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Total Synthesis of Batatoside L

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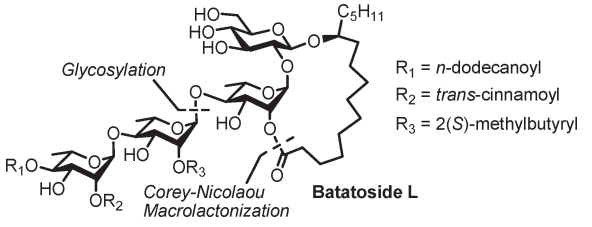

The total synthesis of batatoside L (**1**), a resin glycoside possessing cytotoxicity against laryngeal carcinoma cells, has been completed in a highly convergent manner. The most crucial step in this total synthesis was the efficient construction of the 18-membered macrolactone framework through the Corey−Nicolaou macrolactonization approach.

Resin glycosides, mainly isolated from the morning glory family (Convolvulaceae) of plants, are a class of amphiphilic glycolipids with a characteristic macrolactone skeleton.[1] The hydrophobic aglycons commonly found in these constituents are optically active 11-hydroxyaliphatic acids, namely, jalapinolic acid (11(*S*)-hydroxyhexadecanoic acid) and convolvulinolic acid (11(*S*)-hydroxytetradecanoic acid).[2] While the hydrophilic carbohydrate sections consist typically of four or five monosaccharide units mainly including D-glucose, D-fucose, L-rhamnose, and D-quinovose, and these sugar residues are usually modified with some fatty acyl substituents. The carboxyl group of aglycon esterifies intramolecularly with one hydroxyl group of the complex oligosaccharide chain to form the macrocycle. Besides, resin glycosides are reported to have a wide range of promising bioactivities such as cytotoxic activity against human cancer cell lines,[3] antibacterial,[3a,4] purgative,[3b,5] and ionophoretic activity,[6] as well as plant growth controlling effects.[3a,b,7] It has been shown that all the bioactivities of these lipo-oligosaccharides are associated with their macrocyclic structures. Cleavage of the lactone bond by saponification destroys the activity.[1a]

Batatoside-type resin glycosides were isolated by Kong and co-workers from the tuber of *Ipomoea batatas* (L.) Lam. (Convolvulaceae),[8] a plant with the common name of sweet potato. In Chinese traditional medicine, the tubers of *I. batatas* have been used as a medicinal herb for promoting hemostasis and eliminating abnormal secretions. Bioassays proved that batatosides L (**1**, Scheme 1) and O exhibited significant cytotoxic activity against laryngeal carcinoma (Hep-2) cells with ED_{50} values at 3.5 and 2.0 $\mu g \cdot mL^{-1}$, respectively.[8b]

Because of their appealing structural and bioactive features, several total syntheses of resin glycosides have been accomplished.[9] Producing the unique macrolactone framework in these natural products has been considered a major synthetic challenge, in which two cyclization strategies have been applied so far. One is a macrolactonization approach[10] used by Schmidt and co-workers for their pioneering synthesis of calonyctin A1.[10a] Later, the effectiveness of this method was further demonstrated by the Heathcock,[10c−e] Yu,[10f,g] and Sakairi[10b] laboratories, respectively, in the synthesis of several other resin glycosides. The other strategy is an olefin ring closing metathesis (RCM) method,[11] by which the Fürstner group formed the macrolidic systems[11a] and succeeded in synthesizing tricolorins,[11b] woodrosin I,[11c−e] and ipomoeassins.[11f,g] Recently, the same strategy was employed

