{1}H-NMR signals and comparison to the internal standard Me_4Si. Column chromatography (CC) and flash column chromatography (FC): silica gel *60N* (SiO_2; 60–210 and 40–100 mesh; *Kanto Chemical*, Japan). TLC and prep. TLC: *silica gel* F_{254} pre-coated glass plates (0.25 mm; *Merck*). M.p.: *Yazawa-BY-1* micro-melting-point apparatus; uncorrected. GC: *Shimadzu-GC-14B* apparatus; *J&W-Scientific-DB-5* capillary column (15 m × 0.25 mm, 0.25 mm film thickness). Optical rotations: *Jasco-DIP-360* polarimeter. ^{1}H-, ^{13}C-, and 2D-NMR Spectra: *Bruker-DRX500* spectrometer; at 500 (^{1}H) and 125 MHz (^{13}C); in $CDCl_3$ or $CDCl_3$/CD_3OD 9:1; δ(H) in ppm, rel. to Me_4Si, *J* in Hz; δ(C) in ppm referenced to the solvent $CDCl_3$ (δ 77.00). EI-MS (70 eV) and positive-mode FAB- and HR-FAB-MS: *Jeol-JMS-700* mass spectrometer; matrix 3-nitrobenzyl alcohol. GC/MS: *Jeol-JMS-AM-SUN200* mass spectrometer in EI (70 eV) mode; *Agilent-Technologies-6890A* gas chromatograph; *J&W-Scientific-HP-5* capillary column (30 m × 0.32 mm, 0.25 mm film thickness) or *J&W-Scientific-DB-1* capillary column (30 m × 0.25 mm, 0.25 mm film thickness); t_R in min.

2. *Plant Material.* Young leaves of the *Paulownia tomentosa* were collected in September 2005 on the campus of the Tokyo Institute of Technology. The identity of the plant source was confirmed by *S. K.* A voucher specimen (CMS17-01) was deposited with the Department of Chemistry and Materials Science, Tokyo Institute of Technology.

3. *Extraction and Isolation.* Fresh young leaves (fresh wt. 500 g, 70 leaves, average size 100 cm^2 per leaf) were briefly (*ca.* 10 s) rinsed twice in a beaker containing Et_2O (total volume 600 ml), the Et_2O soln. being concentrated to dryness (720 mg) under reduced pressure. The TLC pattern of the oily residue was identical to that of the sample collected selectively from the glandular trichomes by gently pressing glass fibers on the leaf surface. The resulting residue was subjected to CC (SiO_2, hexane/AcOEt 10:1 → AcOEt, and then AcOEt/MeOH 20:1 → 10:1 (total volume 1 l)): eight fractions (by TLC analysis). The first three fractions were combined (80 mg) and further purified by FC (SiO_2, hexane/AcOEt 5:1 → 2:1): *G-1* (14 mg), *G-2* (18 mg), and *G-3* (38 mg). The next three fractions were combined (440 mg) and further purified by FC (SiO_2, hexane/AcOEt 4:1 → 1:2): *G-4*/*G-5* 1:1 (160 mg), *G-5* (72 mg), and *G-6* (200 mg). The seventh and eighth fractions of the first column were designated as *G-7* (84 mg) and *G-8* (28 mg). *G-1* – *G-8* were present in the original Et_2O extract as established by TLC ($CHCl_3$/MeOH 20:1) analysis, thus ruling out the possibility of formation of the acetylated compounds during extraction and separation as artifacts.

The leaves were wiped with cotton twice, and the cotton was washed with Et_2O to give extract *A*. The leaves were then rinsed in Et_2O to give extract *B*. TLC Comparison of the two extracts established that extract *A* had *ca.* five times more intense spots for *G-1* – *G-8* than extract *B*. The leaves rinsed in Et_2O were then homogenized in MeOH/$CHCl_3$. This extract did not show any TLC spot of *G-1* – *G-8*.

4. *Analysis of the Fatty Acyl Moieties of* G-1 – G-8. 4.1. *Hydrolysis of the Extract and Silylation.* A suspension of the extract (30 mg) in 1,2-dimethoxyethane (800 µl) and LiOH (8 mg)/H_2O (200 µl) was stirred at r.t. for 36 h. Sat. aq. NH_4Cl soln. was added, and the mixture was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ layer was concentrated and the residue was treated with CH_2N_2/Et_2O (200 µl) at r.t. for 1 h. The resulting fatty acid methyl ester mixture (18 mg) showed two spots on TLC (hexane/AcOEt 1:1; R_f 0.8 and 0.3), which were separated by CC (SiO_2, hexane/AcOEt 2:1 → 1:1) to give the mono- and dihydroxy-substituted fatty acid methyl ester fractions (3 and 15 mg). The latter fraction was further purified by prep. TLC (hexane/AcOEt 1:1, developed twice) to give the 3,9-dihydroxy-substituted (5 mg, R_f 0.38), the 3,8-dihydroxy-substituted (4 mg, R_f 0.34), the 3,7-dihydroxy-substituted (*ca.* 1 mg, R_f 0.28), and the 3,6-dihydroxy-substituted fatty acid methyl esters (5 mg, R_f 0.30), separately.

