Total Synthesis of Tricolorin A

Shou-Fu Lu, QinQin O'yang, Zhong-Wu Guo, Biao Yu,* and Yong-Zheng Hui*

State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

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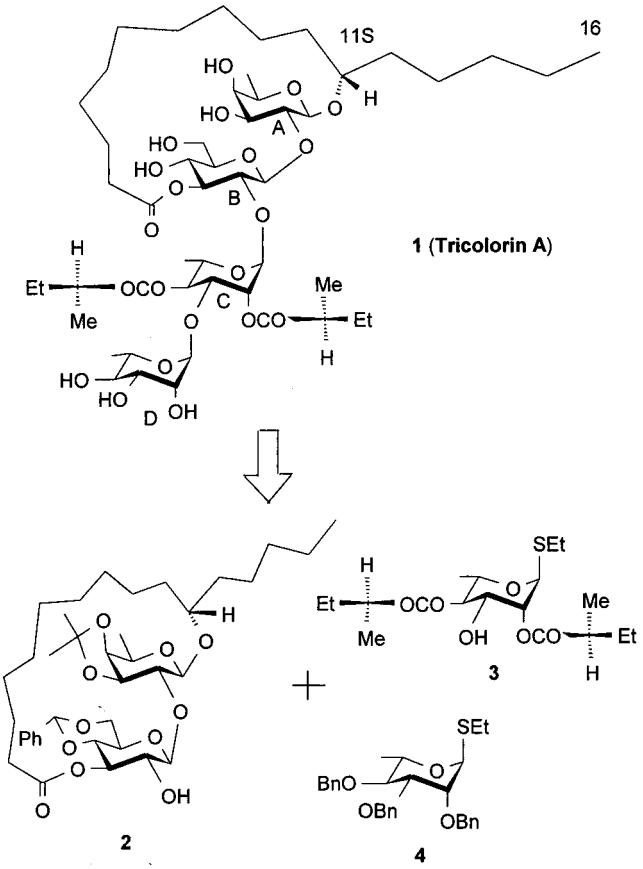
Tricolorin A (**1**), a structurally amazing resin glycoside with promising bioactivities from *Ipomoea tricolor* cav. (convolvulaceae), was synthesized in a total of 45 steps, with the longest linear sequence of 20 steps and overall yield of 0.65% from D-mannitol. The AB disaccharide 19-membered lactone **2** was constructured by a regioselective macrolactonization using Corey−Nicolaou protocol. The macrolactone tetrasaccharide **33** was realized either by "one-pot two-step" glycosylation procedure or by a stepwise assembly employing the "armed-disarmed" glycosylation strategy.

Introduction

Tricolorin A (**1**), a member of the resin glycoside family,[1] was isolated by Pereda-Miranda in 1993 from *Ipomoea tricolor* cav. (convolvulaceae), a plant used in Mexican traditional agriculture as a weed controller.[2] Bioassays showed that tricolorin A not only took major responsibility for the weed growth inhibition of the plant but also possessed significant cytotoxic activity against cultured P-388 and human breast cancer cells (ED_{50} 2.2 μg/mL).[2a] What attracted us more was the beauty of the structure of tricolorin A that, bearing a disaccharide containing 19-membered macrolactone, was in a perfect balance of hydrophobicity and hydrophilicity. Therefore, we made an effort directed toward the total synthesis of this interesting molecule. While our synthesis was underway, Schmidt first accomplished a total synthesis of another molecule of the resin glycoside family (calonyctin A).[3] Recently, Heathcock reported a communication on the synthesis of a macrolactone disaccharide subunit (**2**) of tricolorin A.[4] Coincidentally, we employed a similar strategy to assembly this subunit (**2**) in our total synthesis. Herein, we wish to describe the total synthesis of tricolorin A. The synthesis was highlighted by a regioselective macrolactonization of a 1-(hydroxycarbonyl)pentadec-10(s)-yl disaccharide to build the macrolactone disaccharide **2** and a "one-pot two-step" assembly of two monosaccharide donors (**3** and **4**) to **2**.[5] (Scheme 1).

Scheme 1. Retrosynthesis of Tricolorin A



Results and Discussion

First, four monosaccharide building blocks (**7**, **10**, **3**, and **4**) were prepared as shown in Scheme 2, which were all glycosyl donors either with a neighboring participation group (**7**, **10**, and **3**) or with high anomeric effect (**3** and **4**) to warrant the highly selective β-glycosidation (for **7** and **10**) or α-glycosidation (for **3** and **4**). 2,3,4-Tri-*O*-acetyl-α-D-fucopyranosyl trichloroacetimidate (**7**) was prepared from peracetylated D-fucose (**5**) by selective deacetylation at the anomeric position[6] and trichloroacetonitrile addition, and **5** was readily obtained from D-galactose in four steps by Lerner's procedure.[7] Ethyl 4,6-*O*-benzylidene-2,3-di-*O*-acetyl-1-thio-β-D-glucopyranoside (**10**) was synthesized from ethyl 1-thio-β-D-gluco-

* To whom correspondence should be addressed. Phone: (86) 21-64163300-1407. Fax: (86) 21-64166128. E-mail: byusioc@fudan.ac.cn.

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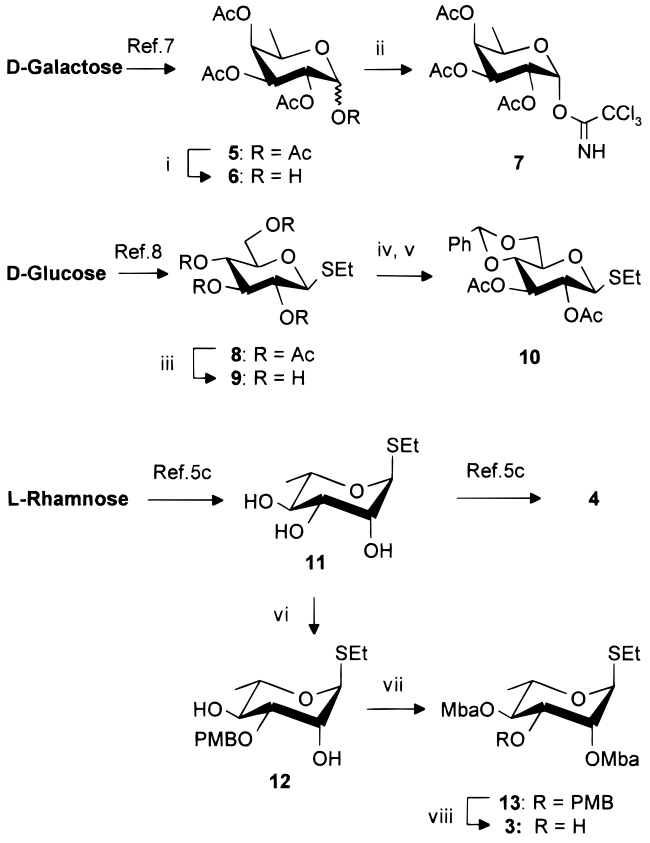
Scheme 2. Preparation of Monosaccharide Building Blocks 7, 10, 3, and 4[a]