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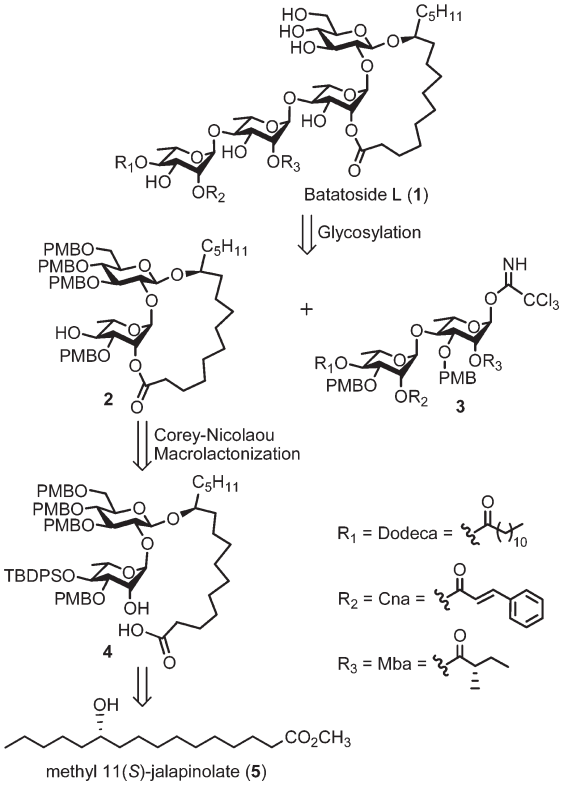
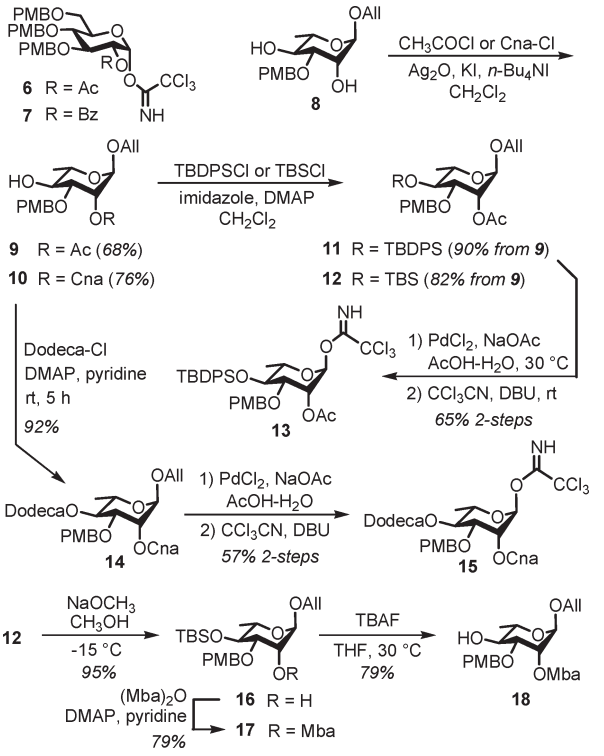
SCHEME 1. Retrosynthetic Analysis



SCHEME 2. Preparation of Monosaccharide Building Blocks



by a team from the Eisai Research Institute, which completed a synthesis of ipomoeassin F.[11h] During our continuing efforts in the synthesis of resin glycosides,[12] we developed a new and efficient synthetic route to chiral methyl 11(*S*)-jalapinolate (**5**) using commercially available (*R*)-glycidol as starting material,[12a,13] and then by taking advantage of the Corey−Nicolaou macrolactonization reaction[14] as a key step, we realized the construction of the 20- and 21-membered cyclic lactones that represent the core structures of merremoside-type resin glycosides.[12a] In this paper, we report the total synthesis of the tetrasaccharidic glycolipid batatoside L (**1**).

As is shown in our retrosynthetic analysis (Scheme 1), batatoside L can be obtained in a highly convergent manner by glycosidic coupling reaction between heterodisaccharide macrolactone **2** and exocyclic dirhamnose trichloroacetimidate **3**. To get the synthetically challenging subunit **2**, we planned to adopt the Corey−Nicolaou macrolactonization method to form the macrocyclic ring from glycosidic acid precursor **4**. For the synthesis of the intermediates **3** and **4**, several suitably functionalized monosaccharide modules were needed including four glycosyl trichloroacetimidate donors **6**, **7**, **13**, and **15**, and one L-rhamnosyl acceptor **18** (Scheme 2). The acyl groups serving as the necessary neighboring participating groups were incorporated at the 2-OH position of each donor to ensure the desired 1,2-trans stereoselectivity of each glycosylation. Additionally, the *p*-methoxybenzyl (PMB) group was chosen as the sole permanent hydroxyl-protecting group, thus reducing the need for functional group transformations and facilitating the final deprotection manipulation.

