Minimally Competent *Lewis* Acid Catalysts: Indium(III) and Bismuth(III) Salts Produce Rhamnosides (=6-Deoxymannosides) in High Yield and Purity

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This paper is dedicated to *Dieter Seebach* for the wonderful science that he has showed us all as a chemist, and for the kindness he has showed me as a person

Glycosylation of decan-1-ol (**2**), (±)-decan-2-ol (**3**), and (±)-methyl 3-hydroxydecanoate (**4**) with L-rhamnose peracetate **5** to produce rhamnosides (=6-deoxymannosides) **6**, **7**, and **8** in the presence of *Lewis* acids $BF_3 \cdot Et_2O$, $Sc(OTf)_3$, $InBr_3$, and $Bi(OTf)_3$ was studied (*Table 1*). While the strong *Lewis* acids $BF_3 \cdot Et_2O$ and $Sc(OTf)_3$ were effective as glycosylation promoters, they had to be used in excess; however, glycosylation required careful control of reaction times and temperatures, and these *Lewis* acids produced impurities in addition to the desired glycosides. Enantiomerically pure rhamnosides (*R*)-**1** and (*S*)-**1** (*Fig.*) were obtained from L-rhamnose peracetate **5** and (±)-benzyl 3-hydroxydecanoate (**9**) *via* the diastereoisomeric rhamnosides **10** (*Table 2*; *Scheme 3*). The much weaker *Lewis* acids $InBr_3$ and $Bi(OTfl)_3$ produced purer products in high yield under a wider range of conditions (higher temperatures), and were effective glycosylation promoters even when used catalytically (<10% catalyst; *Table 2*). We refer to these *Lewis* acids as 'minimally competent *Lewis* acids' (*cf. Scheme 4*).

Introduction. – Earlier studies [1] directed toward the glycosylation of serine and threonine [2] with readily available sugar peracetates [3] for the efficient production of O-linked glycopeptides [4–6] led us to explore the use of weaker rather than stronger *Lewis* acids in conjunction with higher temperatures with these relatively unreactive per-*O*-acetylated glycosyl donors [7]. The discovery that the weak *Lewis* acid $InBr_3$ was effective led us explore this approach in the synthesis of rhamnolipids [8]. *Rademann* and co-workers' synthesis was quite elegant for the production of a rhamnolipid library [9] but did not provide a robust, scalable approach that could be used to produce larger amounts for the study of their surfactant properties [10].

We required rhamnoside diastereoisomers, (*R*)-**1** and (*S*)-**1** (*Fig.*), as well as the ability to produce various chain lengths at will. These single-chain glycosides are related to bacterial rhamnolipids [8][9], which are typically produced as mixtures of various chain lengths [10][11]. Bacterial rhamnolipids, particularly those produced by *Pseudomonas aeruginosa* show a great deal of promise for the environmental remediation of oil spills [12][13] and toxic metals [14][15].

Results. – The first glycosylation reactions were performed with decan-1-ol (**2**) as a model glycosyl acceptor and β-lactose peracetate as a model glycosyl donor. Heating

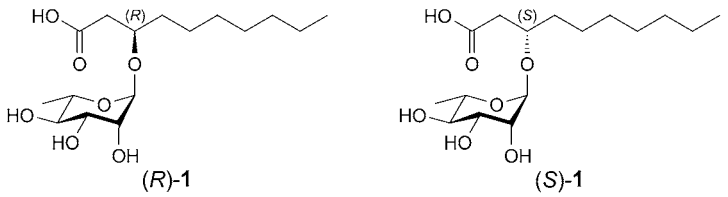
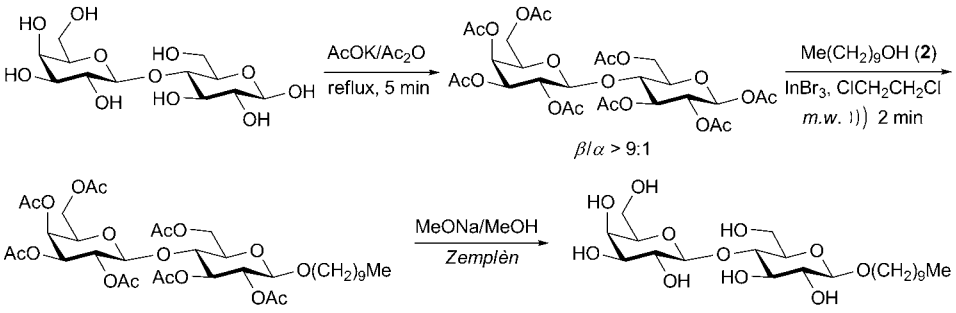


Figure. *Diastereoisomeric glycolipids* (rhamnolipid analogues) *(*R*)- and (*S*)*-**1**

mixtures of the donor and acceptor in a sealed tube (by means of microwaves) in $ClCH_2CH_2Cl$ as solvent in the presence of $InBr_3$ or other *Lewis* acids was used to define reaction conditions (*Scheme 1*). The classical *Zemplèn* deacylation methodology (MeONa/MeOH pH ≈ 9) was used to remove the acetate protecting groups to provide the nonionic surfactant β-decyl lactoside in 50% yield. Higher temperatures (> 80°) or longer reaction times for the glycosylation resulted in the formation of α-lactoside and product degradation.