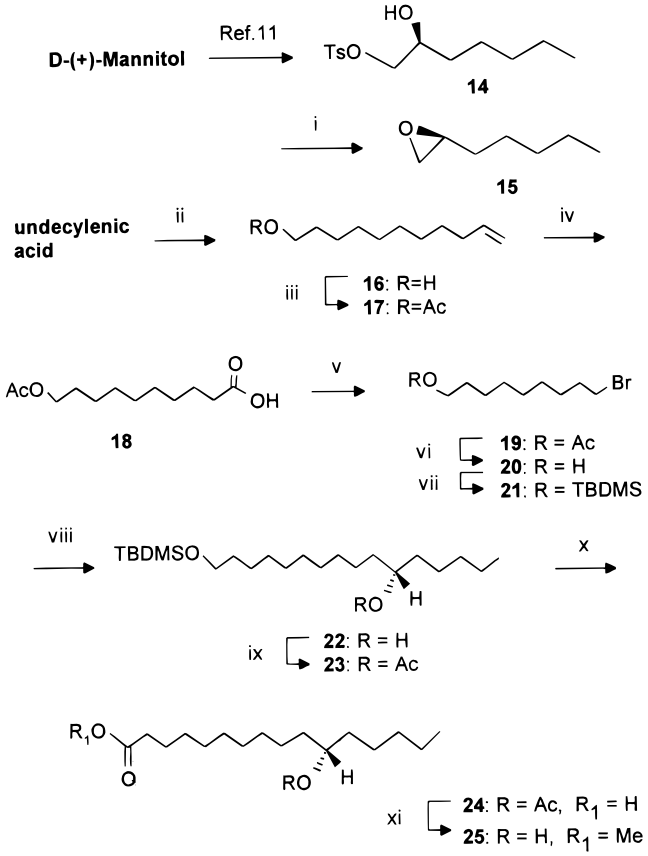


[a] Reagents and Conditions: (i) NH_3, MeOH−THF (3:7), 0 °C, 3 h, 50%; (ii) $CNCCl_3$, DBU, CH_2Cl_2, rt, overnight, 79%; (iii) NaOMe (cat.), MeOH, 0 °C, 2 h, 90%; (iv) $PhCH(OMe)_2$, *p*-TsOH, 50 °C, 4.5 h, 61%; (v) Ac_2O, Py, overnight, 84%; (vi) Bu_2SnO, toluene, reflux, 1 h, then PMBCl, CsF, Bu_4NI, DMF, rt, 33 h, 79%; (vii) 2(S)-methylbutyric anhydride (2.0 equiv), DMAP, Py, rt, 27 h, 70%; (viii) CAN (2.0 equiv), CH_3CN-H_2O (9:1), 25 min, 97%.

pyranoside (**8**), which was readily available from D-glucose,[8] by benzylidenization and acetylation. Ethyl 1-thio-α-L-rhamnopyranoside (**11**), readily prepared from L-rhamnose by a known procedure in three steps,[5c] was selectively protected at 3-OH with a *p*-methoxybenzyl (PMB) group by sequential treatment with Bu_2SnO, PMBCl, CsF, and Bu_4NI in DMF to give ethyl 3-*O*-PMB-1-thio-α-L-rhamnopyranoside (**12**),[9] which was further converted to ethyl 2,4-di-*O*-Mba(2s)-3-*O*-PMB-1-thio-α-L-rhamnopyranoside (**13**) by treatment with commercially available 2(s)-methylbutyric anhydride (from Aldrich) in pyridine in the presence of DMAP. Removal of the 3-*O*-PMB group with cerium(IV) ammonium nitrate (CAN)[9] afforded ethyl 2,4-di-*O*-Mba(2s)-1-thio-α-L-rhamnopyranoside (**3**). Alternatively, **11** was benzylated to provide the ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**4**).[5c]

Secondly, methyl 11(*S*)-jalapinolate [methyl 11(*S*)-hydroxyhexadecanoyl ester (**25**)][10] was prepared employing a chiral pool approach starting from D-(+)-mannitol

Scheme 3. Preparation of Methyl 11(*S*)-Jalapinolate[a]



[a] Reagents and conditions: (i) *t*-BuLi/pentane (1.5 mol/mL), −30 °C to rt, 1 h, 70%; (ii) $LiAlH_4$, THF, reflux, 12 h, 95%; (iii) Ac_2O, Py, rt, 2 h, 95%; (iv) $KMnO_4$, benzene−H_2O−HOAc (4:4:1), Bu_4NI, rt, overnight, 91%; (v) Br_2, HgO, CCl_4, reflux, 5 h, 83%; (vi) *p*-TsOH (cat.), CH_3OH, reflux, 1.5 h, 92%; (vii) TBDMSCl, imidazole, rt, 3 h, 97%; (viii) Mg, THF, reflux, 2 h, then CuI (cat.), **15** (1.0 equiv), −78 °C to rt, 2.5 h, 66%; (ix) Ac_2O, Py, rt, overnight, 91%; (x) Jones reagent, acetone, rt, 1.5 h, 89%; (xi) $BF_3{\cdot}OEt_2$ (3.0 equiv), MeOH, 40 °C, 4 h, 97%.

(Scheme 3). 2(*S*)-Hydroxyheptanyl tosylate (**14**), readily obtained from D-mannitol in seven steps in a yield of 6.7% according to Barry's procedure,[11] was treated with *t*-BuLi to afford the 1,2(*S*)-epoxyheptane (**15**) (overall yield of 4.7% from D-mannitol).[12] On the other hand, transformation of undecylenic acid to ω-bromononanyl (*tert*-butyl dimethyl) silyl ether (**21**) was easily realized in six steps (overall 61% yield): reduction with $LiAlH_4$, acetylation, oxidative cleavage of the double bond by $KMnO_4$,[13] Hunsdieck decarboxylic bromination,[14] deacetylation, and protection of 1-OH with TBDMS. Conversion of **21** into the Grignard reagent followed by treatment with epoxide **15** in the presence of catalytic CuI conveniently afforded 1-(*tert*-butyldimethylsiloxy)-11(*S*)-hexadecanol (**22**) in 66% yield. Protection of the 11(*S*)-hydroxyl of **22** with acetyl, followed by Jones oxidation, provided 11(*S*)-acetoxy-1-hexadecanoic acid (**24**), which was transferred to methyl 11(*S*)-jalapinolate (**25**) in one step by treatment with $BF_3{\cdot}OEt_2$ in MeOH.

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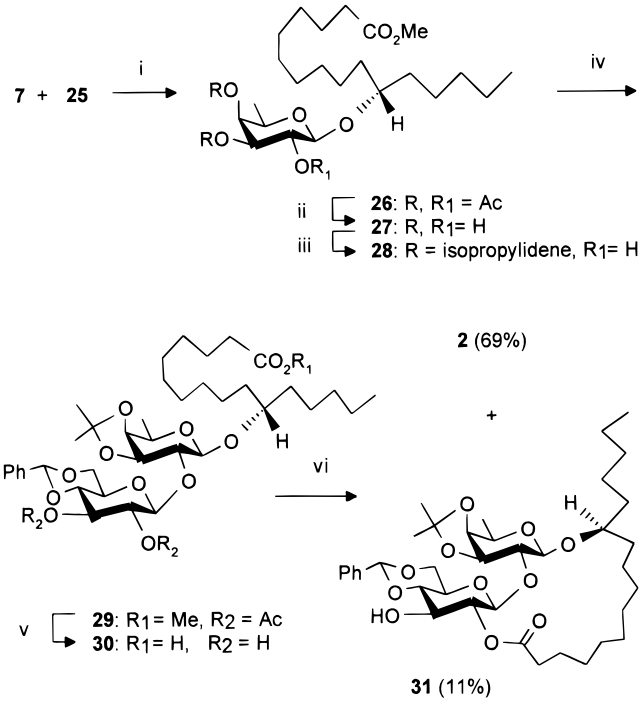
Scheme 4. Preparation of AB Disaccharide Macrolactone Acceptor 2[a]