The glucose derivatives **6** and **7** were prepared according to the literature procedures.[15] The preparation of building blocks **13**, **15**, and **18** was carried out as outlined in Scheme 2. Reaction of the known allyl 3-*O*-PMB-α-L-rhamnopyranoside (**8**)[16] with acetyl chloride (CH_3COCl) and *trans*-cinnamoyl chloride (Cna-Cl) via a Ag_2O-mediated regioselective monoacylation methodology[17] developed by our group provided exclusively C-2 acetate **9** and cinnamate **10**, respectively, in 68% and 76% yield. Protection of the remaining 4-OH in **9** with *tert*-butyldiphenylsilyl (TBDPS) and *tert*-butyldimethylsilyl (TBS) groups secured silyl ethers **11** and **12** in 90% and 82% yield, respectively. The anomeric center of **11** was then unmasked by a $PdCl_2$-catalyzed deallylation[18] of the allyl ether. Activation of the obtained crude hemiacetal for glycoside formation was performed by treatment with trichloroacetonitrile (CCl_3CN) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU),[19] giving rise to the α-L-rhamnopyranosyl trichloroacetimidate **13** in 65% yield over the two steps from **11**. Conversion of **10** to the required **15** involved (i) 4-*O*-*n*-dodecanoylation of **10** with *n*-dodecanoyl chloride (Dodeca-Cl), forming **14** (92%), and (ii) installation of the

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(13) 11(*S*)-Hydroxyhexadecanoic acid (jalapinolic acid) is available by hydrolysis of the crude convolvulaceous resins (ref 1a) and also by total synthesis, see: refs 10b−g and: Kitagawa, I.; Baek, N. I.; Kawashima, K.; Yokokawa, Y.; Yoshikawa, M.; Ohashi, K.; Shibuya, H. *Chem. Pharm. Bull.* **1996**, *44*, 1680–1692.

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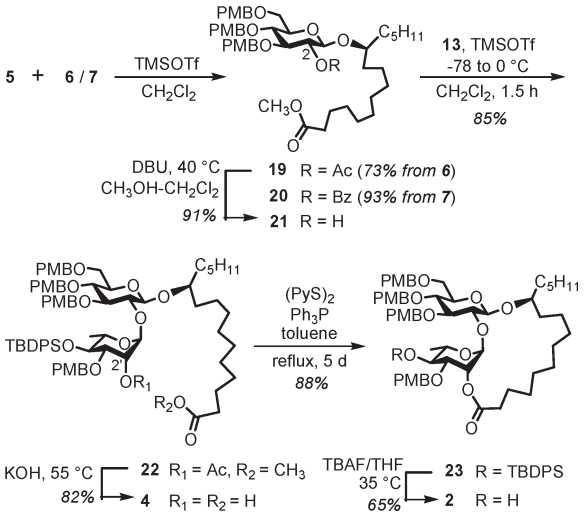
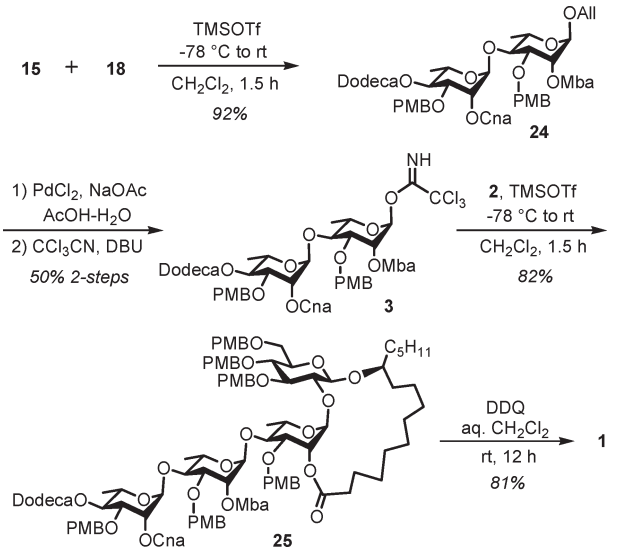
SCHEME 3. Formation of Macrolactone Framework



SCHEME 4. Completion of Total Synthesis of Batatoside L (1)



leaving group following the same two-step sequence as described above at the anomeric carbon of **14**, giving the corresponding imidate **15** (57% for two steps). In addition, the preparation of the rhamnose unit **18** began with methanolysis of sugar **12** with sodium methoxide/methanol at low temperature (−15 °C) to provide alcohol **16** in a yield of 95%. Esterification of **16** with 2(*S*)-methylbutyric anhydride ($(Mba)_2O$) in pyridine gave **17** (79%), which was easily desilylated with tetrabutylammonium fluoride (TBAF) to afford **18** in 79% yield.

