5(5a)-enopyranosylamine] (14). A mixture of **13α** (39 mg, 0.11 mmol), *n*-hexylamine (143 μL, 1.1 mmol), and 2-propanol (0.4 mL) was stirred for a week at room temperature, and then evaporated to dryness. The residue was chromatographed on a silica gel column (4 g, 1:40 MeOH/$CHCl_3$) to give **14** (21 mg, 64%) as a white powder, TLC: R_f 0.46 (1:4 MeOH/$CHCl_3$); $[\alpha]_D^{20}$ −27 ° (*c* 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.88 (br s, 1H, H-5), 4.63 (d 1H, *J* = 6.8 Hz, H-3), 4.18 and 4.26 (ABq, each 1H, *J* = 11.7 Hz, CH_2OH), 4.13 (dd, 1H, *J* = 6.8 and 8.5 Hz, H-2), 3.44 (dd, 1H, *J* = 8.5 and 9.2 Hz, H-1), 3.04 (d, 1H, *J* = 9.2 Hz, H-6), 2.81 and 2.43 (2 dt, each 1H, *J* = 7.3 and 11.2 Hz, $NHCH_2$), 2.58 (br s, 2H, OH), 1.49 and 1.40 (2 s, each 3H, CMe_2), 1.54–1.26 [m, 8H, $NHCH_2(CH_2)_4$], 0.89 (t, 3H, *J* = 6.7 Hz, CH_2CH_3).

4.1.16. (1*S*,2*R*,3*S*,6*R*)-6-Hexylamino-4-(hydroxymethyl)-cyclohex-4-ene-1,2,3-triol [*N*-hexyl-5a-carba-β-L-*arabino*-hex-5(5a)-enopyranosylamine] (18). A mixture of **14** (7.9 mg, 26 μmol) and 80% aqueous acetic acid (2 mL) was stirred for 30 h at 80 °C. The product was purified by a column of Dowex 50 W×2 (H^+) resin (0.7 g) with methanolic 1% ammonia as eluent to give **18** (7.5 mg, ~100%) as a white powder, $[\alpha]_D^{20}$ −1.9° (*c* 0.34, MeOH); ^1H NMR (300 MHz, CD_3OD): δ 5.71 (br s, 1H, H-5), 4.15 (d, 1H, *J* = 4.2 Hz, H-3), 4.12 (br s, 2H, CH_2OH), 3.70 (dd, 1H, *J* = 8.1 and 10.3 Hz, H-1), 3.43 (dd, 1H, *J* = 4.2 and 10.3 Hz, H-2), 3.10 (dd, 1H, *J* = 2.0 and 8.1 Hz, H-6), 2.56 and 2.74 (2 dt, each 1H, *J* = 7.3 and 11.4 Hz, $NHCH_2$), 1.52 (m, 2H, $NHCH_2CH_2$), 1.32 [m, 6H, $CH_2(CH_2)_3CH_3$], 0.91 (t, 3H, *J* = 6.7 Hz, CH_2CH_3); ITMS-ESI (positive mode): *m*/*z* 260 $[M+H]^+$.

4.1.17. (1*S*,4*R*,5*R*,6*S*)-5-Hydroxy-2-(hydroxymethyl)-8,8-dimethyl-4-octylamino-7,9-dioxabicyclo[4.3.0]non-2-ene [*N*-octyl-3,4-*O*-isopropylidene-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (15). A mixture of **13α** (38 mg, 0.105 mmol), *n*-octylamine (174 μL, 1.1 mmol), and 2-propanol (0.4 mL) was stirred for a week at room temperature. The reaction mixture was processed as in the preparation of **14** to give, after chromatography on silica gel, **15** (24 mg, 68%) as a white powder, TLC: R_f 0.46 (1:4 MeOH/$CHCl_3$); $[\alpha]_D^{20}$ −20 ° (*c* 0.24, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.88 (br s, 1H, H-5), 4.64 (d, 1H, *J* = 6.8 Hz, H-3), 4.18 and 4.27 (ABq, each 1H, *J* = 13.7 Hz, CH_2OH), 4.14 (dd, 1H, *J* = 6.8 and 8.7 Hz, H-2), 3.43 (dd, 1H, *J* = 8.7 and 9.0 Hz, H-1), 3.04 (d, 1H, *J* = 9.0 Hz, H-6), 2.81 and 2.55 (dt, each 1H, *J* = 7.3 and 11.3 Hz, H-6), 2.36 (br s, 2H, OH), 1.40 and 1.50 (2 s, each 3H, CMe_2), 1.27–1.53 [m, 12H, $NHCH_2(CH_2)_6$], 0.88 (t, 3H, *J* = 6.5 Hz, CH_2CH_3).