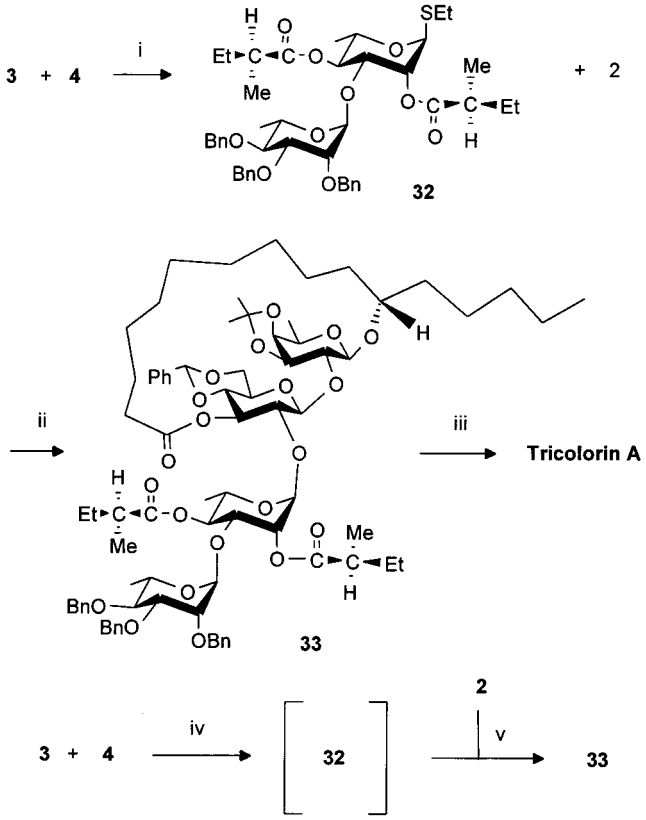


[a] Reagents and conditions: (i) **7** (1.0 equiv), **25** (0.9 equiv), $BF_3{\cdot}OEt_2$ (1.2 equiv), CH_2Cl_2, −15 °C, 1 h, 66%; (ii) 1% NaOMe, MeOH, −15 °C, 25 min; (iii) $Me_2C(OMe)_2$, *p*-TsOH, acetone, overnight, 82% (two steps); (iv) **10** (1.6 equiv), NIS (3.0 equiv), AgOTf (1.0 equiv), 4 Å MS, CH_2Cl_2, −15 °C, 0.5 h, 76%; (v) 3% KOH, MeOH−H_2O (9:1), reflux, 24 h, 91%; (vi) $(PyS)_2$, Ph_3P, toluene, reflux, 7 days, 69% for **2**, 11% for **31**.

With methyl 11(S)-jalapinolate (**25**) and monosaccharide donors **7** and **10** in hand, we sought to construct the macrolactone disaccharide **2** (Scheme 4). Alcohol **25** was readily glycosylated by imidate **7** using Schmidt's procedure[15] to afford **26**, which was sequentially subjected to deacetylation and isopropylidenization to give rise to **28** with only 2′-OH free. Treatment of alcohol **28** with thioglycoside donor **10** in the presence of NIS and AgOTf in CH_2Cl_2 at −15 °C led to the disaccharide **29** in 76% yield, which was saponified with 3% KOH in MeOH−H_2O (9:1) to provide the acid **30** with 2″,3″-OH free. Regioselective macrolactonization of **30** by Corey−Nicolaou's protocol[16] gave the desired 3″-OH macrolactonized product **2** in 69% yield, together with 11% of the 2″-OH macrolactonized product **31**.

Finally, the macrolactone tetrasaccharide **33** was assembled by a facile "one-pot, two-step" glycosylation of **2** with thioglycoside donors **3** and **4** under NIS/TfOH (cat.) in 43% yield (based on consumed **2**)[5] (Scheme 5). Alternatively, **33** was also constructed stepwise. Disaccharide synthon **32**, the intermediate in the above "one-pot" protocol, was efficiently synthesized by the reaction of thioglycosides **3** and **4** involving the well-known "armed-disarmed" glycosidation approach[17] in the presence of IDCP (iodium di-*sym*-collidine perchlorate).[18] Glycosylation of macrolactone disaccharide **2** by disaccharide donor **32** in the presence of promoter (NIS/AgOTf)[19] afforded the important precursor (**33**) of tricolorin A in

Scheme 5. Synthesis of Tricolorin A by a Stepwise or "One-Pot" Procedure[a]



[a] Reagents and conditions: (i) IDCP (2.3 equiv), 4 Å MS, CH_2Cl_2, rt, 0.5 h, 98%; (ii) NIS (4.5 equiv), AgOTf (0.5 equiv), 4 Å MS, CH_2Cl_2, rt, 1 h, 86%; (iii) (a) DDQ (3.0 equiv), CH_3CN-H_2O (9:1), reflux, 4 h; (b) H_2 (6 MPa), 10% Pd−C, 60 °C, 7 h, 70% (two steps); (iv) **3** (1.2 equiv), **4** (1.0 equiv), NIS (1.4 equiv), TfOH (cat.), 4 Å MS, Et_2O−DCE (1:1), −15 °C, 15 min; (v) **2** (1.6 equiv), NIS (1.4 equiv), TfOH (cat.), 4 Å MS, rt, 1 h, 43% (based on **2**).

good yield (86%). Final deprotection of the 3′,4′-*O*-isopropylidene and 4″,6″-*O*-benzylidene of **33** by DDQ[20] followed by removal of the benzyl groups by hydrogenation provided tricolorin A in 70.4% yield. The physical data were in identical to those reported.[2]

In conclusion, we have achieved the first total synthesis of tricolorin A in a total 45 steps, with the longest linear sequence of 20 steps and overall yield of 0.65% from D-(+)-mannitol. The synthetic route is highlighted by the regioselective macrolactonization of a disaccharide bearing 19-membered ring and the "one-pot" glycosidation for construction of a macrolactone tetrasaccharide.

Experimental Section

General Methods. Solvents were purified in the usual way, and melting points were uncorrected. TLC was per-

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formed on precoated plates of silica gel HF_{254} (0.5 mm, Qingdao, China) and detected by 10% concentrated sulfuric acid in methanol. Flash column chromatography was carried out on silica gel H (400 mesh, Qingdao, China). Coupling constants (*J*) are reported in Hz.

2,3,4-Tri-*O*-acetyl-α-D-fucopyranosyl Trichloroacetimidate (7). **5** (4.680 g, 14.08 mmol) was dissolved in a solution of NH_3 in MeOH/THF (200 mL, 3/7 v/v) (prepared by bubbling NH_3 into MeOH−THF until the system was not exothermic). The mixture was stirred for 3 h at 0 °C and then concentrated. The residue was purified by flash chromatography on a silica gel column (petroleum ether−EtOAc, 7:3, then 7:3:1% MeOH) to afford a white solid **6** (1.922 g, 50%, **5** (652 mg, 14%) was recovered).