Scheme 1. *Synthesis of β-Decyl Lactoside from the Peracetate of β-Lactose*



These were the initial conditions used for the synthesis of L-rhamnosides. The requisite fatty acid was prepared from the corresponding β-keto ester by simple reduction with $NaCNBH_3$ [16][17], or by enantioselective reduction by means of *Noyori*'s method [18]. The β-keto ester in turn was prepared from the appropriate acyl chloride and *Meldrum*'s acid [19] as depicted in *Scheme 2*.

L-Rhamnose (= 6-deoxy-L-mannose) was converted to the peracetate donor **5** with Ac_2O and pyridine, and subjected to glycosylation conditions (microwaves) in the presence of one of three different *Lewis* acids. Initially, the $BF_3 \cdot Et_2O$, $Sc(OTf)_3$ (Tfl = CF_3SO_2), and $InBr_3$ in $ClCH_2CH_2Cl$ were examined as promoters in conjunction with the three acceptors decan-1-ol (**2**), (±)-decan-2-ol (**3**), and methyl (±)-3-hydroxydecanoate (**4**) to produce glycosides **6**, **7**, and **8**, respectively (*Table 1*). Other solvent systems were explored: CH_2Cl_2/PhMe 1:5; $CHCl_3$, and CCl_4 were found to be effective, but several other solvents were not useful, *i.e.*, in Et_2O, THF, and DMF, was formed no product. Temperatures above 80° resulted in product mixtures.

Further studies indicated that, similar to $InBr_3$, the bismuth(III) salt $Bi(OTfl)_3$ [20] was also a minimally competent *Lewis* acid, but with properties that were superior to $InBr_3$ for these reactions, as shown in *Table 2*. In addition to being less hygroscopic than

Scheme 2. *Synthesis of Benzyl 3-Hydroxydecanoates from* Meldrum*'s Acid*

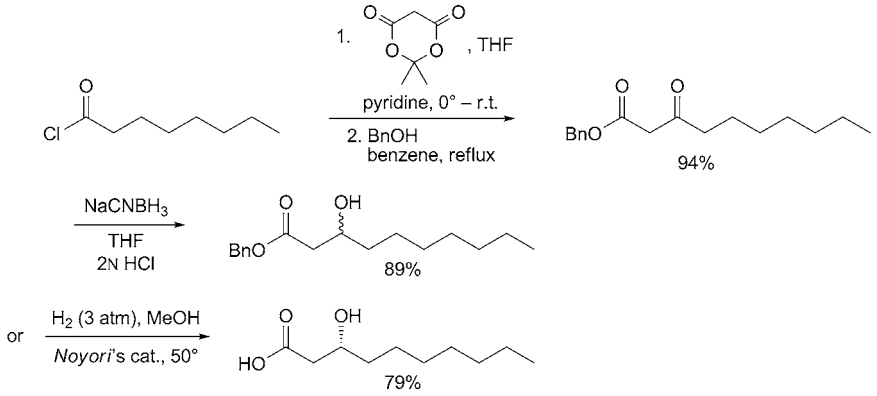
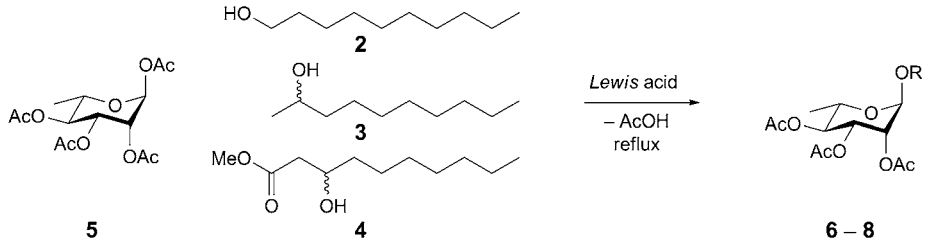


Table 1. *Synthesis of Glycosides from* L*-Rhamnose Peracetate* **5** *and Decanols* **2**–**4** *in* $ClCH_2CH_2Cl$*, in the Presence of Different* Lewis *Acids*[a])



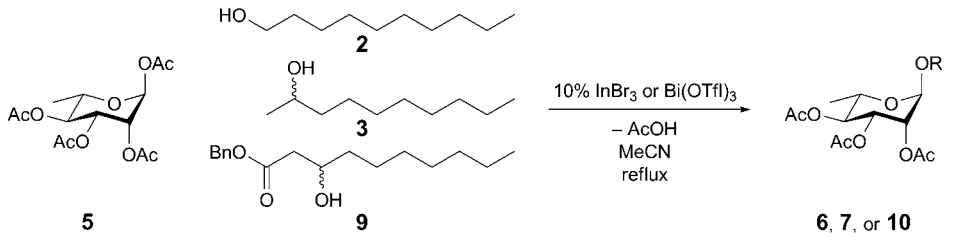
Decanol	Yield[b]) [%]		
	$BF_3 \cdot Et_2O$ (5.0 equiv.)	$Sc(OTfl)_3$ (1.0 equiv.)	$InBr_3$ (0.1 equiv.)
Decan-1-ol (**2**)	52	39	39
(±)-Decan-2-ol (**3**)	71	33	50
Methyl (±)-3-hydroxydecanoate (**4**)	43	16	34