4.1.18. (1*S*,2*R*,3*S*,6*R*)-4-(Hydroxymethyl)-6-octylamino-cyclohex-4-ene-1,2,3-triol [*N*-octyl-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (1). Compound **15** (4.7 mg, 14 μmol) was deprotected as in the preparation of **14** to give, after passage through a column of Dowex 50 W×2 with 1% methanolic ammonia, **1** (2.3 mg, 56%) as a white powder, TLC: R_f 0.38 (1:3:6 AcOH/MeOH/$CHCl_3$); $[\alpha]_D^{20}$ +6.3° (c 0.5, MeOH); ^1H NMR (300 MHz, CD_3OD): δ 5.71 (br s, 1H, H-5), 4.15 (d, 1H, *J* = 4.2 Hz, H-3), 4.12 (br s, 2H, CH_2OH), 3.70 (dd, 1H, *J* = 8.1 and 10.3 Hz, H-1), 3.43 (dd, 1H, *J* = 4.2 and 10.3 Hz, H-2), 3.12 (d, 1H, *J* = 8.1 Hz, H-6), 2.56 and 2.75 (2 m, each 1H, NCH_2), 1.52 (m, 2H, $NHCH_2CH_2$), 1.31 [m, 10H, $CH_2(CH_2)_5CH_3$], 0.89 (t, 3H, *J* = 6.7 Hz, CH_2CH_3); ITMS-ESI (positive mode): *m*/*z* 288 $[M+H]^+$.

4.1.19. (1*S*,4*R*,5*R*,6*S*)-4-Decylamino-5-hydroxy-2-(hydroxymethyl)-8,8-dimethyl-7,9-dioxabicyclo[4.3.0]non-2-ene [*N*-decyl-3,4-*O*-isopropylidene-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (16). A mixture of **13α** (36 mg, 99 μmol), *n*-decylamine (120 μL, 0.59 mmol) was stirred for 3 days at room temperature. The mixture was processed as in the preparation of **14** to give **16** (14 mg, 40%) as a white powder, TLC: R_f 0.44 (1:5 MeOH/$CHCl_3$); $[\alpha]_D^{20}$ −19° (*c* 0.43, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.88 (br s, 1H, H-5), 4.63 (d, 1H, *J* = 6.6 Hz, H-3), 4.17 and 4.27 (ABq, each 1H, *J* = 13.7 Hz, CH_2OH), 4.14 (dd, 1H, *J* = 6.6 and 8.5 Hz, H-2), 3.44 (dd, 1H, *J* = 8.5 and 9.0 Hz, H-1), 3.06 (d, 1H, *J* = 9.0 Hz, H-6), 2.81 and 2.55 (2 dt, each 1H, *J* = 7.2 and 11.2 Hz, $NHCH_2$), 2.66 (br s, 2H, OH), 1.40 and 1.49 (2 s, each 3H, CMe_2), 1.26–1.54 [m, 16H, $(CH_2)_8CH_3$], 0.88 (t, 3H, *J* = 6.6 Hz, CH_2CH_3).

4.1.20. (1*S*,2*R*,3*S*,6*R*)-6-Decylamino-4-(hydroxymethyl)-cyclohex-4-ene-1,2,3-triol [*N*-decyl-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (19). Compound **16** (10.4 mg, 29 μmol) was deprotected as in the preparation of **14** to give **19** (6.7 mg, 73%) as a white powder, TLC: R_f 0.48 (1:3:6 AcOH /MeOH/$CHCl_3$); $[\alpha]_D^{21}$ +12° (*c* 0.12, MeOH); ^1H NMR (300 MHz, CD_3OD): δ 5.62 (d, 1H, *J* = 2.0 Hz, H-5), 4.06 (d, 1H, *J* = 4.2 Hz, H-3), 4.03 (br s, 2H, CH_2OH), 3.60 (dd, 1H, *J* = 7.6 and 10.3 Hz, H-1), 3.34 (dd, 1H, *J* = 4.2 and 10.3 Hz, H-2), 3.01 (d, 1H, *J* = 8.1 Hz, H-6), 2.46 and 2.65 (2 dt, each 1H, *J* = 7.4 and 11.3 Hz, $NHCH_2$), 1.43 (m, 2H, $NHCH_2CH_2$), 1.20 [m, 14H, $CH_2(CH_2)_7CH_3$], 0.80 (t, 3H, *J* = 6.7 Hz, CH_2CH_3); ITMS-ESI (positive mode): *m*/*z* 316 $[M+H]^+$.

