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Note

Synthesis and glycosylation of pyrimidin-2-yl 1-thio-α-D-manno- and -α-L-rhamnopyranoside

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Abstract

Pyrimidin-2-yl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyrano side (**9**), pyrimidin-2-yl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (**10**), pyrimidin-2-yl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**7**), and pyrimidin-2-yl 2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**8**) were prepared almost quantitatively from the corresponding protected 1,2-*O*-methoxyethylidene-β-D-manno-or-β-L-rhamnopyranose with 2-mercaptopyrimidine in the presence of mercuric bromide. Coupling reactions of the thioglycosides promoted by silver triflate with suitable glycosyl acceptors afforded 1,2-*trans* linked disaccharides. © 1998 Published by Elsevier Science Ltd. All rights reserved

Keywords: Pyrimidin-2-yl; 1-Thio-α-D-mannopyranoside; 1-Thio-α-L-rhamnopyranoside

Thioglycosides have attracted much attention recently as versatile glycosyl donors, particularly for synthesis of complex carbohydrates, since they are stable under a variety of reaction conditions but can be activated with appropriate thiophilic reagents [1]. However, an addition to the requirement of more than equimolar amounts of catalysts which are generally sensitive to moisture and are expensive, relatively low glycosyl-donor properties were observed with these systems [2]. These problems were partly overcome with the use of heterocyclic thioglycosides [3]. Hanessian [3a] studied the activity of basic heterocyclic thioglycosides and reported that, with suitable catalysts, unprotected pyrimidin-2-yl 1-thio-β-D-glucopyranoside could effectively glycosylate simple alcohols. Our lab [4] also reported that glycosylation using pyrimidin-2-yl 1-thio-β-D-gluco-, -β-D-galacto-, -β-D-xylo-, and -α-D-arabinopyranoside benzyl ethers as glycosyl donors gave 1,2-*cis* linked disaccharides predominantly. Here, we report the synthesis and glycosylation of pyrimidin-2-yl 1-thio-α-D-manno- and -α-L-rhamnopyranoside.

Pyrimidin-2-yl 1-thio-α-D-manno- and -α-L-rhamnopyranoside were not available by the PTC method [4] or Helferich procedure [5]. However, we found that (**5, 6, 7** and **8**) were prepared almost quantitatively by refluxing protected 1,2-*O*-methoxyethylidene-β-D-manno- (**1,3**) [6] and -β-L-rhamnopyranose (**2,4**) [7] with 2-mercaptopyrimidine in dry acetonitrile in the presence of mercuric bromide.

The pyrimidin-2-yl 1-thio group was sufficiently stable to allow chemical modification at the other

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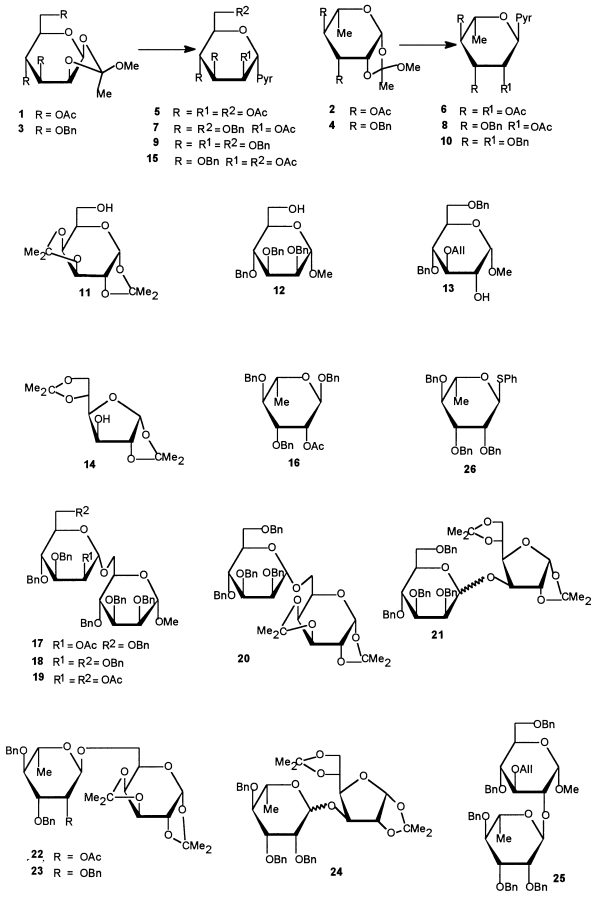

hydroxyl groups of the thioglycosides. For example, selective 6-*O*-debenzylation was successfully carried out by treating **7** with trimethylsilyl triflate [8] in acetic anhydride at −50 °C, affording pyrimidin-2-yl 2,6-di-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (**15**) in 76% yield. In the ^{1}H NMR spectrum of **15**, the H-6, 6′ signals shifted from 3.70–3.90 to 4.25–4.39 ppm, indicating 6-*O*-acetylation.