[a]) Conditions: 2.2 equiv. of L-rhamnose peracetate **5** and 1 equiv. of decanol **2**, **3**, or **4** in $ClCH_2Cl_2Cl$ at 60° in a sealed tube. [b]) Yield of **6** (from **2**), **7** (from **3**), and **8** (from **4**).

indium(III) compounds, bismuth(III) salts are generally regarded as nontoxic, and are much cheaper than the corresponding indium(III) salts [21]. Additionally it was discovered that MeCN was the best solvent for rhamnoside formation [22], and that conventional reflux conditions with this solvent were ideal. The methyl ester **8** was replaced by benzyl ester **9** to permit hydrogenolysis and UV monitoring. The minimally competent $Bi(OTf)_3$ provided higher yields than $InBr_3$, and conventional heating conditions with MeCN as the solvent was reproducible, forming the rhamnosides **6**, **7**, and **10** from decan-1-ol (**2**), (±)-decan-2-ol (**3**), and benzyl (±)-3-hydroxydecanoate (**9**).

Hydrogenolysis of the diastereoisomer mixture of benzyl esters **10** produced a mixture of acids **11** in which the L-rhamnoside head group functioned as a very effective

Table 2. *Comparison of* Lewis *Acids $InBr_3$ and $Bi(OTfl)_3$ in the Glycosylations of* L-*Rhamnose Peracetate* **5** *with Decanols* **2**, **3**, *or* **9** *in MeCN*[a])

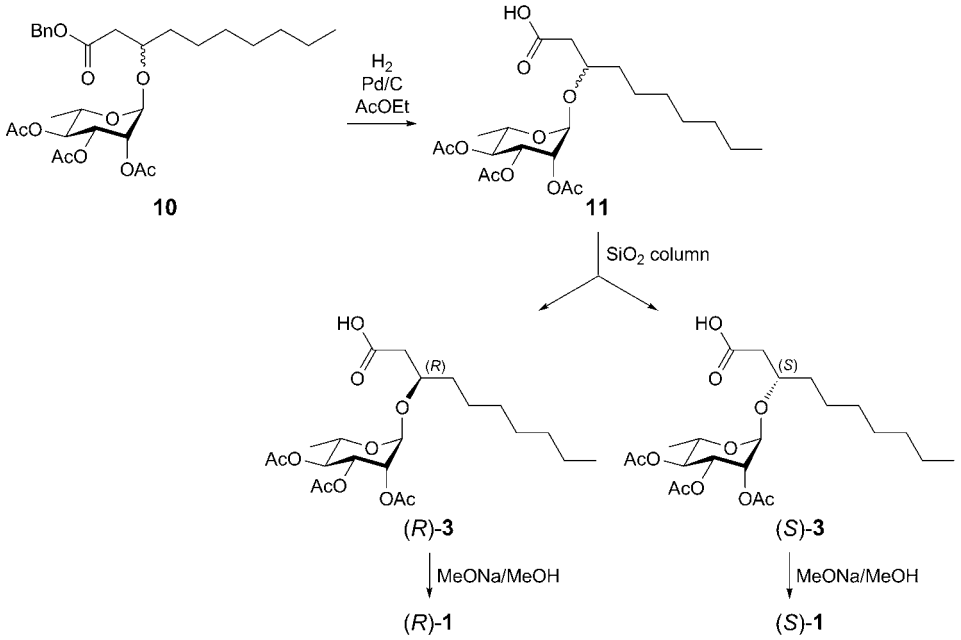


Decanol	Yield[b]) [%]	
	$InBr_3$ (0.1 equiv.)	$Bi(OTfl)_3$ (0.1 equiv.)
Decan-1-ol (**2**)	89	91
(±)-Decan-2-ol (**3**)	83	89
Benzyl (±)-3-hydroxydecanoate (**9**)	38	60

[a]) Conditions: 2.2 equiv. of L-rhamnose peracetate **5** and 1 equiv. of **2**, **3**, or **9** in MeCN under reflux, 2.5 h. [b]) Yield of **6** (from **2**), **7** (from **3**), and **10** (from **9**).