The mono- and dihydroxy-substituted fatty acid methyl esters (100 μg each) were separately mixed with hexamethyldisilazane and trimethylchlorosilane in pyridine (TMS-HT reagent; 30 μl; *Tokyo Chemical Industry Co.*), and the soln. was kept at 65° for 1.5 h. Hexane (50 μl) and H_2O (50 μl) were added to the mixture, and the separated upper layer (containing the trimethylsilylated Me esters) was analyzed by GC (injection temp. 270°, column temp. 215°, detection temp. 270°) and GC/MS (*HP*-5 capillary column; source temp. 250°, injection temp. 250°; column temp. 60° for 1 min, then 20°/min up to 240°, then 240° for 15 min; interface temp. 280°). GC of the Me_3Si derivatives of the monohydroxy-substituted fatty acid methyl esters: t_R 8.3 (rel. abundance 9%), monosilyl derivative of methyl (3*R*)-3-hydroxyoctadecanoate (**32a**); t_R 15.4 (91%), monosilyl derivative of methyl (3*R*)-3-hydroxyeicosanoate (**31a**). GC of the Me_3Si derivatives of the dihydroxy-substituted fatty acid methyl esters; t_R 13.5 (4%), disilyl derivative of methyl (3*R*,6*S*)-3,6-dihydroxyoctadecanoate (**34a**); t_R 13.7 (4%), disilyl derivative of methyl (3*R*,7*R*)-3,7-dihydroxyoctadecanoate (**36a**); t_R 14.1 (2%), disilyl derivative of methyl (3*R*,8*R*)-3,8-dihydroxyoctadecanoate (**38a**); t_R 14.3 (1%), disilyl derivative of methyl (3*R*,9*R*)-3,9-dihydroxyoctadecanoate (**40**a); t_R 25.3 (37%), disilyl derivative of methyl (3*R*,6*S*)-3,6-dihydroxyeicosanoate (**33a**); t_R 25.4 min (3%), disilyl derivative of methyl (3*R*,7*R*)-3,7-dihydroxyeicosanoate (**35a**); t_R 26.3 (27%), disilyl derivative of methyl (3*R*,8*R*)-3,8-dihydroxyeicosanoate (**37a**); t_R 26.7 (22%), disilyl derivative of methyl (3*R*,9*R*)-3,9-dihydroxyeicosanoate (**39a**). For MS data of the peaks obtained by GC/MS see text below.

4.2. *Methyl (3*R*)-3-Hydroxyeicosanoate/Methyl (3*R*)-3-Hydroxyoctadecanoate* (**31a**/**32a**). White solid. ^{1}H-NMR ($CDCl_3$): 3.97–4.03 (*m*, H–C(3)); 3.71 (*s*, MeO); 2.82 (*d*, *J* = 4.0, OH); 2.52 (*dd*, *J* = 16.3, 3.0, H_a–C(2)); 2.41 (*dd*, *J* = 16.3, 9.0, H_b–C(2)); 1.40–1.58 (*m*, CH_2); 1.22–1.30 (*m*, CH_2); 0.88 (*t*, *J* = 7.0, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 173.5 (C(1)); 68.1 (C(3)); 51.7 (MeO); 41.1 (C(2)); 36.6 (C(4)); 31.9 (C(18)/C(16)), 29.4–29.7 (CH_2); 25.5 (C(5)); 22.7 (C(19)/C(17)); 14.1 (C(20)/C(18)). HR-FAB-MS: 343.3244 ($[M+H]^+$, $C_{21}H_{43}O_3^+$; calc. 343.3212).

*Methyl (3*R*)-3-[(Trimethylsilyl)oxy]eicosanoate* (from **31a**). EI-MS: 399 (41, $[M-Me]^+$), 383 (1, $[M-MeO]^+$), 175 (63), 159 (14), 129 (22), 73 (100).

*Methyl (3*R*)-3-[(Trimethylsilyl)oxy]octadecanoate* (from **32a**). EI-MS: 371 (51, $[M-Me]^+$), 355 (2, $[M-MeO]^+$), 175 (58), 129 (21), 73 (100).

2NMA Derivatives of **31a**/**32a**. To a soln. of **31a**/**32a** (300 μg, 0.9 μmol) in $CHCl_3$ (30 μl) were added (*R*)-2NMA-OH (300 μg, 1.4 μmol), EDC·HCl (1.0 mg, 5.2 μmol), DMAP (200 μg, 1.6 μmol), and DMAP·HCl (200 μg, 1.3 μmol), and the mixture was stirred at r.t. for 12 h. The mixture was purified by prep. TLC (hexane/AcOEt 6:1): (*R*)-2NMA derivatives **31b**/**32b** in 80% yield. Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 541 ($[M+H]^+$).

The corresponding reaction of **31a**/**32a** with (*S*)-2NMA-OH gave the (*S*)-2NMA derivatives **31c**/**32c**. Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 541 ($[M+H]^+$).

4.3. *Methyl (3*R*,9*R*)-3,9-Dihydroxyeicosanoate/Methyl (3*R*,9*R*)-3,9-Dihydroxyoctadecanoate* (**39a**/**40a**). White solid. ^{1}H-NMR ($CDCl_3$): 3.97–4.01 (*m*, H–C(3)); 3.72 (*s*, MeO); 3.54–3.60 (*m*, H–C(9)); 2.84 (*d*, *J* = 4.0, OH); 2.51 (*dd*, *J* = 16.4, 3.1, H_a–C(2)); 2.41 (*dd*, *J* = 16.4, 9.0, H_b–C(2)); 1.33–1.58 (*m*, CH_2); 1.22–1.30 (*m*, CH_2); 0.88 (*t*, *J* = 7.0, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 173.5 (C(1)); 72.0 (C(9)); 68.0 (C(3)); 51.7 (MeO); 41.1 (C(2)); 37.6; 37.4 (C(8), C(10)); 36.4 (C(4)); 31.9 (C(18)/C(16)); 29.4–29.7 (CH_2); 25.7; 25.6; 25.5 (C(5), C(7), C(11)); 22.7 (C(19)/C(17); 14.1 (C(20)/C(18). HR-FAB-MS: 359.3123 ($[M+H]^+$, $C_{21}H_{43}O_4^+$; calc. 359.3161).