The activity of the described thioglycosides was examined by coupling with sugar acceptors of diverse structure. Condensation of thioglycosides **8, 9**, and **10** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**11**) [9] using 2 equivalents of silver triflate as the promoter in dichloromethane at room temperature for 30 min gave the sole α-linked disaccharide derivatives **22** (95%), **20** (95%) and **23** (93%), respectively, in spite of the presence or absence of neighboring group participation at C-2. Reducing of the amount of silver triflate to 1 equivalent lowered the disaccharide yield (65%) for coupling of **8** with **11**, and a byproduct, benzyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**16**), formed. Using 0.4 equivalents of silver triflate, the coupling reaction did not occur, and the main product was compound **16**.

Condensation of **7, 9**, and **15** with methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**12**) was also carried out, giving **17** (92%), **18** (97%), and **19** (83%), respectively, indicating that the acetyl group in the thiomannopyranoside lowered its reactivity.

Coupling of the thioglycoside **10** with methyl 3-*O*-allyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (**13**) [10] afforded the sole α-linked disaccharide derivative (**25**) in high yield (87%). However, under the same conditions, condensation of **9** or **10** with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**14**) [9] gave a non-separable α, β anomeric mixture (4:1 for **21**, 1:1 for **24**, estimated from ^{1}H NMR spectra) in relatively low yields (64–57%).

For comparison of the reactivity, phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**26**) [11] was reacted with **11** in dichloromethane in the presence of 2 equivalents of silver triflate at room temperature, but no coupling product was observed, indicating that as a leaving group the pyrimidin- 2-yl-1-thio group is much more active than the phenylthio group. Compound **26** was readily obtained via the Helferich procedure [5] from treatment of 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose with phenylthiol followed by deacetylation and benzylation, but the same procedure failed to yield the corresponding pyrimidin-2-yl 1-thio-manno- or -rhamnopyranoside. This result is also a clear indication of the difference between the phenylthio group and pyrimidin-2-yl-1-thio group.

In summary, protected pyrimidin-2-yl 1-thio-α-D-manno- and -α-L-rhamnopyranoside were readily synthesized, and their stability and relatively high reactivity should prove beneficial in the synthesis of complex oligosaccharides.

1. Experimental

General methods.—See reference [6a]. Compounds **17, 19, 20, 22**, and **23** have been reported previously, and their ^{1}H NMR data were in agreement with those previously published.

Pyrimidin-2-yl 2,3,4,6-tetra-O-*acetyl-1-thio*-α-D-*mannopyranoside* (**5**) *and pyrimidin-2-yl 2,3,4-tri*-O-*acetyl-1-thio*-α-L-*rhamnopyranoside* **(6)**.—To a stirred solution of **1** or **2** (4 mmol) and 2-mercaptopyrimidine (5.6 mmol) in dry acetonitrile (30 mL) was added mercuric bromide (0.4 mmol). The mix-

ture was stirred and refluxed for 30 min. TLC (1:2 ethyl acetate–petroleum ether) indicated that the reaction was complete. The mixture was filtered, washed with acetonitrile and concentrated. The residue was chromatographed on silica gel with 1:2 ethyl acetate–petroleum ether (v/v) to give the syrupy products **5** (95%) and **6** (95.6%). For compound **5** $[\alpha]_D$ +42.7° (*c* 4.5, $CHCl_3$); ^1H NMR: δ 8.58, 7.10 (s, t, 3 H, Pyrim-H), 6.54 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.55 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4}$ 9.0 Hz, $J_{4,5}$ 9.1 Hz, H-4), 5.26 (dd, 1 H, H-3), 4.36–4.04 (m, 3 H, H-5, 6, 6′), 2.24–2.00 (4 s, 12 H, 4 COCH_3); Anal. Calcd for $C_{18}H_{22}N2O_9S$: C, 48.87; H, 4.98. Found: C, 49.02; H, 5.10. For compound **6** $[\alpha]_D$ −79.7° (*c* 12.5, $CHCl_3$); ^1H NMR: δ 8.58, 7.10 (s, t, 3 H, Pyrim-H), 6.46 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.55 (dd, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 5.37 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.20 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.20–4.05 (m, 1 H, H-5), 2.20–2.00 (3 s, 9 H, 3 COCH_3), 1.24 (d, 3 H, *J* 4.4H_2, CH_3); Anal. Calcd for $C_{16}H_{20}N_2O_7S$: C, 50.00; H, 5.21, Found: C 50.04; H, 5.32.