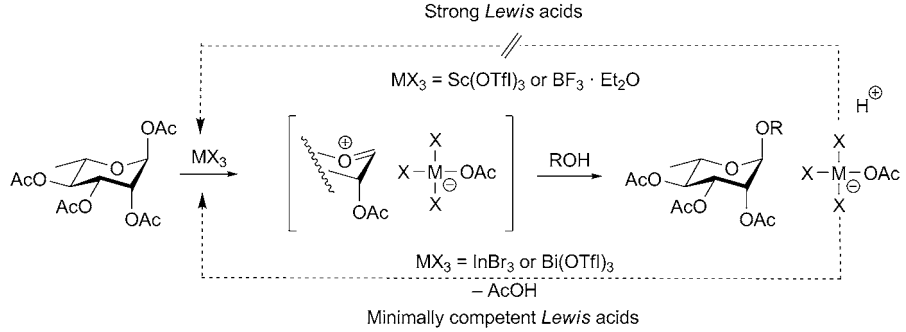
chiral auxiliary during chromatography (*Scheme 3*), permitting facile separation of the diastereoisomeric acids (*R*)-**11** and (*S*)-**11**. Subsequent *Zemplèn* deacylation of the purified diastereoisomers provided the corresponding rhamnosides (*R*)-**1** and (*S*)-**1** in excellent yield and purity.

Scheme 3. *Chromatographic Separation of Diasteroisomeric Monolipids* **11**



Discussion. – A major benefit of minimally competent *Lewis* acid is the fact that it can be used as a true catalyst, rather than stoichiometrically as a promoter of glycosylation. Stronger *Lewis* acids will retain the acetate leaving group from the donor, essentially becoming *Brønsted* acids as the glycosylation reaction proceeds. The minimally competent *Lewis* acids release the acetate to form acetic acid during the reaction, with concomitant regeneration of the catalyst (*Scheme 4*). Thus, the use of an 'H-atom acceptor' such as tetramethylurea [23] is not necessary or even desirable for such glycosylations.

Scheme 4. *Minimally Competent* Lewis *Acids Releasing the Acetate Moiety to Regenerate the Active* Lewis *acid.* Stronger *Lewis* acids retain the acetate to produce strong *Brønsted* acids.



Discovery of a second minimally competent *Lewis* acid, $Bi(OTfl)_3$, augers well for the discovery of more catalysts for glycosylation. It is noteworthy that the use of the relatively simple and robust sugar peracetates in conjunction with these mild *Lewis* acids allows for considerable leeway in the development of glycosylation conditions. Thus, the use of highly reactive glycosyl donors (*e.g.*, bromides, trichloroacetimidates, sulfoxides) for use with stoichiometric or even excess amounts of expensive, unstable, and/or exotic promoters (Ag^+, Hg^{2+} salts, $BF_3 \cdot Et_2O$ [Me_2SSMe](OTfl), *etc.*), and long reaction times are no longer required. Although above-described reactions were performed with 10% $Bi(OTfl)_3$ and nominally dry MeCN so that the reactions go to completion within a few hours, scrupulously dry conditions permit the use of much smaller amounts of catalyst. Further experimentation with more complex glycosides, polysaccharides, and glycolipids is clearly warranted.

Experimental Part

1. *General.* All glassware was flame-dried prior to reactions, and all reactions were done under Ar. Microwave: 900 W *Emerson MW8992SB* microwave oven, purchased from a *Target* department store. Flash chromatography (FC): silica gel *60* (SiO_2, 200–400 mesh; *Geduran* No. EM-11567-1); *Horizon* HPFC system (*Biotage*, *Inc.*). HPLC: *Varian-Prostar* HPLC system, with a *Prostar-330* photodiode array detector and a *Phenomenex-Jupiter* (250 mm × 21.2 mm, 15 μm) C_{18} semi-prep. column. M.p.: uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-DRX-400* (400 MHz), *-DRX-500* (500 MHz), and *-DRX-600* (600 MHz) spectrometers; in $CDCl_3$, (D_6)DMSO, or CD_3OD; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; all NMR spectra were analyzed and interpreted with the MestReNova® software. ESI-MS: *Thermo-Finnigan LCQ Deca* with pos. and neg. detection, MeOH/H_2O 1:1 solvent system; in *m*/*z* (rel. %).

2. *Decyl β-Lactoside.* A mixture of AcOK (6.56 g, 66.8 mmol) and Ac_2O (21 ml, 220 mmol) was heated under reflux, followed by slow addition of lactose (1.01 g, 2.79 mmol) to the boiling mixture. The mixture was stirred for 5 min and allowed to cool to r.t., where it was then diluted with CH_2Cl_2 and washed with ice-cold H_2O, 1% $NaHCO_3$, sat. $NaHCO_3$, and sat. NaCl soln. The org. layer was dried ($MgSO_4$) and concentrated to a colorless oil which was then dissolved in a minimal amount of CH_2Cl_2 and recrystallized by addition of Et_2O: *β-lactose peracetate* (58%). White, crystalline solid. M.p. 104–106°.