*Methyl (3*R*,9*R*)-3,9-Bis[(trimethylsilyl)oxy]eicosanoate* (from **39a**). EI-MS: 487 (1, $[M-Me]^+$), 397 (5, $[M-Me-Me_3SiOH]^+$), 347 (1), 315 (11), 257 (24), 247 (2), 225 (1), 175 (8), 143 (3), 129 (10), 73 (100).

*Methyl (3*R*,9*R*)-3,9-Bis[(trimethylsilyl)octadecanoate* (from **40a**): EI-MS: 459 (1, $[M-Me]^+$), 369 (6, $[M-Me-Me_3SiOH]^+$), 347 (2), 315 (8), 247 (2), 229 (22), 225 (1), 175 (4), 143 (3), 129 (5), 73 (100).

2NMA Derivatives of **39a**/**40a**. As described in *Sect. 4.2*, with **39a**/**40a** (300 μg, 0.8 μmol), $CHCl_3$ (30 μl), (*R*)-2NMA-OH (200 μg, 1.0 μmol), EDC·HCl (1.0 mg, 5.2 μmol), DMAP (200 μg, 1.6 μmol), and DMAP·HCl (200 μg, 1.3 μmol). Prep. TLC (hexane/AcOEt 4:1) gave 3-*O*- and 9-*O*-(*R*)-2NMA derivatives **39b**/**40b** and **39d**/**40d**) as an inseparable 1:1 mixture in 60% yield. Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$).

The corresponding reaction of **39a**/**40a** with (*S*)-2NMA-OH gave the (*S*)-2NMA derivatives **39c**/**40c** and **39e**/**40e**. Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$).

4.4. *Methyl (3*R,*8*R*)-3,8-Dihydroxyeicosanoate*/*Methyl (3*R,*8*R*)-3,8-Dihydroxyoctadecanoate* (**37a**/**38a**). White solid. ^{1}H-NMR ($CDCl_3$): 3.98–4.04 (*m*, H–C(3)); 3.72 (*s*, MeO); 3.55–3.61 (*m*, H–C(8)); 2.86 (*d*, *J* = 4.0, OH); 2.51 (*dd*, *J* = 16.4, 3.1, H_a–C(2)); 2.42 (*dd*, *J* = 16.4, 9.0, H_b–C(2)); 1.33–1.58 (*m*, CH_2); 1.22–1.30 (*m*, CH_2); 0.88 (*t*, *J* = 7.0, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 173.5 (C(1)); 71.9 (C(8)); 68.0 (C(3)); 51.7 (MeO); 41.1 (C(2)); 37.6; 37.3; 36.5 (C(4), C(7), C(9)); 31.9 (C(18)/C(16)); 29.4–29.7 (CH_2); 25.7; 25.6 (C(5), C(10)); 22.7 (C(19)/C(17)); 14.1 (C(20)/C(18)). HR-FAB-MS: 359.3126 ($[M+H]^+$, $C_{21}H_{43}O_4^+$; calc. 359.3161).

*Methyl (3*R,*8*R*)-3,8-Bis[(trimethylsilyl)oxy]eicosanoate* (from **37a**). EI-MS: 487 (1, $[M-Me]^+$), 397 (5, $[M-Me-Me_3SiOH]^+$), 333 (2), 301 (26), 271 (24), 247 (3), 243 (1), 211 (4), 175 (7), 143 (3), 129 (13), 73 (100).

*Methyl (3*R,*8*R*)-3,8-Bis[(trimethylsilyl)oxy]octadecanoate* (from **38a**). EI-MS: 459 (1, $[M-Me]^+$), 369 (5, $[M-Me-Me_3SiOH]^+$), 333 (1), 301 (18), 247 (2), 243 (22), 211 (3), 175 (8), 143 (4), 129 (7), 73 (100).

2NMA Derivatives of **37a**/**38a**. From **37a**/**38a** and (*R*)-2NMA-OH as described for **39a**/**40a** (*Sect. 4.3*). Prep. TLC (hexane/AcOEt 4:1, twice) gave 8-*O*-(*R*)-2NMA derivatives **37d**/**38d** (30%; R_f 0.38) and 3-*O*-(*R*)-2NMA derivatives **37b**/**38b** (29%; R_f 0.32). Data of **37d**/**38d** and **37b**/**38b**: Colorless oils. ^{1}H-NMR: *Table 2*. FAB-MS: both 557 ($[M+H]^+$). The corresponding reaction of **37a**/**38a** with (*S*)-2NMA-OH gave the 3-*O*- and 8-*O*-(*S*)-2NMA derivatives **37c**/**38c** and **37e**/**38e** as an inseparable 1:1 mixture (62% yield). Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$).