Pyrimidin 2-yl 2,3,4,6-tetra-O-*benzyl-1-thio*-α-D-*mannopyranoside* (**9**) *and pyrimidin 2-yl 2,3,4-tri*-O-*benzyl-1-thio*-α-L-*rhamnopyranoside* (**10**).—To a solution of **5** or **6** (10 mmol) in anhydrous methanol (15 mL) was added sodium methoxide (11 mg, 0.2 mmol), and the solution was stirred at room temperature for 3 h. Concentration of the solution gave a solid residue which was dissolved in *N,N*-dimethylformamide (15 mL) and subjected to benzylation with sodium hydride (80% in oil, 66 mmol) and benzyl bromide (8.0 mL, 64 mmol). The mixture was stirred at room temperature for 5 h, at the end of which time TLC (1:2 ethyl acetate–petroleum ether) indicated that the reaction was complete. The mixture was poured into water, the solution was extracted repeatedly with dichloromethane, and the combined extracts were concentrated to a syrup. Purification by column chromatography with 1:3 ethyl acetate–petroleum ether as the eluent afforded syrupy **9** (95.3%) and **10** (96%). For compound **9** $[\alpha]_D$ +54.8° (*c* 2.5, $CHCl_3$); ^1H NMR: δ 8.54, 7.00 (s, t, 3 H, Pyrim-H), 7.46–7.18 (m, 20 H, Ph), 6.70 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.91, 4.54 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.65–4.47 (m, 7 H, H-2, 3 CH_2Ph), 4.41 (dd, 1 H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.2 Hz, H-4), 4.02–3.96 (m, 1 H, H-5), 3.90–3.79 (m, 2 H, H-3, 6′), 3.71 (dd, 1 H, $J_{5,6}$ 1.7 Hz, $J_{6,6'}$ 12 Hz, H-6); Anal. Calcd for $C_{38}H_{38}N_2O_5S$: C, 71.92; H, 5.99. Found: C, 72.07; H, 6.03. For compound **10** $[\alpha]_D$ −47.3° (*c* 2.5, $CHCl_3$); ^1H NMR: δ 8.58, 7.00 (s, t, 3 H, Pyrim-H), 7.45–7.20 (m, 15 H, Ph), 6.59 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.98, 4.65 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.87, 4.71 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 4.56 (s, 2 H, CH_2Ph), 4.00 (dd, $J_{2,3}$ 2.9 Hz, H-2), 3.95–3.85 (m, 1 H, H-5), 3.82 (dd, $J_{3,4}$ 9.0 Hz, H-3), 3.70 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 1.35 (d, 3 H, *J* 4.4 Hz, CH_3); Anal. Calcd for $C_{31}H_{32}N_2O_4S$: C, 70.45. H, 6.06. Found: C, 69.98; H, 6.04.

Pyrimidin 2-yl 2-O-*acetyl-3,4,6-tri*-O-*benzyl-1-thio*-α-D-*mannopyranoside* (**7**) *and pyrimidin 2-yl 2*-O-*acetyl-3,4-di*-O-*benzyl-1-thio*-α-L-*rhamnopyranoside* (**8**).—The syrupy products **7** (97%) and **8** (97%) were obtained using the same procedure as described in the preparation of **5** and **6**. For compound **7** $[\alpha]_D$ +46.7° (*c* 4.5, $CHCl_3$); ^1H NMR: δ 8.58, 7.02 (s, t, 3 H, Pyrim-H), 7.44–7.10 (m, 15 H, Ph), 6.62 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.65 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 4.89, 4.59 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.76, 4.52 (2 d, 2 H, *J* 11 Hz, CH_2Ph). 4.68–4.46 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.10–4.02 (m, 2 H, H-5, 6), 3.92 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 3.84 (dd, 1 H, $J_{4,5}$ 7.3 Hz, H-4), 3.70 (dd, 1 H, $J_{5,6}$ 0.7 Hz, $J_{6,6'}$ 11 Hz, H-6′), 2.22 (s, 3 H, COCH_3); Anal. Calcd for $C_{33}H_{34}N_2O_6S$: C, 67.58; H, 5.80. Found: C, 67.47. H, 5.72. For compound **8** $[\alpha]_D$ 58.4° (*c* 2.5, $CHCl_3$); ^1H NMR: δ 8.58, 7.00 (s, t, 3 H, Pyrim-H), 7.46–7.20 (m, 10 H, Ph), 6.44 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.64 (dd, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.94, 4.62 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.69 (s, 2 H, CH_2Ph), 4.00 (m, 1 H, H-5), 3.85 (dd, $J_{3,4}$ 9.3 Hz, H-3), 3.70 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 2.22 (s, 3 H, COCH_3), 1.36 (d, 3 H, *J* 4.4 Hz, CH_3); Anal. Calcd for $C_{26}H_{28}N_2O_5S$: C, 65.00; H, 5.83. Found: C, 64.88; H, 5.97.