The β-lactose peracetate (1.78 g, 2.62 mmol), decan-1-ol (**2**; 0.50 ml, 2.62 mmol), and $InBr_3$ (0.093 g, 0.262 mmol) were added to a 50 ml triple-walled resealable vessel (internally threaded with a *Teflon* plug), dissolved in $ClCH_2CH_2Cl$ (3–4 ml), and irradiated in a 900 W *Emerson-MW8992SB* microwave oven (power level 6) for 2 min. The crude yellow oil was purified b FC (gradient AcOEt/hexanes 1:9 → 2:8 → 3:7 → 4:6): *decyl β-lactoside peracetate* (60%). White foam. M.p. 94–99°. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.31 (*d*, *J* = 3.2, 1 H); 5.16 (*t*, *J* = 9.3, 1 H); 5.07 (*dd*, *J* = 10.4, 7.9, 1 H); 4.92 (*dd*, *J* = 10.4, 3.4, 1 H); 4.85 (*dd*, *J* = 9.5, 8.0, 1 H); 4.49–4.38 (*m*, 3 H); 4.15–4.01 (*m*, 3 H); 3.87–3.72 (*m*, 3 H); 3.56 (*ddd*, *J* = 9.8, 5.0, 1.9, 1 H); 3.41 (*dt*, *J* = 9.6, 6.8, 1 H); 2.12 (*s*, *J* = 2.9, 3 H); 2.09 (*s*, *J* = 7.8, 3 H); 2.06–1.97 (*m*, 12 H); 1.93 (*s*, *J* = 5.9, 3 H); 1.58–1.45 (*m*, 2 H); 1.33–1.16 (*m*, 14 H); 0.85 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.2; 170.2; 170.0; 169.9; 169.6; 169.4; 168.9; 101.0; 100.6; 76.3; 72.9; 72.6; 71.8; 71.0; 70.7; 70.2; 69.2; 66.7; 62.1; 60.8; 31.9; 29.6; 29.5; 29.4; 29.3; 29.3; 25.8; 22.7; 20.8; 20.8; 20.7; 20.6; 20.5; 14.1. ESI-MS (pos.): 815.1 (17, $[M+K]^+$), 799.2 (99, $[M+Na]^+$), 794.1 (53, $[M+NH_4]^+$).

The *decyl β-lactoside peracetate* (2.93 g, 3.77 mmol) was dissolved in dry MeOH (30 ml) under Ar, and a 25% (wt./*v*) MeONa/MeOH soln. (0.5 ml) was added dropwise until the soln. reached pH 9–10. The mixture was stirred for 24 h (TLC monitoring) and then neutralized by *Dowex® 50WX8–100* ion-exchange resin. The mixture was filtered and the filtrate concentrated: *decyl β-lactoside* (72%). White solid. M.p. 140–160° (dec.). ^{1}H-NMR (500 MHz, (D_6)DMSO): 6.04 (*s*, 1 H); 5.84–5.31 (*m*, 4 H); 5.17 (*dd*, *J* = 19.1, 7.5, 2 H); 4.73 (*dt*, *J* = 6.6, 5.8, 2 H); 4.67–4.14 (*m*, 19 H); 3.99 (*t*, *J* = 8.2, 1 H); 3.50 (*dt*, *J* = 3.6, 1.8, 1 H); 2.37–2.13 (*m*, 14 H); 1.85 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (125 MHz, (D_6)DMSO): 103.8; 102.5; 80.8; 75.5; 75.0; 74.8; 73.2; 73.1; 70.6; 68.7; 68.1; 60.6; 60.4; 31.3; 29.3; 29.0; 29.0; 28.9; 28.7; 25.5; 22.1; 14.0. ESI-MS (pos.): 987.0 (100, $[2M+Na]^+$), 964.9 (13, $[2M+H]^+$), 505.4 (12, $[M+Na]^+$), 482.9 (10, $[M+H]^+$).

3. *Microwave Procedure for Rhamnosides* **6**–**8** (*Table 1*). Rhamnose peracetate **5** (1.2 equiv.), alcohol (1 equiv.), and $Sc(OTf)_3$ (1 equiv.), $InBr_3$ (0.1 equiv.), or $BF_3 \cdot Et_2O$ (5 equiv.) were dissolved in dry $ClCH_2CH_2Cl$ (1.5 ml) in a flame-dried triple-walled resealable vessel (internally threaded with a *Teflon* plug), and the vessel was microwave-irradiated (900 W *Emerson MW8992SB*) for 2 min on power level 6. The slightly yellow mixture was neutralized with sat. $NaHCO_3$ soln., the org. layer washed with H_2O, dried ($MgSO_4$), and concentrated, and the obtained oil purified by FC (20% AcOEt/hexanes). Yields of **6**–**8** in *Table 1*.