4.5. *Methyl* (*3*R,*7R*)-*3,7-Dihydroxyeicosanoate*/*Methyl (3*R,*7*R*)-3,7-Dihydroxyoctadecanoate* (**35a**/**36a**). White solid. ^{1}H-NMR ($CDCl_3$): 4.00–4.06 (*m*, H–C(3)); 3.72 (*s*, MeO); 3.57–3.63 (*m*, H–C(7)); 2.93 (*m*, OH); 2.52 (*dd*, *J* = 16.5, 3.2, H_a–C(2)); 2.43 (*dd*, *J* = 16.5, 9.0, H_b–C(2)); 1.40–1.60 (*m*, CH_2); 1.22–1.30 (*m*, CH_2); 0.88 (*t*, *J* = 7.0, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 173.5 (C(1)); 71.8 (C(7)); 67.9 (C(3)); 51.8 (MeO); 41.0 (C(2)); 37.5; 37.1 (C(6), C(8)); 36.3 (C(4)); 31.9 (C(18)/C(16)); 29.4–29.7 (CH_2); 25.7 (C(9)); 22.7 (C(19)/C(17)); 21.5 (C(5)); 14.1 (C(20)/C(18)). HR-FAB-MS: 359.3160 ($[M+H]^+$, $C_{21}H_{43}O_4^+$; calc. 359.3161), 331.2837 ($[M+H]^+$, $C_{19}H_{41}O_4^+$; calc. 331.2848).

*Methyl (3*R,*7*R*)-3,7-Bis[(trimethylsilyl)oxy]eicosanoate* (from **35a**). EI-MS: 487 (1, $[M-Me]^+$), 397 (6, $[M-Me-Me_3SiOH]^+$), 319 (6), 287 (23), 285 (22), 247 (4), 229 (1), 197 (1), 175 (4), 143 (2), 129 (11), 73 (100).

*Methyl (3*R,*7*R*)-3,7-Bis[(trimethylsilyl)oxy]octadecanoate* (from **36a**). EI-MS: 459 (1, $[M-Me]^+$), 369 (3, $[M-Me-Me_3SiOH]^+$), 319 (5), 287 (21), 257 (24), 247 (2), 229 (1), 197 (1), 175 (6), 143 (3), 129 (11), 73 (100).

2NMA Derivatives of **35a**/**36a**. From **35a**/**36a** and (*R*)-2NMA-OH as described in *Sect. 4.3:* 3-*O*- and 7-*O*-(*R*)-2NMA derivatives **35b**/**36b** and **35d**/**36d** as an inseparable 1:1 mixture (59% yield). Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$). The corresponding reaction of **35a**/**36a** with (*S*)-2NMA-OH gave 3-*O*- and 7-*O*-(*S*)-2NMA derivatives **35c**/**36c** and **35d**/**36d** as an inseparable 1:1 mixture (58% yield). Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$).

4.6. *Methyl (3*R,*6*S*)-3,6-Dihydroxyeicosanoate*/*Methyl (3*R,*6*S*)-3,6-Dihydroxyoctadecanoate* (**33a**/**34a**). White solid. ^{1}H-NMR ($CDCl_3$): 4.02–4.08 (*m*, H–C(3)); 3.72 (*s*, MeO); 3.65–3.59 (*m*, H–C(6)); 2.86 (*m*, OH); 2.51 (*dd*, *J* = 16.3, 3.7, H_a–C(2)); 2.46 (*dd*, *J* = 16.3, 8.3, H_b–C(2)); 1.40–1.68 (*m*, CH_2); 1.22–1.30 (*m*, CH_2); 0.88 (*t*, *J* = 7.0, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 173.4 (C(1)); 71.8 (C(6)); 67.9 (C(3)); 51.8 (MeO); 41.2 (C(2)); 37.7 (C(7)); 33.7 (C(5)); 33.1 (C(4)); 31.9 (C(18)/C(16)); 29.4–29.7 (CH_2); 25.7 (C(9)); 22.7 (C(19)/C(17)); 14.1 (C(20)/C(18)). HR-FAB-MS: 359.3139 ($[M+H]^+$, $C_{21}H_{43}O_4^+$; calc. 359.3161).

*Methyl (3*R,*6*S*)-3,6-Bis[(trimethylsilyl)oxy]eicosanoate* (from **35a**). EI-MS: 487 (1, $[M-Me]^+$), 397 (4, $[M-Me-Me_3SiOH]^+$), 305 (4), 299 (21), 273 (1), 247 (3), 215 (45), 183 (1), 175 (3), 143 (5), 129 (2), 73 (100).

*Methyl (3*R,*6*S*)-3,6-Bis[(trimethylsilyl)oxy]octadecanoate* (from **36a**). EI-MS: 459 (1, $[M-Me]^+$), 369 (9, $[M-Me-Me_3SiOH]^+$), 305 (3), 273 (2), 271 (21), 247 (4), 215 (43), 183 (1), 175 (4), 143 (10), 129 (3), 73 (100).

2NMA Derivatives of **33a**/**34a**. From **33a**/**34a** and (*R*)-2NMA-OH as described in *Sect. 4.3:* 3-*O*- and 6-*O*-(*R*)-2NMA derivatives **33b**/**34b** and **33d**/**34d** as an inseparable 1:1 mixture (60% yield). Colorless oil. ^{1}H-NMR: *Table 2*. FAB-MS: 557 ($[M+H]^+$).

The corresponding reaction of **33a**/**34a** with (*S*)-2NMA-OH gave, after separation by prep. TLC (hexane/AcOEt 4:1, twice), 3-*O*-(*S*)-2NMA derivatives **33c**/**34c** (31%; R_f 0.30) and 6-*O*-(*S*)-2NMA derivatives **33e**/**34e** (30%; R_f 0.34). Data of **33c**/**34c** and **33e**/**34e**. Colorless oils. ^{1}H-NMR: *Table 2*. FAB-MS: both 557 ($[M+H]^+$).