Pyrimidin-2-yl 2,6-di-O-*acetyl-3,4-di*-O-*benzyl-1-thio*-α-D-*mannopyranoside* (**15**).—To a solution of **7** (100 mg, 0.17 mmol) in acetic anhydride (2 mL) was added 1:1 (v/v) trimethyisilytrifluoromethane sulfonate–dichloromethane (0.2 mL) at −50 °C, and the solution was stirred for 1 h at the same temperature. The mixture was poured into 1:1 (v/v) dichloromethane–saturated $NaHCO_3$ solution (50 mL) and stirred for 0.5 h, and the organic layer was washed with water, dried, and concentrated under reduced pressure. The residue was applied to a column of silica gel and **15** (62 mg, 76%) was obtained as a syrup. $[\alpha]_D$ +67.6° (*c* 5.0, $CHCl_3$); ^1H NMR: δ 8.55, 7.05 (s, t, 3 H, Pyrim-H), 7.40–7.20 (m, 10 H, Ph), 6.55 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.63 (dd, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.94, 4.58 (2 d, 2 H, *J* 11 Hz, CH_2Ph), 4.75, 4.52 (2 d, 2 H, *J* 11 Hz,

CH_2Ph), 4.39 (dd, 1 H, $J_{5,6}$ 4.4 Hz, $J_{6,6'}$ 12 Hz, H-6), 4.25 (dd, 1 H, $J_{5,6'}$ 12 Hz, H-6′), 4.10–4.02 (m, 2 H, H-5), 3.95 (dd, 1 H, $J_{3,4}$ 7.3 Hz, H-3), 3.88 (dd, 1 H, $J_{4,5}$ 7.1 Hz, H-4), 2.22, 2.00 (2 s, 6 H, 2 COCH_3); Anal. Calcd for $C_{28}H_{30}N_2O_7S$: C, 62.45; H, 5.58. Found: C, 62.79; H, 5.70.

*Coupling reaction using pyrimidin-2-yl 1-thio-α-*D*-manno- and -*L*-rhamnopyranosides as donors.*—To a solution of a donor (**7, 8, 9**, or **10**) (0.5 mmol) and an acceptor (**11, 12, 13**, or **14**) (0.45 mmol) in dry dichloromethane (5 mL) was added 4 Å molecular sieves (500 mg), and the mixture was stirred at room temperature. To the mixture was added silver triflate (0.9 mmol) and the mixture was stirred for 30 min to 2 h. The reaction was monitored by TLC (1:2 ethyl acetate–petroleum ether). After completion of the reaction, the reaction mixture was filtered, and the filtrate was concentrated under diminished pressure. The residue was chromatographed on silica gel to give disaccharide.

*Benzyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-*L*-rhamnopyranoside* (**16**).—Compound **16** was obtained as a syrupy byproduct in the coupling of **8** with **11** when the quantity of promoter was decreased to 1 equivalent or less. $[\alpha]_D$ −25.0° (*c* 2.0, $CHCl_3$); ^{1}H NMR: δ 7.41–7.22 (m, 15 H, Ph), 5.43 (dd, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 3.4 Hz, H-2), 4.92, 4.61 (2 d, 2 H, *J* 10.8 Hz, CH_2Ph), 4.82 (d, 1 H, H-1), 4.70, 4.52 (2 d, 2 H, *J* 11.2 Hz, CH_2Ph), 4.68, 4.47 (2 d, 2 H, *J* 11.6 Hz, CH_2Ph), 3.98 (dd, $J_{3,4}$ 9.5 Hz, H-3), 3.80 (m, 1 H, H-5), 3.45 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 2.16 (s, 3 H, COCH_3), 1.32 (d, 3 H, *J* 4.4 Hz, CH_3); Anal. Calcd for $C_{29}H_{32}O_6$: C, 73.11; H, 6.72. Found: C, 73.33; H, 6.80.