*Decyl 6-Dexoy-α-*L*-mannopyranoside Triacetate* (**6**): Colorless oil. R_f (30% AcOEt/hexanes) 0.64. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.28 (*dd*, *J* = 10.1, 3.5, 1 H); 5.20 (*dd*, *J* = 3.5, 1.7, 1 H); 5.03 (*t*, *J* = 9.9, 1 H); 4.68 (*d*, *J* = 1.5, 1 H); 3.84 (*dq*, *J* = 9.9, 6.3, 1 H); 3.63 (*dt*, *J* = 9.5, 6.8, 1 H); 3.39 (*dt*, *J* = 9.6, 6.6, 1 H); 2.12 (*s*, 3 H); 2.02 (*s*, 3 H); 1.96 (*s*, 3 H); 1.59–1.53 (*m*, 2 H); 1.35–1.21 (*m*, 14 H); 1.19 (*d*, *J* = 6.3, 3 H); 0.86 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.2; 170.0; 169.9; 97.4; 71.3; 70.0; 69.2; 68.2; 66.2; 31.9; 29.6; 29.5; 29.4; 29.3; 29.3; 26.1; 22.7; 20.9; 20.8; 20.7; 17.4; 14.1.

*(1*R*)- and (1*S*)-1-Methylnonyl 6-Deoxy-α-*L*-mannopyranoside Triacetate* (**7**; diastereoisomer mixture 1:1): Colorless oil. R_f (30% AcOEt/hexanes) 0.68. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.28 (*dd*, *J* = 10.1, 3.5, 1 H); 5.25 (*dd*, *J* = 10.1, 3.5, 1 H); 5.15–5.11 (*m*, 2 H); 5.02 (*t*, *J* = 9.9, 1 H); 5.01 (*t*, *J* = 10.0, 1 H); 4.79 (*d*, *J* = 1.7, 1 H); 4.77 (*d*, *J* = 1.7, 1 H); 3.92 (*dq*, *J* = 9.8, 6.3, 1 H); 3.89 (*dq*, *J* = 9.8, 6.3, 1 H); 3.70 (*dt*, *J* = 11.8, 6.0, 1 H); 3.64 (*dt*, *J* = 12.4, 6.1, 1 H); 2.11 (*s*, 6 H); 2.01 (*s*, 3 H); 2.01 (*s*, 3 H); 1.95 (*s*, 6 H); 1.60–1.44 (*m*, 2 H); 1.44–1.30 (*m*, 2 H); 1.26 (*dd*, *J* = 26.5, 8.0, 24 H); 1.16 (*d*, *J* = 6.3, 9 H); 1.08 (*d*, *J* = 6.1, 3 H); 0.84 (*t*, *J* = 6.9, 3 H); 0.84 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 170.2; 170.1; 170.0; 169.9; 169.9; 97.0; 94.9; 75.8; 73.1; 71.4; 71.2; 70.6; 70.4; 69.2; 69.2; 66.4; 66.2; 36.9; 36.2; 31.8; 31.8; 29.6; 29.5; 29.5; 29.5; 29.2; 29.2; 25.6; 25.3; 22.6; 21.1; 20.9; 20.8; 20.7; 18.9; 17.3; 17.3; 14.1.

*Methyl (3*R*)- and (3*S*)-3-[(2,3,4-Tri-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl)oxy]decanoate* (**8**; diastereoisomer mixture 1:1): Colorless oil. R_f (pair of diastereoisomers) 0.45 and 0.40. ^{1}H-NMR

(500 MHz, $CDCl_3$): 5.21 (*d*, *J* = 3.4, 1 H); 5.19 (*d*, *J* = 3.4, 1 H); 5.11 (*dd*, *J* = 3.4, 1.8, 1 H); 5.07 (*dd*, *J* = 3.4, 1.8, 1 H); 5.01 (*t*, *J* = 9.9, 1 H); 4.99 (*t*, *J* = 10.0, 1 H); 4.83 (*d*, *J* = 1.5, 1 H); 4.80 (*d*, *J* = 1.5, 1 H); 4.10–3.97 (*m*, 2 H); 3.94–3.82 (*m*, 2 H); 3.66 (*s*, 3 H); 3.65 (*s*, 3 H); 2.54 (*dd*, *J* = 15.3, 8.1, 1 H); 2.50 (*dd*, *J* = 15.5, 7.5, 1 H); 2.44 (*dd*, *J* = 15.4, 6.4, 1 H); 2.43 (*dd*, *J* = 15.4, 6.9, 1 H); 2.10 (*d*, *J* = 2.8, 6 H); 2.00 (*d*, *J* = 3.0, 6 H); 1.93 (*d*, *J* = 1.9, 6 H); 1.63–1.40 (*m*, 4 H); 1.36–1.17 (*m*, 16 H); 1.16 (*d*, *J* = 6.3, 1 H); 1.15 (*d*, *J* = 6.2, 1 H); 0.83 (*td*, *J* = 6.9, 3.5, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.7; 171.6; 170.1; 170.0; 169.9; 169.9; 169.9; 97.5; 95.9; 76.3; 74.9; 71.1; 70.3; 70.2; 69.1; 69.0; 66.7; 66.6; 51.7; 51.6; 39.9; 39.3; 35.0; 33.3; 31.7; 31.7; 29.4; 29.4; 29.1; 29.1; 25.1; 24.7; 22.6; 22.6; 20.9; 20.9; 20.8; 20.7; 17.2; 17.2; 14.0.