5. *Data of the Fractions* G-1 – G-8. 5.1. *Fraction* G-1 (= **1**). Colorless oil. $[\alpha]_D^{26} = 0.0$ ($c = 0.72$, $CHCl_3$). ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 170.5 (2 Ac); 170.3 (Ac); 169.5 (C(1)); 71.3 (C(6)); 70.0 (C(3); 69.4 (*sn*-C(2)); 62.2 (*sn*-C(1), *sn*-C(3)); 39.2 (C(2)); 37.7 (C(7)); 32.5 (C(5)); 31.9 (C(18)); 30.1 (C(4)); 29.4 – 29.7 (CH_2); 25.7 (C(8)); 22.7 (C(19)); 21.0 (Ac); 20.7 (2 Ac); 14.1 (C(20)). HR-FAB-MS: 545.3680 ($[M+H]^+$, $C_{29}H_{53}O_9^+$; calc. 545.3690).

Mosher *Esters of* G-1. *G-1* (1.0 mg, 1.8 μmol) was treated with (*R*)-MTPA – Cl (1.2 μl, 6.4 μmol) in pyridine (30 μl) at r.t. After 30 min, MeOH (100 μl) was added to the mixture, and the soln. was purified by prep. TLC (hexane/AcOEt 4:1): (*S*)-MTPA derivative (1.3 mg, 93%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 7.26 – 7.58 (*m*, 5 H); 5.22 – 5.28 (*m*, H–*sn*-C(2)); 5.19 – 5.25 (*m*, H–C(3)); 5.06 – 5.12 (*m*, H–C(6)); 4.30 (*dd*, $J = 12.1$, 4.6, H_a–*sn*-C(1)/H_a–*sn*-C(3)); 4.28 (*dd*, $J = 12.1$, 4.2, H_a–*sn*-C(3)/H_a–*sn*-C1)); 4.14 (*dd*, $J = 12.1$, 5.9, 2 H, H_b–*sn*-C(1), H_b–*sn*-C(3)); 3.54 (*s*, MeO); 2.60 (*dd*, $J = 15.5$, 7.5, H_a–C(2)); 2.52 (*dd*, $J = 15.5$, 5.0, H_b–C(2)); 2.07 (*s*, Ac); 2.06 (*s*, Ac); 2.01 (*s*, Ac); 1.25 – 1.70 (CH_2); 0.88 (*t*, $J = 6.8$, Me(20)). FAB-MS: 761 ($[M+H]^+$).

The corresponding reaction of *G-1* (1.0 mg, 1.8 μmol) with (*S*)-MTPA – Cl (1.2 μl, 6.4 μmol) gave the (*R*)-MTPA derivative (1.2 mg, 86%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 7.26 – 7.58 (*m*, 5 H); 5.22 – 5.28 (*m*, H–*sn*-C(2)); 5.19 – 5.13 (*m*, H–C(3)); 5.06 – 5.12 (*m*, H–C(6)); 4.30 (*dd*, $J = 12.0$, 4.3, H_a–*sn*-C(1)); 4.28 (*dd*, $J = 12.0$, 4.2, H_a–*sn*-C(3)/H_a–*sn*-C(1)); 4.14 (*dd*, $J = 12.0$, 5.8, H_b–*sn*-C(1)/H_b–*sn*-C(3)); 4.13 (*dd*, $J = 12.0$, 5.9, H_b–*sn*-C(3)/H_b–*sn*-C(1)); 3.55 (*s*, MeO); 2.53 (*dd*, $J = 15.7$, 8.1, H_a–C(2)); 2.43 (*dd*, $J = 15.7$, 4.8, H_b–C(2)); 2.07 (*s*, 2 Ac); 2.01 (*s*, Ac); 1.25 – 1.70 (CH_2); 0.88 (*t*, $J = 6.8$, Me(20)). FAB-MS: 761 ($[M+H]^+$).

Acetylation of G-1. *G-1* (2.0 mg, 3.7 μmol) was treated with Ac_2O and pyridine at r.t. overnight. Extractive workup gave a crude product which was purified by prep. TLC (hexane/AcOEt 4:1): *G-1* acetate (2.1 mg, 97%). Colorless oil. ^{1}H- and ^{13}C-NMR ($CDCl_3$): essentially identical with those of *G-5* acetate. FAB-MS: 587 ($[M+H]^+$).

5.2. *Fraction* G-2 (= **2**/**3**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 170.9 (2 Ac); 170.2 (C(1)); 72.8 (*sn*-C(2)); 70.7 (C(3)); 62.2; 61.4 (*sn*-C(1), *sn*-C(3)); 39.6 (C(2)); 34.3 (C(4)); 31.9 (C(18)/C(16)); 29.3 – 29.7 (CH_2); 25.1 (C(5)); 22.7 (C(19)/C(17)); 21.1 (Ac); 20.7 (Ac); 14.1 (C(20)/C(18)). HR-FAB-MS: 487.3613 ($[M+H]^+$, $C_{27}H_{51}O_7^+$; calc. 487.3635).