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**18**).—Compound **18** was obtained as a syrup from the condensation of **9** with **12** in a yield of 97%. $[\alpha]_D$ +28.7° (*c* 4.7, $CHCl_3$); ^{1}H NMR: δ 7.40–7.10 (m, 30 H, Ph), 5.15 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.70 (d, 1 H, $J_{1',2'}$ 2.2 Hz, H-1′), 4.95–4.42 (m, 14 H, 7 CH_2Ph), 4.10–3.60 (m, 12 H, H-2, 2′, 3, 3′, 4, 4′' 5, 5′, 6a, 6b, 6′a, 6′b), 3.24 (s, 3 H, OCH_3); Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.46. H, 6.69. Found: C, 76.07; H, 6.89.

O-*(2,3,4,6-Tetra-*O*-benzyl-*D*-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose* (**21**) *and* O-*(2,3,4-tri-*O*-benzyl-*L*-rhamnopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose* (**24**).—Compounds **21** (64%) and **24** (57%) were obtained as non-separable α, β mixtures from the condensation of **9** and **10** with **14** respectively. For **21** ^{1}H NMR: δ 7.40–7.20 (m, 20 H, Ph), 5.94 (d, 0.8 H, $J_{1,2}$ 3.7 Hz, H-1), 5.80 (d, 0.2 H, $J_{1,2}$ 3.7 Hz, H-1), 4.90–3.60 (m, 21 H, H-1′, 2, 2′, 3, 3′, 4, 4′, 5, 5′, 6a, 6′a, 6b, 6′b, 4 CH_2Ph), 1.50, 1.48, 1.44, 1.40, 1.38, 1.36, 1.33, 1.26 (8 s, 12 H, 4 CCH_3). For **24** ^{1}H NMR: δ 7.40–7.22 (m, 15 H, Ph), 5.95 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1), 5.75 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1), 4.94–3.60 (m, 20 H, H-1′, 2, 2′, 3, 3′, 4, 4′, 5, 5′, 6a, 6b, 3 CH_2Ph), 1.52, 1.48, 1.44, 1.36, 1.36, 1.32, 1.32, 1.30 (8 s, 12 H, 4 CCH_3), 1.26, 1.24 (2 d, 3 H, *J* 4.4 Hz, CH_3).

*Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-rhamnopyranosyl)-α-*D*-glucopyranoside* (**25**).—Disaccharide **25** was obtained as a syrup from the coupling of **10** with **13** in a yield of 87%. $[\alpha]_D$ +28.7° (*c* 3.0, $CHCl_3$); ^{1}H NMR: δ 7.42–7.10 (m, 15 H, Ph), 5.80 (m, 1 H, −CH = CH_2), 5.30–5.00 (m, 2 H, −CH = CH_2), 5.00–4.40 (m, 12 H, 5 CH_2Ph, CH_2−CH = CH_2), 4.80 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.72 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1′), 4.16 (dd, 1 H, $J_{2',3'}$ 2.0 Hz, 4, 4′, 7.8 Hz, H-3′), 3.90–3.50 (m, 9 H, H-2, 2′, 3, 4, 4′, 5, 5′, 6, 6′), 3.34 (s, 3 H, OCH_3), 1.30 (d, 3 H, *J* 4.4 Hz, CH_3); Anal. Calcd for $C_{51}H_{58}O_{10}$: C, 73.73; H, 6.99. Found: C, 73.43; H, 6.89.

Table 1
Optical rotation data for isolated compounds

Compound	Yield (%)	$[\alpha]_D$ (*c*, $CHCl_3$)	Lit: [Ref.]
17	92	+29.1° (5.5)	+29° [6a]
19	83	+32.6° (3.5)	+34° [12]
20	95	+36.0° (1.5)	+39° [3b]
21	64	−2.4° (2.5)	[13][a]
22	95	−35.7° (14.0)	[14][a]
23	93	−38.7° (3.5)	−47° [3b]
24	57	−0.10° (3.5)	[3b][a]

[a] Optical rotation data were not reported for this compound in the cited article.

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