To a solution of **6** (439 mg, 1.3 mmol) in CH_2Cl_2 (5 mL) were added $CNCCl_3$ (2.5 mL, 24.6 mmol) and DBU (0.2 mL, 1.3 mmol). The mixture was stirred at rt overnight under argon and then concentrated and flash chromatographed on a silica gel column (petroleum ether−EtOAc, 7:3) to give **7** (480 mg, 79%) as a white amorphous solid: $[\alpha]^{16}_D$ +132.8 (*c* 0.30, $CHCl_3$) (lit.[3c] $[\alpha]^{16}_D$ +106.4 (*c* 3.2, $CHCl_3$)); IR (KBr) 3333, 1746, 1677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 8.61 (1H, s), 6.55 (1H, d, *J* = 3.4), 5.45−5.39 (2H, m), 5.34 (1H, dd, *J* = 10.4), 4.37 (1H, m), 2.19, 2.02 and 2.01 (3H each, s each), 1.19 (3H, d, *J* = 6.5).

Ethyl 4,6-*O*-Benzylidene-2,3-di-*O*-acetyl-1-thio-β-D-glucopyranoside (10). A mixture of **9** (1.026 g, 4.58 mmol), $PhCH(OMe)_2$ (6 mL, 39 mmol), and *p*-TsOH (0.05 g) in DMF (50 mL) (PH 3.0) was stirred at 50 °C for 4.5 h and then was neutralized by addition of anhydrous K_2CO_3. After removal of DMF and $PhCH(OMe)_2$ under vacuum, the residue was diluted with EtOAc (50 mL), filtered through a short column of silica gel, and concentrated. Flash chromatography on a silica gel column (CH_2Cl_2−CH_3OH, 9:1) gave rise to ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (0.897 g, 61%) as a white needle.

The above product (265 mg, 0.85 mmol) was dissolved in Py (15 mL) and Ac_2O (2 mL). The solution was stirred at rt overnight. After removal of Py and Ac_2O under vacuum, the residue was purified by chromatography on a silica gel column (petroleum ether−EtOAc, 80:7) to afford **10** (284 mg, 84.4%) as a white needle: mp 139−141 °C; $[\alpha]^{24}_D$ −72.45 (*c* 0.62, $CHCl_3$); IR (KBr) 1753, 1731 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.45−7.35 (5H, m), 5.51 (1H, s), 5.35 (1H, t, *J* = 9.13), 5.05 (1H, dd, *J* = 10.1, 9.3), 4.59 (1H, d, *J* = 10.1), 4.38 (1H, dd, *J* = 10.5, 4.9), 3.79 (1H, t, *J* = 10.1), 3.70 (1H, t, *J* = 9.5), 3.57 (1H, m), 2.72 (2H, m), 2.08, 2.05 (3H each, s each), 1.27 (3H, t, *J* = 7.52); EIMS *m/z* 335 (M^+ − EtS, 1.6%). Anal. Calcd for $C_{19}H_{24}O_5S$: C, 57.56; H, 6.10; S, 8.09. Found: C, 57.26; H, 5.84; S, 8.16.

Ethyl 2,4-Di-*O*-[2(*S*)-methylbutyryl]-3-*O*-(*p*-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (13). A mixture of **11** (3.256 g, 15.7 mmol) and Bu_2SnO (4.873 g, 19.6 mmol) in toluene (100 mL) was refluxed for 1 h in a Soxhlet apparatus with a thimble containing 4 Å molecular sieves. Then the solution was concentrated. The residue was suspended in DMF (75 ML), and finely powdered CsF (4.8 g, 31.7 mmol), Bu_4NI (14.5 g, 19 mmol), and PMBCl (5.7 mL, 3.9 mmol) were added. After being stirred at rt for 33 h, the mixture was diluted with Et_2O (300 mL) and washed with H_2O (300 mL × 3). The separated water phase was extracted with Et_2O (100 mL × 2). The combined organic phase was washed with ice water, dried over Na_2SO_4, and then filtered through a short column of silica gel (containing a thin layer of active charcoal). The eluent was concentrated to a residue, which was purified by flash chromatography on a silica gel column (CH_2Cl_2−CH_3OH, 95:2) to afford a colorless syrup **12** (4.068 g, 79%), which was directly used in the next step.

A mixture of **12** (4.068 g, 12.4 mmol), 2(S)-methylbutyric anhydride (5 mL, 25 mmol, purchased from Aldrich), and catalytic DMAP in Py (30 mL) was stirred for 27 h under Argon at rt. After the solvent was removed under reduced pressure, the residue was diluted with EtOAc, washed with aqueous $NaHCO_3$ and brine, and then dried with anhydrous Na_2SO_4 and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 100:3) afforded a colorless syrup **13** (4.292 g, 69.7%): $[\alpha]^{18}_D$ −34.30 (*c* 3.65, $CHCl_3$); IR (neat) 1741, 1613 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.15, 6.81 (4H, m), 5.42 (1H, dd, *J* = 1.5, 2.9), 5.19 (1H, s), 5.06 (1H, t, *J* = 9.7), 4.52 (1H, d, *J* = 11.2), 4.30 (1H, d, *J* = 11.2), 4.11 (1H, dq, *J* = 9.8, 6.2), 3.77 (3H, s), 3.76 (1H, dd, *J* = 3.2, 8.3), 2.62 (2H, m), 2.48 (1H, m), 2.32 (1H, m), 1.67, 1.45 (2H each, m), 1.28 (3H, t, *J* = 7.2), 1.18 (3H, d, *J* = 6.4), 1.15 (3H, d, *J* = 7.2), 1.11 (3H, d, *J* = 6.9), 0.88 (3H, t, *J* = 7.5), 0.87 (3H, t, *J* = 7.3); FABMS *m/z* 496 (M^+), 495 (M^+ − 1), 435 (M^+ − EtS).

Ethyl 2,4-Di-*O*-[2(*S*)-methylbutyryl]-1-thio-α-L-rhamnopyranoside (3). To a solution of **13** (1.027 g, 2.07 mmol) in CH_3CN−H_2O (30 mL, 10:1) was added cerium(IV) ammonium nitrate (2.280 g, 4.17 mmol) at rt. The mixture was stirred for 25 min and then quenched with saturated aqueous $NaCO_3$ solution and diluted with EtOAc. The mixture was washed with brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (petroleum−EtOAc, 9:1, then 4:1) gave rise to a colorless syrup **3** (641 mg, 97.5% based on reacted **13**, 159 mg **13** was recovered): $[\alpha]^{16}_D$ −62.13 (*c* 21.9, $CHCl_3$); IR (neat) 3484, 1741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 5.24 (1H, d, *J* = 1.3), 5.15 (1H, dd, *J* = 1.5, 3.5), 4.88 (1H, t, *J* = 9.3), 4.19 (1H, dq, *J* = 9.9, 6.3), 3.89 (1H, ddd, *J* = 3.5, 9.8, 8.3), 2.64 (2H, m), 2.54−2.41 (2H, m), 2.17 (1H, d, *J* = 8.2), 1.78−1.64, 1.60−1.46 (2H each, m), 1.30 (3H, t, *J* = 7.4), 1.23 (3H, d, *J* = 6.4), 1.20 (3H, d, *J* = 7.2), 1.18 (3H, d, *J* = 6.9), 0.94 (3H, t, *J* = 7.4), 0.94 (3H, t, *J* = 7.4); EIMS *m/z* 315 (M^+ − EtS, 63.1). Anal. Calcd for $C_{18}H_{32}O_6S$: C, 57.42; H, 8.57. Found: C, 57.38; H, 8.74.