Silylation of G-2. A mixture of *G-2* (8 mg, 16 μmol), 1*H*-imidazole (4.0 mg, 59 μmol), and ^{t}BuPh$_2$-SiCl (8 μl, 31 μmol) in DMF (30 μl) was stirred at r.t. for 3 h. Et_2O was added, and the Et_2O-soluble portion was washed with sat. aq. NH_4Cl soln. and then brine, dried (Na_2SO_4), and concentrated. The residue was dissolved in CH_2Cl_2 (100 μl) and stirred at $-78°$, after addition of 1.0M DIBAL in hexane (100 μl) for 2 min under N_2 (DIBAL = diisobutylaluminium hydride). Et_2O and sat. aq. NH_4Cl were added, and the Et_2O layer was washed with brine, dried (Na_2SO_4), and concentrated. The residue was subjected to CC (SiO_2, hexane/AcOEt 2:1) to give 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (4.2 mg, 77% from *G-2*). White solid. Crystallization from hexane/AcOEt 5:1 gave needles. M.p. 56 – 57°. $[\alpha]_D^{26} = +5.4$ ($c = 0.56$, $CHCl_3$). ([17]: $[\alpha]_D^{26} = +6.5$ and m.p. 54° for 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol). FAB-MS: 331 ($[M+H]^+$).

The 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (0.5 mg 1.5 μmol) was treated with (*R*)-MTPA – Cl (1.0 μl, 5.4 μmol) as described for *G-1* (*Sect. 5.1*), and the crude product was purified by prep. TLC (hexane/AcOEt 7:1) to give the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (90%). White powder. ^{1}H-NMR ($CDCl_3$): 7.27 – 7.58 (*m*, 20 H); 5.33 – 5.39 (*m*, H–*sn*-C(2)); 4.75 (*dd*, $J = 12.4$, 3.2, H_a–*sn*-C(1)); 4.50 (*dd*, $J = 12.4$, 6.4, H_b–*sn*-C(1)); 3.70 – 3.73 (*m*, 2 H–*sn*-C(3)); 3.44 (*s*, MeO); 3.38 (*s*, MeO); 1.01 (*s*, ^{t}Bu). FAB-MS: 763 ($[M+H]^+$).

5.3. *Fraction* G-3 (= **4**/**5**/**6**/**7**/**8**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 171.0 (Ac); 170.8 (Ac); 170.7 (Ac); 170.1, 170.0, 169.9 (C(1)); 74.3, 74.1, 73.9 (C(7)/C(8)/C(9)); 72.9, 72.8, 72.7 (*sn*-C(2));

70.5, 70.4, 70.3 (C(3)); 62.2 (*sn*-C(1)/*sn*-C(3)); 61.3 (*sn*-C(3)/*sn*-C(1)); 39.6, 39.5, 39.4 (C(2)); 34.1; 34.0; 33.9; 33.7; 31.9 (C(18)/C(16)); 29.7–29.1 (CH_2); 25.3; 25.1; 25.0; 24.9; 22.7 (C(19)/C(17)); 21.2 (Ac); 21.1 (Ac); 20.9 (Ac); 20.7 (Ac); 14.1 (C(20)/C(18)). HR-FAB-MS: 545.3652 ($[M+H]^+$, $C_{29}H_{53}O_9^+$; calc. 545.3690), 517.3392 ($[M+H]^+$, $C_{27}H_{49}O_9^+$; calc. 517.3377).

Silylation of G-3. *G-3* (8 mg, 15 μmol) was converted to 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (3.6 mg, 75%) as described for *G-2* (*Sect. 5.2*): Colorless needles. $[\alpha]_D^{26} = +5.6$ ($c = 0.48$, $CHCl_3$). This was further converted to the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol as described for the corresponding silyl derivative of *sn*-glycerol derived from *G-2*. The ^{1}H-NMR spectrum of the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol was essentially identical to that derived from *G-2*.

5.4. *Fraction* G-4 (= **9**/**10**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 171.5 (Ac); 170.4 (C(1)); 75.8 (*sn*-C(2)); 71.0 (C(3)); 62.4 (*sn*-C(1)/*sn*-C(3)); 62.1 (*sn*-C(3)/*sn*-C(1)); 40.4 (C(2)); 34.5 (C(4)); 31.9 (C(18)/(16)); 29.3–29.7 (CH_2); 25.2 (C(5)); 22.7 (C(19)/(17)); 21.1 (Ac); 14.1 (C(20)/C(18)). HR-FAB-MS: 445.3574 ($[M+H]^+$, $C_{25}H_{49}O_6^+$; calc. 445.3529).

Acetylation of G-4. *G-4*/*G-5* (10 mg) was acetylated at r.t. overnight in the standard manner (Ac_2O/pyridine). Prep. TLC (hexane/AcOEt 6:1) purification of the crude product gave the less polar *G-4* diacetate (4.2 mg, R_f 0.68). Colorless oil. ^{1}H-NMR: 5.22–5.28 (*m*, H–*sn*-C(2)); 5.18–5.24 (*m*, H–C(3)); 4.31 (*dd*, $J = 12.0, 4.2$, H_a–*sn*-C(1)/H_a–*sn*-(3)); 4.29 (*dd*, $J = 12.0, 4.2$, H_a–*sn*-C(3)/H_a–*sn*-C(1)); 4.15 (*dd*, $J = 12.0, 5.9$, H_b–*sn*-C(1)/H_b–*sn*-C(3)); 4.14 (*dd*, $J = 12.0, 5.9$, H_b–*sn*-C(3)/H_b–*sn*-C(1)); 2.62 (*dd*, $J = 15.4, 7.5$, H_a–C(2)); 2.57 (*dd*, $J = 15.4, 10.0$, H_b–C(2)); 2.07 (*s*, 2 Ac); 2.03 (*s*, Ac); 1.51–1.62 (CH_2); 1.22–1.30 (CH_2); 0.88 (*t*, $J = 6.9$, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 170.5 (2 Ac); 170.3 (Ac); 169.6 (C(1)); 70.4 (C(3)); 69.3 (*sn*-C(2)); 62.2 (*sn*-C(1), *sn*-C(3)); 39.1 (C(2)); 34.0 (C(4)); 31.9 (C(18)/Me(16); 29.4–29.7 (CH_2); 25.1 (C(5)); 22.7 (C(19)/C(17)); 20.9 (Ac); 20.7 (2 Ac); 14.1 (C(20)/C(18)). HR-FAB-MS: 529.3730 ($[M+H]^+$, $C_{29}H_{53}O_8^+$; calc. 529.3740).