For the total synthesis of batatoside L (**1**), our first task was the preparation of the macrolactone **2** (Scheme 3). Under the standard Schmidt glycosylation conditions,[19,20] the chiral hydroxyl ester **5**[12a] was glycosylated with D-glucosyl donors **6** and **7** in methylene chloride (CH_2Cl_2) activated by a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) to deliver β-D-glucopyranosides **19** and **20**, respectively, in 73% and 93% yield. In the glycosylation of **5** with the C-2 acetate donor **6**, the possible orthoester byproduct formed by participation of the acetyl moiety was not detected. At this junction, we encountered difficulties in selectively cleaving the C-2 ester functionalities from **19** and **20** under various hydrolysis conditions. Initial attempts employing $NaOCH_3/CH_3OH$ for **19** and **20** and CH_3COCl/CH_3OH[21] for **19** were found to be ineffective and no reactions were realized. This is probably because of the steric hindrance around the secondary 2-OH position that resulted from the bulkiness of the anomeric substituent and the PMB group at C-3. Gratifyingly, dissolution of the conjugate **19** in a solvent mixture of CH_3OH/CH_2Cl_2 (7:1), addition of 7.0 equiv of DBU,[22] and heating to 40 °C effected 2-*O*-deacetylation, and thus the hydrolyzed product **21** bearing the point for the next glycosylation step was obtained as a sole product (91% yield). Subsequent coupling of **21** and donor **13** (2.0 equiv) took place smoothly in the presence of TMSOTf as the promoter at −78→0 °C, providing the lipo-disaccharide **22** in a good yield and with complete α-stereoselectivity.

Then, compound **22** was saponified with potassium hydroxide (KOH) in a CH_3OH/tetrahydrofuran/water (9:9:1) cosolvent at 55 °C to release the 2′-OH and the aglycon carboxyl groups, affording the acid **4** in 82% yield.

The efficient construction of the 18-membered macrocycle core must be the most critical step for this total synthesis. With the key precursor **4** in hand, we then centered on the ring-closing reaction using the Corey−Nicolaou method.[14] After screening several conditions, we found that the desired cyclized product **23** was obtained efficiently (88% yield) under the typical Corey−Nicolaou's lactonization protocol using 2,2′-pyridyl disulfide ($(PyS)_2$) and triphenylphosphine (Ph_3P) in highly dilute toluene (7.5×10^{-4} M) upon heating to reflux for 5 days. The resulting **23** was then exposed to fluoride ion at 35 °C to remove the silyl moiety, which yielded the lactone alcohol **2** in 65% yield without damaging the macrolactone ring (Scheme 3).

The next task was to prepare the exocyclic dirhamnopyranose fragment. The imidate donor **15** was readily reacted with the L-rhamnose building block **18** by means of a similar TMSOTf-catalyzed glycosylation procedure to furnish disaccharide glycoside **24** (92% yield) with α-anomeric configuration at the new glycosidic linkage (Scheme 4). After subjecting **24** again to the same series of transformations as that used for **11**→**13**, we obtained the corresponding imidate **3** (50% yield over the two steps).