1,2(*S*)-Epoxyheptane (15). To a solution of **14** (5.1 g, 17.8 mmol) in Et_2O (50 mL) was added dropwise ^{t}BuLi/pentane (1.5 M, 14 mL, 21 mmol, purchased from Janssen Chemica) at −30 °C, then the mixture was warmed to 20 °C and stirred for 1 h. After the mixture was cooled to −20 °C, a saturated aqueous solution of NH_4Cl (2 mL) was added to quench the reaction. The mixture was extracted with Et_2O (70 mL × 3), washed with brine, dried over Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (pentane−Et_2O, 100:3) furnished a yellow oil **15** (1.429g, 70%): $[\alpha]^{20}_D$ −9.46 (*c* 0.43, $CHCl_3$) (lit.[12] $[\alpha]^{21}_D$ −12.3 (*c* 6.0, dioxane); ^1H NMR (300 MHz, $CDCl_3$) 2.87 (1H, m), 2.70 (1H, pseudo-t, *J* = 4.8, 4.1), 2.43 (1H, dd, *J* = 2.5, 5.0), 1.50 (4H, m), 1.28 (4H, m), 0.86 (3H, t, *J* = 7.0); EIMS *m/z* 113 (M^+ − 1, 0.3), 71 (M^+ − C_2H_3O, 100.0), 43 (M^+ − C_5H_{11}, 31.8).

ω-Bromononanyl Dimethyl-*tert*-butylsilyl Ether (21). A mixture of **20** (28 g, 118 mmol), TBDMSCl (23 g, 152 mmol), imidazole (12 g, 176 mmol), and catalytic DMAP in CH_2Cl_2 (300 mL) was stirred for 3 h at rt under nitrogen. The reaction mixture was filtered and concentrated. Flash chromtography on a silica gel column (petroleum−EtOAc, 9:1) gave rise to **21** (39g, 97%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) 3.59 (2H, t, *J* = 6.6), 3.40 (2H, t, *J* = 6.9), 1.84 (2H, m), 1.52−1.29 (12H, m); EIMS *m/z* 339 (M^+ − 1, 6). Anal. Calcd for $C_{15}H_{33}$-BrOSi, C, 53.39; H, 9.86; Br, 23.68. Found: C, 53.42; H, 9.68; Br, 23.70.

1-(*tert*-Butyldimethylsiloxy)-11(S)-hexadecanol (22). To flame-dried three-neck round-bottom flask (1 L) was added a mixture of magnesium scrubbers (300 mg), catalytic I_2, and a 1 mL solution of **21** in THF (4g/20 mL, 11.9 mmol). The mixture was heated to start the reaction, and then the remaining solution of **21** in THF was added into the flask dropwise. After being refluxed for 2 h, the reaction system was cooled to −78 °C and catalytic CuI was added. The mixture was stirred for 15 min and then was added to a solution of **15** in THF (1.118 g/15 mL, 3.31 mmol) by drop funnel followed by slow warming to rt for 1.5 h. The reaction proceeded for an additional 1 h at rt and then was quenched with a saturated aqueous solution of NH_4Cl (4 mL) at −78 °C. The mixture was dried over Na_2SO_4, filtered, and concentrated. Flash chromatography on a silica gel column (petroleum−EtOAc, 80:5) gave rise to **22** (2.411 g, 66.0%) as a white waxy solid: mp 35−38 °C; $[\alpha]^{21}_D$ +0.28 (*c* 4.0, $CHCl_3$); IR (KBr) 3400 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 3.55 (3H, t, *J* = 6.6), 1.56 (2H, m), 1.38 (4H, m), 1.25 (20H, m), 0.85 (6H, s), 0.85 (3H, t, *J* = 6.9), 0.00 (6H, s); EIMS *m/z* 355 (M^+ − OH, 1.0),

301 ($M^+ - C_5H_{11}$, 6.2). Anal. Calcd for $C_{22}H_{48}O_2Si$: C, 70.90; H, 12.98. Found: C, 70.82; H, 13.26.

1-(*tert*-Butyldimethylsiloxy)-11(*S*)-hexadecanyl acetate (23). A mixture of **22** (1.577 g, 4.2 mmol) and Ac_2O (3 mL) in Py (15 mL) was stirred overnight at rt. After Py and the remaining Ac_2O were removed under vacuum, the residue was purified by flash chromatography on a silica gel column (petroleum ether−EtOAc, 100:0.6) to afford **23** (1.794 g, 90.5%) as a colorless oil: $[\alpha]^{22}_D$ −1.02 (*c* 11.39, $CHCl_3$); IR (film) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.79 (1H, m), 3.52 (2H, t, *J* = 6.6), 1.96 (3H, s), 1.43 (6H, m), 1.19 (20H, br), 0.82 (9H, s), 0.81 (3H, t, *J* = 7.1), 0.3 (6H, s); EIMS *m/z* 415 ($M^+ + 1$, 1.5), 343 ($M^+ - C_5H_{11}$, 3.3). Anal. Calcd for $C_{24}H_{50}O_3Si$: C, 69.50; H, 12.15. Found: C, 69.30; H, 11.82.

11(S)-Acetoxy-1-hexadecanoic Acid (24). To a solution of **23** (657 mg, 1.53 mmol) in acetone (15 mL) was added Jones reagent (2.0 mL) by drop funnel at 0 °C. After the mixture was stirred for 1.5 h at rt, a saturated aqueous solution of $NaHCO_3$ was added to quench the reaction. The mixture was filtered, and the liquid portion was diluted with EtOAc (80 mL), washed successively with 10% aqueous citric acid and brine, dried over Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 7:3) gave rise to **24** (429 mg, 89.4%) as a colorless oil: $[\alpha]^{23}_D$ −0.79 (*c* 14.85, $CHCl_3$); IR (film) 3050−2500, 1738, 1711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.86 (1H, m), 2.35 (2H, t, *J* = 7.5), 2.04 (3H, s), 1.62 (2H, m), 1.49 (4H, m), 1.26 (22H, br), 0.88 (3H, t, *J* = 6.6); EIMS *m/z* 315 ($M^+ + 1$, 36.7. Anal. Calcd for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.84; H, 10.98.

Methyl 11(*S*)-Jalapinolate (25). A solution of **24** (367 mg 1.2 mmol) and $BF_3{\cdot}OEt_2$ (0.5 mL, 0.6 mmol) in absolute CH_3OH (4 mL) was stirred at 40 °C for 4 h, and then Et_3N was added to quench the reaction. After removal of CH_3OH and Et_3N, the residue was purified by flash chromatography on a silica gel column (petroleum ether−EtOAc, 70:6) to give **25** (323 mg, 96.9%) as a colorless plate crystal: mp 48−49 °C; $[\alpha]^{25}_D$ +1.37 (*c* 2.18, $CHCl_3$) (lit.[21] $[\alpha]_D$ +1.2 (*c* 10.0 $CHCl_3$)); IR (KBr) 3334, 1746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 3.66 (3H, s), 3.57 (1H, m), 2.30 (2H, t, *J* = 7.5), 1.61 (2H, m), 1.42−1.28 (22H, m), 0.89 (3H, t, *J* = 6.6); EIMS *m/z* 269 ($M^+ - OH$, 57.2), 215 ($M^+ - C_5H_{11}$, 12.0). Anal. Calcd for $C_{17}H_{34}O_3$: C, 71.28; H, 11.96. Found: C, 71.11; H, 11.68.