The more polar product (5.0 mg, R_f 0.30) was identified as *G-5* diacetate.

5.5. *Fraction* G-5 (= **11**/**12**/**13**/**14**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 170.9 (Ac); 170.8 (Ac); 169.9 (C(1)); 72.9 (C(6)); 71.0 (*sn*-C(2)); 70.1 (C(3)); 62.2 (*sn*-C(1)/*sn*-C(3)); 61.3 (*sn*-C(3)/*sn*-C(1)); 39.7 (C(2)); 37.6 (C(7)); 32.3 (C(5)); 31.9 (C(18)/C(16)); 30.0 (C(4)); 29.3–29.7 (CH_2), 25.7 (C(7)); 22.7 (C(19)/C(17)); 21.1 (Ac); 20.7 (Ac); 14.1. HR-FAB-MS: 503.3586 ($[M+H]^+$, $C_{27}H_{51}O_8^+$; calc. 503.3584).

Silylation of G-5. *G-5* (10 mg, 20 μmol) was converted to 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (4.2 mg, 64%): $[\alpha]_D^{26} = +5.3$ ($c = 0.56$, $CHCl_3$), and the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol as described for *G-2* (*Sect. 5.2*). The ^{1}H-NMR of the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol was essentially identical with that derived from *G-2*.

Acetylation of G-5. *G-5* (5.1 mg, 10 μmol) was converted to the acetate (5.6 mg, 98%) as described for *G-1* (*Sect. 5.1*). Colorless oil. ^{1}H-NMR ($CDCl_3$): 5.22–5.28 (*m*, H–*sn*-C(2)); 5.20–5.26 (*m*, H–C(3)); 4.83–4.89 (*m*, H–C(6)); 4.31 (*dd*, $J = 12.0, 4.2$, H_a–*sn*-C(1)/H_a–*sn*-C(3)); 4.29 (*dd*, $J = 12.0, 4.2$, H_a–*sn*-C(3)/H_a–*sn*-C(1)); 4.15 (*dd*, $J = 12.0, 5.9$, H_b–*sn*-C(1)/H_b–*sn*-C(3)); 4.14 (*dd*, $J = 12.0, 5.9$, H_b–*sn*-C(3)/H_b–*sn*-C(1)); 2.62 (*dd*, $J = 15.6, 7.6$, H_a–C(2)); 2.57 (*dd*, $J = 15.6, 5.2$, H_b–C(2)); 2.08 (*s*, 2 Ac); 2.04 (*s*, Ac); 2.03 (*s*, Ac); 1.25–1.67 (CH_2); 0.88 (*t*, $J = 6.9$, Me(20)/Me(18)). ^{13}C-NMR ($CDCl_3$): 170.8 (Ac); 170.5 (2 Ac); 170.2 (Ac); 169.4 (C(1)); 73.6 (C(6)); 69.9 (C(3)); 69.4 (*sn*-C(2)); 62.1 (*sn*-C(1), *sn*-C(3)); 39.7 (C(2)); 34.1 (C(7)); 31.9 (C(18)/C(16)); 29.3–29.8 (CH_2); 25.3 (C(8)); 22.7 (C(19)/C(17)); 22.0 (Ac); 21.0 (Ac); 20.7 (2 Ac); 14.1 (C(20)/C(18)). HR-FAB-MS: 587.3760 ($[M+H]^+$, $C_{31}H_{55}O_{10}^+$; calc. 587.3584).

5.6. *Fraction* G-6 (= **15**/**16**/**17**/**18**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 171.4 (Ac); 171.1 (Ac); 170.3 (C(1)); 75.9 (*sn*-C(2)); 74.3, 74.1 (C(8)/C(9)); 70.9/70.7 (C(3)); 62.6 (*sn*-C(1)/*sn*-C(3)); 62.3 (*sn*-C(3)/*sn*-C(1)); 40.4, 40.3 (C(2)); 34.4; 34.2; 34.0; 33.9; 31.9 (C(18)/C(16)); 29.3–29.7 (CH_2); 25.3; 25.1; 25.0; 24.9; 22.7 (C(19)/C(17)); 21.2 (Ac); 21.1 (Ac); 14.1. HR-FAB-MS: 503.3627 ($[M+H]^+$, $C_{27}H_{51}O_8^+$; calc. 503.3584), 475.3256 ($[M+H]^+$, $C_{25}H_{47}O_8^+$; calc. 475.3271).

5.7. *Fraction* G-7 (= **19**/**20**/**21**/**22**/**23**/**24**/**25**/**26**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR ($CDCl_3$): 171.5, 171.3 (Ac); 170.4, 170.2 (C(1)); 75.8 (*sn*-C(2)); 69.9–71.9; 62.1–63.2; 40.3, 40.2, 40.1, 39.7 (C(2)); 37.1–37.7; 34.1–34.3; 32.2; 31.9 (C(18)/C(16)); 30.1; 29.2–29.7 (CH_2); 25.0–25.7; 22.7; 21.1 (Ac); 14.1

(C(20)/C(18)). HR-FAB-MS: 461.3453 ($[M+H]^+$, $C_{25}H_{49}O_7^+$; calc. 461.3478), 433.3202 ($[M+H]^+$, $C_{25}H_{47}O_8^+$; calc. 433.3165).