Finally, we investigated the methods for connecting the macrocycle acceptor **2** and the fully elaborated disaccharide donor **3** (Scheme 4). Although this coupling reaction using the similar glycosylation conditions outlined above afforded our desired product **25**, the lability of the donor **3** in the presence of the Lewis acid (TMSOTf) resulted in low yield (only 40%). Alternatively, we turned to the "inverse glycosylation" procedure developed by Schmidt et al.,[23] with the goal of minimizing the exposure of the glycosyl donor to the Lewis acidic solutions. In such an experiment, premixing the acceptor **2** with catalytic amounts of TMSOTf (0.38 equiv) and 4 Å molecular sieves in anhydrous CH_2Cl_2, followed by slow addition of a CH_2Cl_2 solution of excess donor **3**

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(3.0 equiv) at −78 °C, did bring about a considerably improved 82% yield of **25**. Then, under the influence of 8.0 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in aqueous CH_2Cl_2 at ambient temperature, exhaustive oxidation cleavage of PMB-ether functions in **25** produced the target molecule **1** in 81% yield. Synthetic batatoside L (**1**) was found to be identical with the natural isolate[8b] on the basis of ^1H and ^{13}C NMR spectra and specific rotation comparisons (see the Supporting Information).

In summary, we have reported the total synthesis of architecturally novel resin glycoside batatoside L (**1**). The use of the trichloroacetimidate glycosylation method provided an entry to the oligosaccharide motif, and application of the Corey−Nicolaou macrolactonization method allowed an efficient formation of the key 18-membered lactone ring. The attachment of the disaccharide donor **3** to the macrocycle acceptor **2** was conducted through an "inverse glycosylation" technique in order to prevent the hydrolysis of the donor,[24] thus generating the fully protected product **25** in good yield. The final removal of all PMB protecting groups in **25** finished the total synthesis of **1**.

Experimental Section

Synthesis of Compound 23. A solution of **4** (110 mg, 0.09 mmol), $(PyS)_2$ (99.8 mg, 0.47 mmol), and Ph_3P (119 mg, 0.47 mmol) in deoxygenated anhydrous toluene (2.37 mL) was stirred at 25 °C for 5 h. The mixture was diluted with deoxygenated anhydrous toluene (7.87 mL) and then the resulting solution was added dropwise by a syringe pump to refluxing dry deoxygenated toluene (109 mL) over 10 h. The solution was refluxed under nitrogen for 5 days. After removal of toluene under reduced pressure, the residue was purified by column chromatography (10:1, petroleum ether−EtOAc) to afford **23** as a white amorphous solid (95.5 mg, 88%). R_f 0.34 (5:1, petroleum ether−EtOAc). $[\alpha]^{20}_D$ −5.34 (*c* 6.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.34−7.57 (m, 26H), 5.30 (s, 1H), 5.07 (s, 1H), 4.90 (d, 1H, J = 11.6 Hz), 4.87 (d, 1H, J = 11.6 Hz), 4.69 (d, 1H, J = 10.4 Hz), 4.54 (d, 1H, J = 12.0 Hz), 4.51 (d, 1H, J = 10.8 Hz), 4.49 (d, 1H, J = 11.2 Hz), 4.46 (d, 1H, J = 5.6 Hz), 4.46 (d, 1H, J = 10.8 Hz), 4.01 (m, 1H), 3.88 (d, 1H, J = 10.0 Hz), 3.80 (s, 6H), 3.75 (s, 3H), 3.66 (s, 3H), 3.47−3.80 (m, 9H), 2.07−2.09 (m, 2H), 1.23−1.50 (m, 27H), 0.90 (s, 9H), 0.87 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 14.1, 19.1, 19.7, 22.7, 24.3, 24.5, 24.8, 27.1, 27.3, 27.4, 27.8, 29.4, 31.9, 32.2, 32.8, 34.0, 55.07, 55.16, 67.1, 68.5, 69.1, 69.9, 73.1, 74.2, 74.5, 74.6, 74.8, 76.7, 82.4, 84.0, 97.9, 103.4, 112.8, 113.7, 113.8, 125.0, 127.0, 127.1, 128.3, 129.0, 129.2, 129.3, 129.6, 129.7, 130.0, 130.2, 130.3, 130.8, 133.1, 134.5, 135.7, 136.3, 158.4, 158.6, 158.9, 159.2, 172.4; IR (KBr) ν_{max} 3439, 2925, 1728, 1615, 1515, 1254 cm^{-1}; HR ESIMS calcd for $C_{76}H_{100}O_{15}Si$ $[M + Na]^+$ 1303.6729, found m/z 1303.6743.