1-(Methoxycarbonyl)pentadec-10(*S*)-yl 2,3,4-Tri-*O*-acetyl-*β*-D-fucopyranoside (26). A mixture of **7** (480 mg, 1.0 mmol), **25** (370 mg, 1.3 mmol), and 4 Å MS (0.8 g) in CH_2Cl_2 (4 mL) was stirred for 15 min at rt under argon and then cooled to −30 °C, and a solution of $BF_3{\cdot}OEt_2$−CH_2Cl_2 (0.6 mL, 1:40, v/v) was added in one portion. After being warmed to 0 °C, the reaction was proceeded for another 1 h. Saturated aqueous $NaHCO_3$ was added to quench the reaction. The mixture was dried over Na_2SO_4, filtered, and concentrated. Chromatography on a silica gel column afforded a yellow oil **26** (334 mg, 65.7%, based on reacted **25**, the acetyl transfer product (109 mg) was also obtained): $[\alpha]^{18}_D$ +4.45 (*c* 2.56, $CHCl_3$); IR (film) 1755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 5.21 (1H, dd, *J* = 2.9, 0.8), 5.16 (1H, dd, *J* = 7.8, 10.4), 5.01 (1H, dd, *J* = 10.3, 3.4), 4.44 (1H, d, *J* = 8.0), 3.77 (1H, dq, *J* = 0.8, 6.5), 3.67 (3H, s), 3.53 (1H, m), 2.31 (2H, t, *J* = 7.6), 2.17, 2.03, 1.98 (3H each, s each), 1.64−1.28 (24H, m), 1.20 (3H, d, *J* = 6.5), 0.88 (3H, t, *J* = 7.0); ^{13}C NMR (75 MHz, $CDCl_3$) 14.19, 16.14, 16.23, 20.80, 22.63, 24.79, 24.98, 29.17, 29.28, 29.47, 29.62, 29.92, 31.91, 34.12, 34.77, 51.47, 68.94, 69.49, 70.47, 71.63, 81.33, 100.92, 169.40, 170.33, 170.85, 174.32; FABMS 559 ($M^+ + 1$). Anal. Calcd for $C_{29}H_{50}O_{11}$: C, 62.34; H, 9.02. Found: C, 62.65; H, 9.09.

1-(Methoxycarbonyl)pentadec-10(*S*)-yl *O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (29). A mixture of **26** (229 mg, 0.41 mmol) in NaOMe−MeOH (1%, 5 mL) was stirred at −15 °C for 25 min under argon. The solution, neutralized with Dowex-50w (H^+), was then filtered, concentrated, and dried under vacuum. The residue was dissolved in acetone (5 mL) and $Me_2C(OMe)_2$ (1 mL, 8.21 mmol), and TsOH (15 mg) was added. The reaction proceeded overnight at rt under argon, neutralized with powdered K_2CO_3, and then filtered through a short column of silica gel. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 7:1) furnished **28** (154 mg, 82%) as a oil: ^1H NMR (300 MHz, $CDCl_3$) 4.16 (1H, d, *J* = 8.3), 4.04−4.00 (2H, m), 3.84 (1H, m), 3.67 (3H, s), 3.60 (1H, t, *J* = 5.7), 3.51 (1H, m), 2.30 (2H, t, *J* = 7.5), 1.54, 1.36 (3H each, s each), 1.40 (3H, d, *J* = 6.5), 1.65−1.27 (24H, m), 0.89 (3H, t, *J* = 7.1).

A mixture of **28** (642 mg, 1.4 mmol), **10** (1.1 g, 2.8 mmol), and 4 Å MS (2 g) in CH_2Cl_2 (20 mL) was stirred at rt for 15 min under nitrogen. The reaction system was then cooled to −15 °C, and NIS (1.1 g, 5.0 mmol) was added immediately followed by a solution of AgOTf (300 mg, 1.4 mmol) in toluene (5 mL). After the mixture was stirred for 0.5 h, Et_3N (1 mL) was added to quench the reaction. The mixture was filtered through a short column of silica gel and diluted with CH_2Cl_2 (150 mL). The solution was washed with 10% aqueous $Na_2S_2O_3$ and ice water, dried over Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 7:1) afforded **29** (838 mg, 76.5%) as a yellow syrup: $[\alpha]^{16}_D$ −21.02 (*c* 4.2, $CHCl_3$); IR (neat) 1757 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 7.5−7.4 (5H, m), 5.50 (1H, s), 5.31 (1H, m), 5.01−4.96 (2H, m), 4.34 (1H, dd, *J* = 5.0, 10.3), 4.12 (1H, d, *J* = 8.0), 4.03 (1H, t, *J* = 5.8), 3.95 (1H, dd, *J* = 1.9, 5.7), 3.83−3.72 (3H, m), 3.66 (3H, s), 3.64−3.52 (3H, m), 2.30 (2H, t, *J* = 7.5), 2.09, 2.05 (3H each, s each), 1.51, 1.33 (3H, each, s each), 1.36 (3H, d, *J* = 6.5), 1.7−1.2 (24H, m), 0.87 (3H, t); ^{13}C NMR (150 MHz, $CDCl_3$) 14.10, 16.59, 20.80, 20.84, 22.62, 24.71, 24.96, 25.15, 26.18, 26.31, 27.84, 27.96, 28.79, 28.97, 29.17, 29.31, 29.51, 29.69, 29.92, 31.96, 33.84, 34.10, 34.65, 51.40, 66.28, 68.49, 68.79, 72.07, 72.93, 76.43, 78.38, 79.24, 79.60, 80.49, 100.14, 100.70, 101.48, 109.66, 126.14, 128.22, 129.08, 136.93, 169.65, 170.15, 174.28; FABMS *m/z* 805 ($M^+ - 1$). Anal. Calcd for $C_{63}H_{66}O_{14}$: C, 64.00; H, 8.24. Found: C, 63.82; H, 8.37.

1-(Hydroxycarbonyl)pentadec-10(*S*)-yl *O*-(4,6-*O*-Benzylidene-*β*-D-glucopyranosyl)-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (30). A mixture of **29** (741 mg, 0.92 mmol) and KOH (500 mg, 9 mmol) in CH_3OH−H_2O (20 mL, 9:1, v/v) was refluxed for 10 h under argon. The mixture was neutralized with IRC-85 Amberlite (weak H^+), filtered, and concentrated. Flash chromatography on a silica gel column afforded **30** (597 mg, 91%) as an amorphous solid: IR (KBr) 3430, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.49−7.26 (5H, m), 5.53 (1H, s), 4.65 (1H, d, *J* = 7.7), 4.31 (1H, dd, *J* = 4.8, 10.5), 4.28 (1H, d, *J* = 8.1), 4.15 (1H, dd, *J* = 5.5, 7.2), 4.01 (1H, dd, *J* = 2.0, 5.4), 3.87−3.46 (5H, m), 2.31 (2H, t), 1.50, 1.34 (3H, each, s each), 1.37 (3H, d, *J* = 6.6), 1.7−1.2 (24H, m), 0.88 (3H, t, *J* = 7.0); FABMS *m/z* 437; ^{13}C NMR (75.6 MHz, $CDCl_3$) 179.0, 137.1, 129.2, 128.3, 126.4, 110.3, 104.1, 101.9, 100.3, 80.8, 80.7, 79.8, 78.6, 76.6, 76.0, 68.8, 68.5, 67.0, 34.5, 34.0, 33.7, 32.0, 30.0, 29.6, 29.4, 29.2, 29.0, 27.8, 26.2, 25.0, 24.7, 24.5, 22.6, 16.5, 14.2.