5.8. *Fraction* G-8 (=**27**/**28**/**29**/**30**). Colorless oil. ^{1}H-NMR: signals of 2-*O*-(fatty acyl)glycerol listed in *Table 1* and of the corresponding 1-*O*-(fatty acyl)glycerol (($CDCl_3$/CD_3OD 9:1): 4.17–4.23 (*m*, H–C(3)); 3.86–3.42 (*m*, 0.33 H); 3.65 (*dd*, *J* = 11.0, 4.0, 0.33 H), 3.58 (*dd*, *J* = 11.0, 6.0, 0.33 H)). HR-FAB-MS: 419.3413 ($[M+H]^+$, $C_{27}H_{51}O_8^+$; calc. 419.3373).

6. *GC and GC/MS Analysis of the Et_2O Extract and of the Fractions* G-1–G-8 *in the Form of Me_3Si Ether Derivatives.* Each sample (*ca.* 1 mg) was converted to the corresponding Me_3Si ether derivatives as described in *Sect. 4.1*, and the resulting Me_3Si ether derivatives were analyzed by GC (injection temp. 290°; column temp. from 240° to 280° at 2°/min, then 280° for 10 min; detection temp. 290°) and GC/MS (*DB-1* capillary column; source temp. 250°; injection temp. 250°; column temp. 60° for 1 min, then up to 280° at 2°/min, and 280° for 15 min; interface temp. 280°). The results are summarized in *Table 3*. In particular, the Me_3Si ether derivatives from *G-8* showed eight GC peaks due to tetrakis(trimethylsilyl) ethers of the 2-*O*-(fatty acyl)glycerides **27**–**30** at t_R 12.0, 12.3, 12.6, and 12.9 and their respective 1-*O*-(fatty acyl) isomers at t_R 13.2, 13.4, 13.7, and 13.9 in a 22:4:25:13:12:3:14:7 ratio.

Tetrakis(trimethylsilyl) Derivative of Isomer of **27**: EI-MS: 691 (1, $[M-Me]^+$), 603 (2), 513 (4), 509 (4), 471 (1), 451 (6), 429 (1), 419 (5), 339 (24), 299 (15), 273 (18), 219, (10), 218 (8), 147, (20), 129 (21), 103 (20), 73 (100).

Tetrakis(trimethylsilyl) Derivative of Isomer of **28**: EI-MS: 691 (1, $[M-Me]^+$), 603 (2), 523 (1), 513 (3), 471 (1), 451 (6), 429 (2), 339 (4), 287 (18), 285 (14), 219 (6), 218 (6), 147 (11), 129 (18), 103 (18), 73 (100).

Tetrakis(trimethylsilyl) Derivative of Isomer of **29**: EI-MS: 691 (1, $[M-Me]^+$), 603 (2), 513 (2), 471 (1), 451 (6), 429 (2), 339 (2), 301 (12), 271 (12), 219 (6), 218 (6), 147 (9), 129 (12), 103 (21), 73 (100).

Tetrakis(trimethylsilyl) Derivative of Isomer of **30**: EI-MS: 691 (1, $[M-Me]^+$), 603 (2), 551 (3), 513 (1), 471 (1), 451 (4), 429 (1), 339 (4), 315 (4), 257 (13), 219; (5), 218 (5), 147 (10), 129 (11), 103 (22), 73 (100).

7. *1,2-Bis-(S)-MTPA Derivative of 3-*O*-[(*tert*-Butyl)diphenylsilyl]-*sn*-glycerol and 2,3-Bis-(S)-MTPA Derivative of 1-*O*-[(*tert*-Butyl)diphenylsilyl]-*sn*-glycerol.* The 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (m.p. 56–57°; $[\alpha]_D^{26} = +5.0$ ($c = 0.20$, $CHCl_3$)), prepared from (4*S*)-2,2-dimethyl-1,3-dioxolane-4-methanol according to [17], was converted to the 1,2-bis-(*S*)-MTPA derivative of 3-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol, as described for *G-2* (*Sect. 5.2*). White powder. ^{1}H-NMR ($CDCl_3$): identical to those of the sample derived from *G-2*. FAB-MS: 763 ($[M+H]^+$).

The 1-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol (m.p. 56–57°; $[\alpha]_D^{26} = -5.6$ ($c = 0.26$, $CHCl_3$)), prepared from (*4*R)-2,2-dimethyl-1,3-dioxolane-4-methanol, was converted to the 2,3-bis-(*S*)-MTPA derivative of 1-*O*-[(*tert*-butyl)diphenylsilyl]-*sn*-glycerol as described above. White powder. FAB-MS: 763 ($[M+H]^+$). ^{1}H-NMR ($CDCl_3$): 7.58–7.27 (*m*), 5.37–5.42 (*m*, H–*sn*-C(2)); 4.63 (*dd*, *J* = 12.3, 3.2, H_a–*sn*-C(3)); 4.39 (*dd*, *J* = 12.4, 5.2, H_b–*sn*-C(3)); 3.79–3.83 (*m*, 2 H–*sn*-C(1)); 3.43 (*s*, MeO), 3.37 (*s*, MeO), 1.01 (*s*, ^{t}Bu). FAB-MS: 763 ($[M+H]^+$).

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