Synthesis of Compound 25. The donor **3** (51 mg, 0.047 mmol) and the acceptor **2** (12.9 mg, 0.016 mmol) were dried separately under high vacuum for 3 h. Then, compound **2** was dissolved in CH_2Cl_2 (184 μL) followed by addition of freshly activated 4 Å molecular sieves (70 mg). The resulting slurry was stirred at room temperature for 15 min, after which it was cooled to −78 °C and a solution of TMSOTf (1.14 μL, 0.006 mmol) in CH_2Cl_2 (356 μL) was added. After 5 min, a solution of **3** in CH_2Cl_2 (131 μL) was added dropwise at −78 °C. After being stirred for 1 h at the same temperature, the reaction was gradually warmed to ambient temperature, and then was quenched with triethylamine and filtered. The filtrate was concentrated in vacuo to give a residue, which was purified by column chromatography (7:1, petroleum ether−EtOAc) to afford **25** as a colorless syrup (20 mg, 82%). R_f 0.48 (3:1, petroleum ether−EtOAc). $[\alpha]^{20}_D$ +2.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 1H, J = 16.0 Hz), 7.54 (m, 2H), 7.40 (t, 3H, J = 3.2 Hz), 6.70−7.37 (m, 24H), 6.52 (d, 1H, J = 16.0 Hz), 5.60 (s, 1H), 5.49 (s, 1H), 5.42 (s, 1H), 5.39 (s, 1H), 5,19 (s, 1H), 5.11 (s, 1H), 5.06 (t, 1H, J = 9.6 Hz), 4.84 (d, 1H, J = 10.8 Hz), 4.81 (d, 1H, J = 9.2 Hz), 4.72 (d, 1H, J = 10.4 Hz), 4.68 (d, 1H, J = 11.6 Hz), 4.65 (d, 1H, J = 7.2 Hz), 4.63 (d, 1H, J = 10.0 Hz), 4.61 (d, 1H, J = 10.0 Hz), 4.52 (d, 1H, J = 9.6 Hz), 4.72 (d, 1H, J = 10.8 Hz), 4.37 (d, 1H, J = 11.2 Hz), 4.34 (d, 1H, J = 9.6 Hz), 4.32 (d, 1H, J = 8.8 Hz), 4.14 (d, 1H, J = 10.0 Hz), 3.49−3.89 (m, 33H), 2.42−2.48 (m, 1H), 2.28−2.33 (m, 2H), 2.23−2.28 (m, 2H), 1.68−1.71 (m, 1H), 1.20−1.50 (m, 1H), 1.18−1.40 (m, 51H), 1.04 (d, 3H, J = 6.8 Hz), 0.80−0.88 (m, 6H), 0.78 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 Hz, $CDCl_3$) δ 11.4, 14.1, 16.3, 17.4, 18.4, 18.9, 19.7, 22.2, 22.7, 24.7, 24.9, 25.0, 26.6, 27.1, 27.4, 27.8, 29.2, 29.3, 29.35, 29.4, 29.5, 29.6, 29.7, 29.9, 31.87, 31.9, 32.1, 33.5, 33.9, 34.3, 40.8, 54.8, 55.1, 55.2, 67.2, 67.3, 67.6, 67.7, 68.4, 69.1, 70.1, 70.8, 72.1, 73.1, 74.5, 75.7, 75.8, 76.4, 77.2, 77.3, 77.8, 78.1, 82.2, 82.6, 83.8, 98.1, 99.0, 99.1, 103.1, 113.5, 113.69, 113.7, 113.9, 117.8, 128.2, 128.5, 128.8, 129.2, 129.4, 129.5, 129.6, 129.7, 130.1, 130.2, 130.25, 130.3, 130.5, 134.3, 145.5, 158.9, 159.0, 159.1, 159.2, 165.8, 172.75, 172.8, 175.3; IR (KBr) ν_{max} 3453, 2923, 1738, 1614, 1513, 1461 cm^{-1}; HR ESIMS calcd for $C_{114}H_{154}O_{28}$ $[M + Na]^+$ 1994.0524, found m/z 1994.0533.

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Supporting Information Available: Experimental procedures, compound characterization data, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) An inverse Schmidt glycosylation has also played a key role in Fürstner's total synthesis of woodrosin I, see refs 11d and 11e.