4.1.21. (1*S*,4*R*,5*R*,6*S*)-4-Dodeylamino-5-hydroxy-2-(hydroxymethyl)-8,8-dimethyl-7,9-dioxabicyclo[4.3.0]non-2-ene [*N*-dodeyl-3,4-*O*-isopropylidene-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (17). A mixture of **13α** (40 mg, 0.11 mmol), *n*-dodecylamine (203 mg, 1.1 mmol), and 2-propanol (0.4 mL) was stirred for a week at room temperature. The mixture was processed as in the preparation of **14** to give, after chromatography on silica gel to give **17** (14 mg, 40%) as a white powder, TLC: R_f 0.39 (1:5 MeOH/$CHCl_3$); $[\alpha]_D^{20}$ −11 ° (*c* 0.35, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.90 (br s, 1H, H-5), 4.63 (d, 1H, *J* = 6.8 Hz, H-3), 4.18 and 4.27 (ABq, each 1H, *J* = 13.7 Hz, CH_2OH), 4.14 (dd, 1H, *J* = 6.8 and 8.7 Hz, H-2), 3.45 (dd, 1H, *J* = 8.7 and 9.1 Hz, H-1), 3.07 (d, 1H, *J* = 9.1 Hz, H-6), 2.56 and 2.82 (2 dt, each 1H, *J* = 7.2 and 11.3 Hz, $NHCH_2$), 2.69 (br s, 2H, OH), 1.40 and 1.50 (2 s, each 3H, CMe_2), 1.26–1.56 [m, 20H, $(CH_2)_{10}CH_3$], 0.88 (t, 3H, *J* = 6.6 Hz, CH_2CH_3).

4.1.22. (1*S*,2*R*,3*S*,6*R*)-6-Dodecylamino-4-(hydroxymethyl)-cyclohex-4-ene-1,2,3-triol [*N*-dodecyl-5a-carba-α-L-*arabino*-hex-5(5a)-enopyranosylamine] (20). Compound **17**

(7.0 mg, 18 μmol) was deprotected as in the preparation of **18** to give **20** (5.4 mg, 87%) as a white powder, TLC: R_f 0.41 (1:2:6 AcOH/MeOH/$CHCl_3$); $[\alpha]_D^{21}$ +0.7° (*c* 0.27, MeOH); ^{1}H NMR (300 MHz, CD_3OD): δ 5.71 (br s, 1H, H-5), 4.15 (d, 1H, J = 4.1 Hz, H-3), 4.12 (br s, 2H, CH_2OH), 3.69 (dd, 1H, J = 8.1 and 9.6 Hz, H-1), 3.43 (dd, 1H, J = 4.1 and 9.6 Hz, H-2), 3.10 (d, 1H, J = 8.1 Hz, H-6), 2.56 and 2.74 (2 dt, each 1H, J = 7.1 and 11.5 Hz, $NHCH_2$), 1.52 (m, 2H, $NHCH_2CH_2$), 1.28 [m, 18H, $CH_2(CH_2)_9CH_3$], 0.89 (t, 3H, J = 6.6 Hz, CH_2CH_3); ITMS-ESI (positive mode): *m/z* 344 $[M+H]^+$.

4.2. Biological assay

Compounds were assayed[13] for enzyme inhibitory activity (IC_{50}) against six glycohydrolases: α-glucosidase (Baker's yeast), β-glucosidase (almonds), α-galactosidase (green coffee beans), β-galactosidase (bovine liver), α-mannosidase (Jack beans), and α-fucosidase (bovine kidney). All compounds did not exhibit any inhibitory activity toward α-glucosidase and α-fucosidase.

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