4. *Conventional Reflux Procedure for Rhamnosides* **6**, **7**, *and* **10** (*Table 2*). To a soln. of rhamnose peracetate **5** (2.2 equiv.) in dry MeCN, the alcohol (1 equiv.) and either $Bi(OTf)_3$ (0.10 equiv.) or $InBr_3$ (0.10 equiv.) were added. The mixture was refluxed under a *Liebig* condenser for 2.5 h and then allowed to cool to r.t. For $Bi(OTf)_3$, the yellow-brown mixture was diluted with CH_2Cl_2, *Celite*® was added, the mixture filtered, and the filtrate concentrated to a yellow-brown syrup. For $InBr_3$, the yellow mixture was diluted with CH_2Cl_2 and neutralized with sat. $NaHCO_3$ soln., and the org. layer washed with H_2O, dried ($MgSO_4$), and concentrated. Purification was achieved by FC (gradient hexanes/AcOEt 0 → 20%). Yields of **6**, **7**, and **10** in *Table 2*.

*Phenylmethyl (3*R*)- and (3*S*)-3-[(2,3,4-Tri*-O*-acetyl-6-deoxy-α-*L*-mannopyranosyl)oxy]decanoate* (**10**; diastereoisomer mixture 45 : 55): Colorless oil. R_f (30% AcOEt/hexanes) 0.55. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.36–7.27 (*m*, 10 H); 5.23 (*ddd*, *J* = 10.1, 3.4, 1.0, 2 H); 5.14 (*dt*, *J* = 4.4, 2.2, 1 H); 5.13–5.10 (*m*, 5 H); 5.02 (td, *J* = 10.0, 5.9, 2 H); 4.87 (*d*, *J* = 1.6, 1 H); 4.83 (*d*, *J* = 1.6, 1 H); 4.14–4.02 (*m*, 2 H); 3.95–3.86 (*m*, 2 H); 2.66–2.46 (*m*, 4 H); 2.12 (*d*, *J* = 5.9, 6 H); 2.04–1.99 (*m*, 6 H); 1.96 (*d*, *J* = 1.5, 6 H); 1.63–1.43 (*m*, 4 H); 1.37–1.19 (*m*, 23 H); 1.18 (*d*, *J* = 6.3, 3 H); 1.15 (*d*, *J* = 6.3, 3 H); 0.85 (*td*, *J* = 6.9, 3.7, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 171.1; 170.9; 170.1; 170.0; 169.9; 135.7; 135.7; 128.5; 128.5; 128.4; 128.2; 128.2; 97.4; 96.2; 76.1; 75.1; 71.1; 70.3; 70.2; 69.1; 69.1; 66.7; 66.7; 66.5; 66.4; 40.2; 39.5; 35.0; 33.4; 31.7; 29.5; 29.4; 29.1; 29.1; 25.1; 24.7; 22.6; 22.6; 20.9; 20.8; 20.7; 17.3; 14.1.

5. *(3*R*)- and (3*S*)-3-[(2,3,4-Tri*-O*-acetyl-6-deoxy-α-*L*-mannopyranosyl)oxy]decanoic Acid* ((*R*)-**11** *and* (*S*)-**11**, resp.). To a soln. of **10** (8.57 g, 15.6 mmol) in dry THF (100 ml) at r.t., a small amount of 10% (wt.) Pd/C was added under Ar. By means of a balloon, the flask was filled with H_2 gas (1 atm) and the mixture stirred vigorously at r.t. for 24 h. Then the mixture was purged with Ar, diluted with CH_2Cl_2, and filtered through *Celite*®, the filtrate concentrated, and the resulting oil purified by FC (Et_2O/hexanes 1 : 1 with 1% AcOH): (*R*)-**11** (38%) and (*S*)-**11** (33%).

*Data of (*R*)-***11***:* Colorless oil. $[\alpha]_D = -30.6$ (*c* = 1.0, $CHCl_3$). R_f (Et_2O/hexanes 1 : 1 with 1% (*v*/*v*) AcOH) 0.26. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.24 (*dd*, *J* = 10.1, 3.5, 1 H); 5.12 (*dd*, *J* = 3.4, 1.8, 1 H); 5.03 (*t*, *J* = 9.9, 1 H); 4.89 (*d*, *J* = 1.8, 1 H); 4.04 (*dq*, *J* = 11.7, 5.9, 1 H); 3.93 (*dq*, *J* = 9.8, 6.3, 1 H); 2.57 (*dd*, *J* = 15.8, 7.5, 1 H); 2.49 (*dd*, *J* = 15.8, 5.3, 1 H); 2.11 (*s*, 3 H); 2.03 (*s*, 3 H); 1.96 (*s*, 3 H); 1.65–1.50 (*m*, 2 H); 1.32–1.22 (*m*, 10 H); 1.18 (*d*, *J* = 6.3, 3 H); 0.89–0.84 (*m*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 176.2; 170.2; 170.1; 170.1; 97.5; 76.2; 71.1; 70.3; 69.1; 66.8; 39.3; 35.0; 31.7; 29.4; 29.1; 25.1; 22.6; 20.9; 20.8; 20.7; 20.7; 17.3; 14.0.