1,3-(B)-Lactone of (*S*)-1-(Hydroxycarbonyl)pentadec-10-yl *O*-(4,6-Benzylidene-*β*-D-glucopyranosyl)-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (2) and 1,2(B)-Lactone of (*S*)-1-(Hydroxycarbonyl)pentadec-10-yl *O*-(4,6-Benzylidene-*β*-D-glucopyranosyl)-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (31). A solution of **30** (400 mg, 0.56 mmol), $(PyS)_2$ (640 mg, 3.0 mmol), and Ph_3P (750 mg, 3.0 mmol) in deoxygenated anhydrous toluene (15 mL) was stirred for 5 h at rt under argon. The mixture was diluted with deoxygenated anhydrous toluene (50 mL) and then was added dropwise to the refluxing dry deoxygenated toluene (700 mL) over 10 h. The solution was refluxed under argon for 7 days. After removal of toluene, the residue was chromatographed on a silica gel column (petroleum-EtOAc, 8:2) to afford **2** (270 mg, 69%) as colorless needles together with **31** (45 mg, 11%) as a white amorphous solid. **2:** mp 209−211 °C; $[\alpha]^{19}_D$ −59.09 (*c* 0.07, $CHCl_3$); IR (KBr) 3484, 1742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.45−7.35 (5H, m), 5.52 (1H, s), 5.22 (1H, t, *J* = 8.8), 5.06 (1H, d, *J* = 7.4) 4.30−4.23 (2H, m), 4.16 (1H, t, *J* = 6.0), 3.97−3.73 (5H, m), 3.60−3.54 (2H, m), 3.42 (1H, m), 2.79 (1H, br), 2.51, 2.31 (1H each, m each), 1.67−1.25 (22H, m), 1.49, 1.34 (3H each, s each), 1.38 (3H, d, *J* = 6.7), 0.88

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3H, t, $J = 6.9$); ^{13}C NMR (75.6 MHz, $CDCl_3$) 174.9, 137.2, 129.2, 128.3, 109.9, 102.5, 101.8, 98.9, 83.2, 79.5, 78.4, 75.2, 74.8, 68.9, 66.3, 36.0, 35.7, 34.8, 32.0, 30.6, 29.8, 29.4, 28.5, 28.4, 27.9, 27.0, 26.6, 25.9, 22.7, 16.8, 14.2; ESIMS 713 ($M + Na^+$), 729 ($M + K^+$). Anal. Calcd for $C_{38}H_{58}O_{11}$: C, 66.07; H, 8.46. Found: C, 65.88; H, 8.59.

31: $[\alpha]^{19}_D$ −38.60 (*c* 0.27, $CHCl_3$); IR (KBr) 3484, 1751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.50−7.36 (5H, m), 5.55 (1H, s), 5.23 (1H, d, $J = 7.4$), 4.91 (1H, t, $J = 8.1$), 4.28 (1H, dd, $J = 4.8, 10.4$), 4.16 (1H, d, $J = 8.3$), 4.07 (1H, m), 4.00 (1H, m), 3.92−3.67 (5H, m), 3.50 (2H, m), 3.07 (1H, br), 2.45 (2H, m), 1.53, 1.36 (3H each, s each), 1.75−1.26 (25H, m), 0.88 (3H, t, $J = 6.2$); ^{13}C NMR (75.6 MHz, $CDCl_3$) 173.8, 137.1, 129.2, 128.3, 126.3, 110.0, 101.8, 100.4, 97.3, 80.0, 79.4, 75.2, 75.1, 73.0, 68.8, 68.7, 66.1, 35.1, 33.7, 31.9, 27.9, 26.8, 26.5, 26.33, 26.27, 26.1, 25.2, 23.8, 23.6, 22.6, 16.6; FABMS *m/z* 690 (M^+). Anal. Calcd for $C_{38}H_{58}O_{11}$: C, 66.07; H, 8.46. Found: C, 66.22; H, 8.76.

Ethyl *O*-[2,3,4-Tri-*O*-benzyl-1-thio-α-L-rhamnopyranosyl]-(1→3)-2,4-di-*O*-[2(*S*)-methylbutyryl]-1-thio-α-L-rhamnopyranoside (32). A mixture of **3** (700 mg, 1.47 mmol, 2.5 equiv), **4** (222 mg, 0.59 mmol), and 4 Å MS (1 g) in Et_2O−$ClCH_2CH_2Cl$ (18 mL, 5:1) was stirred for 15 min under nitrogen at rt, and then IDCP (1.076 mg, 2.31 mmol) was added. After being stirred for 0.5 h, the resulting mixture was filtered through a short column of silica gel and diluted with Et_2O (200 mL). The organic phase was washed with 10% aqueous $Na_2S_2O_3$ and ice−water, dried with Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 100:3) furnished **32** as a colorless syrup (457 mg, 98%): $[\alpha]^{22}_D$ −35.85 (*c* 1.89, $CHCl_3$); IR (neat) 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.13 (1H, m), 5.12 (1H, s), 5.02 (1H, t, $J = 9.7$), 4.84 (1H, s), 4.79, 4.52 (1H each, d, $J = 11.3$), 4.66, 4.56 (1H each, d, $J = 12.2$), 4.51, 4.48 (1H each, d, $J = 11.9$), 4.03 (1H, m), 3.95 (1H, dd, $J = 2.4, 9.8$), 3.65 (1H, dd, $J = 8.3$), 3.63 (1H, s), 3.49 (2H, m), 2.56 (2H, m), 2.38 (1H, m), 2.17 (1H, m), 1.65, 1.57, 1.39, 1.31 (1H each, m each), 1.18 (3H, d, $J = 5.1$), 1.09 (3H, d, $J = 5.1$), 1.09 (3H, d, $J = 6.1$), 1.02 (3H, d, $J = 7.1$), 0.83 (3H, t, $J = 7.4$), 0.76 (3H, t, $J = 7.3$); ^{13}C NMR (150 MHz, $CDCl_3$) 14.97, 17.53, 17.84, 25.74, 67.43, 69.01, 72.39, 72.47, 72.91, 73.65, 74.64, 75.46, 75.64, 80.03, 80.17, 82.11, 100.82, 127.26, 127.41, 127.46, 127.50, 128.10, 128.28, 138.38, 138.48, 138.88, 11.66, 11.77, 16.55, 16.65, 26.37, 26.52, 41.09, 41.19, 175.30, 175.89; FABMS *m/z* 792 (M^+). Anal. Calcd for $C_{45}H_{60}O_{10}S$: C, 68.16; H, 7.63; S, 4.04. Found: C, 68.02; H, 7.74; S, 4.44.