*Data of (*S*)-***11***:* Clear oil. $[\alpha]_D = -47.9$ (*c* = 1.0, $CHCl_3$); R_f (Et_2O/hexanes 1 : 1 with 1% (*v*/*v*) AcOH) 0.38. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.23 (*dd*, *J* = 10.1, 3.4, 1 H); 5.14 (*dd*, *J* = 3.4, 1.8, 1 H); 5.02 (*t*, *J* = 9.9, 1 H); 4.82 (*d*, *J* = 1.7, 1 H); 4.07 (*dq*, *J* = 7.5, 5.9, 1 H); 3.93 (*dq*, *J* = 9.9, 6.3, 1 H); 2.63 (*dd*, *J* = 15.9, 7.6, 1 H); 2.52 (*dd*, *J* = 15.9, 4.8, 1 H); 2.12 (*s*, 3 H); 2.02 (*s*, 3 H); 1.96 (*s*, 3 H); 1.52 (*ddd*, *J* = 23.0, 14.2, 5.3, 2 H); 1.32–1.21 (*m*, 10 H); 1.15 (*d*, *J* = 6.3, 3 H); 0.87–0.82 (*m*, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$): 176.7; 170.2; 170.1; 170.0; 96.4; 75.1; 71.1; 70.3; 69.1; 66.8; 39.9; 33.6; 31.7; 29.5; 29.1; 24.8; 22.6; 20.9; 20.8; 20.7; 17.2; 14.0.

6. *(3*R*)- and (3*S*)-3-(6-Deoxy-α-*L*-mannopyranosyloxy)decanoic Acid* ((*R*)-**1** and (*S*)-**1**, resp.). To a soln. of (*R*)-**11** (5.77g, 12.5 mmol) in dry MeOH (50 ml) at r.t., MeONa was added while stirring to achieve a pH 9–10 (monitoring by a drop of the mixture onto a moistened pH-indicator strip). The mixture was stirred at r.t. for 3.5 h and then quenched with *Dowex* H^+ resin. The resin was removed by filtration and the filtrate concentrated to an oil. No further purification was required. However, redissolving of the product in a minimal amount of hexanes, followed by filtration, was occasionally required to remove residual Na^+ salts: (*R*)-**1** (99%). Colorless oil. $[\alpha]_D = -34.8$ (*c* = 1.0, MeOH). R_f (10% MeOH/CH_2Cl_2 with 1% (*v*/*v*) AcOH) 0.20. ^{1}H-NMR (400 MHz, CD_3OD): 4.75 (*d*, *J* = 1.7, 1 H);

3.96–3.89 (*m*, 1 H); 3.65 (*dd*, *J* = 3.4, 1.7, 1 H); 3.61–3.53 (*m*, 1 H); 3.51 (*dd*, *J* = 9.5, 3.4, 1 H); 3.29–3.24 (*m*, 1 H); 2.34 (*qd*, *J* = 15.0, 6.4, 2 H); 1.54–1.43 (*m*, 2 H); 1.26–1.17 (*m*, 10 H); 1.14 (*d*, *J* = 6.3, 3 H); 0.80 (*dd*, *J* = 7.9, 6.0, 3 H). ^{13}C-NMR (100 MHz, CD_3OD): 176.2; 101.6; 76.9; 73.9; 72.7; 72.4; 70.2; 41.2; 36.4; 33.0; 30.7; 30.3; 26.3; 23.7; 17.9; 14.4. ESI-MS (neg.): 334.1 (12, M^-), 333.1 (99, $[M-H]^-$).

Glycolipid (*S*)-**1** was obtained in the same fashion: Yield 99%. Colorless oil. $[\alpha]_D = -47.0$ ($c = 1.0$, MeOH). R_f (10% MeOH/CH_2Cl_2 with 1% (*v*/*v*) AcOH) 0.25. ^{1}H-NMR (400 MHz, CD_3OD): 4.66 (*d*, *J* = 1.7, 1 H); 3.93 (*dq*, *J* = 7.5, 5.7, 1 H); 3.62 (*dd*, *J* = 3.4, 1.7, 1 H); 3.58–3.45 (*m*, 2 H); 3.20 (*t*, *J* = 9.5, 1 H); 2.33 (*ddd*, *J* = 20.4, 14.8, 6.6, 2 H); 1.42 (*dt*, *J* = 9.1, 6.2, 2 H); 1.21–1.13 (*m*, 10 H); 1.09 (*d*, *J* = 6.2, 3 H); 0.77–0.73 (*m*, 3 H). ^{13}C-NMR (100 MHz, CD_3OD): 176.5; 100.3; 75.9; 74.0; 72.7; 72.3; 70.1; 42.2; 34.5; 33.0; 30.7; 30.3; 25.9; 23.7; 17.9; 14.4. ESI-MS (neg.): 334.1 (12, M^-), 333.1 (99, $[M-H]^-$).

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