1,3(B)-Lactone of (S)-1-(Hydroxycarbonyl)pentadec-10-yl *O*-(2,3,4-Tri-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-(2S-methylbutyryl)-α-L-rhamnopyranosyl-(1→2)-4,6-benzylidene-*β*-D-glucopyranosyl-(1→2)-3,4-*O*-isopropylidene-*β*-D-fucopyranoside (33). Method A. A mixture of **2** (139 mg, 0.2 mmol), **32** (242 mg, 0.3 mmol), and 4 Å MS (1 g) in CH_2Cl_2 (5 mL) was stirred at rt under argon for 15 min. NIS (200 mg, 0.9 mmol) was added followed by a solution of AgOTf (33 mg) in toluene (0.5 mL) immediately. After the mixture was stirred for 1 h, Et_3N (0.2 mL) was added to quench the reaction, and the mixture was filtered through a short column of silica gel and diluted with CH_2Cl_2 (150 mL). The solution was washed with 10% aqueous $Na_2S_2O_3$ and ice−water, dried over Na_2SO_4, and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 90:8) afforded **33** (245 mg, 86%) as a colorless amorphous solid.

Method B ("One-Pot" Procedure). A mixture of **3** (11 mg, 0.029 mmol), **4** (16 mg, 0.034 mmol), and 4 Å MS (100 mg) in Et_2O−DCE (2 mL, 1/1, v/v) was stirred at rt under nitrogen for 0.5 h. The mixture was cooled to −15 °C, and then NIS (9 mg, 0.04 mmol) and a solution of TfOH−DCE (1:300, ∼20 μL) were added. After stirring for 0.5 h (TLC showed that **4** was consumed), 4 Å MS (50 mg), **2** (56 mg, 0.04 mmol), NIS (14 mg, 0.046 mmol), and a catalytic solution of TfOH−DCE (1:300, ∼20 μL) was added successively. The reaction system was warmed to rt and stirred for another 0.5 h. To the resulting mixture was added Et_3N (0.1 mL), and the mixture was diluted with CH_2Cl_2 (70 mL), washed with 10% aqueous $Na_2S_2O_3$ and, ice−water, dried over Na_2SO, and concentrated. Flash chromatography on a silica gel column (petroleum ether−EtOAc, 20:1) afforded **33** (7 mg, 43%, 48 mg **2** recovered) as a colorless amorphous solid: $[\alpha]^{19}_D$ −11.01 (*c* 0.39, $CHCl_3$); IR (KBr) 1743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.35−7.26 (20H, m), 5.53 (1H, s), 5.33 (1H, dd, $J = 7.1, 9.3$), 5.20 (1H, dd, $J = 6.3$), 5.13 (1H, t, $J = 2.2$), 5.09 (1H, d, $J = 1.6$), 5.05 (1H, t, $J = 9.9$), 4.98 (1H, d, $J = 1.6$), 4.87, 4.59 (1H each, d, $J = 11.4$), 4.73, 4.69 (1H each, d, $J = 11.7$), 4.55, 4.51 (1H each, d, $J = 11.7$), 4.32−4.26 (2H, m), 4.15−4.09 (3H, m), 4.01 (1H, m), 3.91−3.47 (11H, m), 2.5 (3H, m), 2.2 (1H, m), 1.49, 1.31 (3H each, s each), 1.37 (3H, d, $J = 6.5$), 1.26 (6H, m), 1.15 (3H, m), 1.07 (3H, d, $J = 7.0$), 0.89 (6H, m), 0.81 (3H, m); ^{13}C NMR (75.6 MHz, $CDCl_3$): 175.4, 175.3, 172.3, 139.0, 138.4, 137.1, 129.0, 128.3, 128.2, 128.1, 127.6, 127.4, 127.2, 126.1, 109.7, 101.5, 101.3, 100.5, 98.0, 97.4, 82.1, 80.7, 80.2, 80.0, 79.2, 78.2, 75.7, 75.1, 74.9, 74.7, 73.5, 72.4, 72.2, 72.0, 71.7, 68.8, 68.7, 67.3, 65.2, 41.3, 41.2, 35.3, 34.8, 34.3, 31.9, 30.4, 29.7, 29.2, 27.9, 27.8, 27.7, 26.9, 26.6, 26.5, 26.4, 25.2, 24.0, 22.6, 17.8, 17.4, 16.8, 16.75, 16.7; ESIMS *m/z* 1445 ($M + Na^+$), 1468 ($M + 2Na^+$). Anal. Calcd for $C_{81}H_{112}O_{21}$; C, 68.43; H, 7.94. Found: C, 68.39; H, 8.14.

Tricolorin A (1). A solution of **33** (127 mg, 0.09 mmol) and DDQ (94 mg) in CH_3CN−H_2O (10 mL, 9:1) was refluxed for 4 h. After being diluted with Et_2O (200 mL), the solution was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was decolored by active charcoal and chromatographed to afford a colorless syrup (92 mg) that was subjected to hydrogenation (H_2, 6 MPa) with catalytic 10% Pd−C in 95% ethanol (5 mL) for 7 h. After being filtered through a short column of silica gel and concentrated, the residue was chromatographed on a silica gel column (CH_2Cl_2:CH_3OH, 9:1) to give tricolorin A (64 mg, 70%) as a colorless amorphous solid: $[\alpha]^{20}_D$ −27.27 (*c* 0.89, CH_3OH) (lit.[2] $[\alpha]_D$ −30.32 (*c* 1.5, CH_3OH); IR (KBr) 3429, 2934, 1739 cm^{-1}; ^{1}H NMR (600 MHz, C_5D_5N) 5.82−5.76 (3H, m), 5.69 (1H, t, $J = 9.6$), 5.55 (1H, s), 5.50 (1H, br s), 4.77 (1H, m), 4.71 (1H, m), 4.65 (1H, m), 4.50 (1H, br s), 4.40 (1H, m), 4.34 (1H, m), 4.23 (3H, m), 4.12 (2H, m), 4.01 (1H, br s), 3.89 (1H, m), 3.82 (2H, m), 3.47 (1H, m), 2.98 (1H, m), 2.45(1H, m), 2.31 (1H, m), 1.70 (3H, d, $J = 5.4$), 1.63 (3H, d, $J = 5.4$), 1.57 (3H, d, $J = 6.6$), 1.16 (3H, d, $J = 7.8$), 1.10 (3H, d, $J = 7.2$), 0.91 (3H, t, $J = 6.6$), 0.82 (6H, m); ^{13}C NMR (75.6 MHz, C_5D_5N) 175.6, 175.5, 172.1, 104.5, 102.9, 99.7, 98.2, 80.8, 80.5, 78.8, 76.2, 76.1, 75.8, 74.5, 73.23, 73.18, 73.0, 72.6, 72.4, 72.2, 71.1, 70.4, 69.4, 67.1, 61.1, 41.7, 41.4, 41.3, 35.0, 34.3, 31.9, 31.6, 29.8, 29.4, 27.8, 26.9, 26.7, 26.5, 25.5, 24.6, 23.5, 22.7, 18.4, 18.2, 17.2, 16.83, 16.78, 14.1, 11.7; ESIMS *m/z* 1046 ($M + Na^+$), 1069 ($M + 2Na^+$).

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Supporting Information Available: Reproductions of ^{1}H NMR spectra for compounds **1**−**3**, **7**, **13**, **21**, **22**, **25**, **26**, and **29**−**33**, ^{13}C NMR spectra for compounds **1**−**3**, **26**, and **30**−**33**, IR and MS spectra for compounds **1** and **33**, and 2D NMR spectra (ROESY, HMQC, DQCOSY, TOCSY) for **1** (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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