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Synthesis of cholic acid amino analogues by oxime reduction with $TiCl_3$−$NaBH_3CN$

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Methyl 3α,7α,12α-trihydroxy-5β-cholan-24-oate **4**: $[\alpha]_D^{20}$ +24 (*c* 1, $CHCl_3$). Found (%): C 71.27; H 10.13. Calc. for $C_{25}H_{42}O_5$ (%): C 71.05; H 10.02. ^{1}H NMR (300 MHz): 0.61 (3 H, s, 18-Me), 0.82 (3 H, s, 19-Me), 0.91 (3 H, d, *J* = 6.3, 21-Me), 1.01-2.40 (27 H, m, steroid protons), 3.34-3.43 (1 H, m, 3β-H), 3.60 (3 H, s, OMe), 3.78 (1 H, m, 7β-H), 3.91 (1 H, m, 12β-H). ^{13}C NMR (75 MHz): 12.43, 17.44, 22.45, 23.36, 26.40, 27.66, 28.26, 30.47, 31.05, 31.25, 34.81, 34.91, 35.45, 39.57, 41.70, 46.54, 47.10, 51.65, 68.58, 72.03, 73.22, 175.02.

Methyl 3,7,12-trioxo-5β-cholan-24-oate **5**: $[\alpha]_D^{20}$ +22 (*c* 1, $CHCl_3$). Found (%): C 71. 88; H 8.71. Calc. for $C_{25}H_{36}O_5$ (%): C 72.08; H 8.71. ^{1}H NMR (200 MHz): 0.77 (3 H, d, *J* = 6.3, 21-Me), 1.00 (3 H, s, 18-Me), 1.33 (3 H, s, 19-Me), 1.16-2.40 (21 H m, steroid protons), 2.70-2.92 (3 H m, steroid protons), 3.60 (3 H, s, OMe). ^{13}C NMR (50 MHz): 11.91, 18.69, 21.96, 25.19, 27.67, 30.49, 31.33, 35.33, 35.56, 36.06, 36.54, 38.9, 42.85, 45.03, 45.59, 45.69, 46.90, 49.04, 51.57, 51.80, 56.93, 174.61, 208.80, 209.15, 212.03.

Methyl 12-oximino-3α,7α-dihydroxy-5β-cholan-24-oate **7**: $[\alpha]_D^{20}$ +82 (*c* 1, $CHCl_3$). MS, *m/z*: 435.964 $[M]^+$; ^{1}H NMR (400 MHz): 0.85 (3 H, s, 18-Me), 0.88 (3 H, d, *J* = 6.3, 21-Me), 0.90 (3 H, s, 19-Me), 0.93-2.37 (23 H, m, steroid protons), 3.25-3.41 (2 H, m, 3β-H, 1 H steroid), 3.60 (3 H, s, OMe), 3.80-3.85 (1 H, m, 7β-H). ^{13}C NMR (100 MHz): 12.18, 19.28, 20.15, 22.41, 23.81, 28.28, 30.63, 30.81, 31.56, 34.87, 35.05, 35.72, 35.81, 36.10, 39.61, 39.75, 41.57, 46.97, 49.79, 51.61, 54.12, 68.21, 71.95, 166.47, 175.07.

Methyl 12β-amino-3α,7α-dihydroxy-5β-cholan-24-oate **8b**: MS, *m/z*: 422.019 $[M+H]^+$, 444.025 $[M+Na]^+$.^{1}H NMR (300 MHz): 0.75 (3 H, s, 18-Me), 0.83 (3 H, s, 19-Me), 0.94 (3 H, d, *J* = 6.3, 21-Me), 0.88-2.38 (24 H m, steroid protons), 3.38-3.53 (2 H, m, 3β-H, 12α-H), 3.60 (3 H, s, OMe), 3.72-3.77 (1 H, m, 7β-H).

*12α-(*tert-*Butyloxycarbonyl)amino-3α,7α-dihydroxy-5β-cholan-24-oic acid* **8c**: MS, *m/z*: 530.157 $[M+Na]^+$; ^1H NMR (300 MHz): 0.72 (3 H, s, 18-Me), 0.82 (3 H, s, 19-Me), 0.86 (3 H, d, *J* = 6.3, 21-Me), 0.88-2.45 (24 H m, steroid protons), 1.36 (9 H, s, ^{t}Bu), 3.34-3.42 (1 H, m, 3β-H), 3.74-3.81 (1 H, m, 7β-H), 3.85-3.89 (1 H, m, 12β-H).

Methyl 12α-hydroxy-3,7-dioxo-5β-cholan-24-oate **9**: $[\alpha]_D^{20}$ –83 (*c* 1, $CHCl_3$). Found (%): C 71.48; H 9.12. Calc. for $C_{25}H_{38}O_5$ (%): C 71.74; H 9.15. ^1H NMR (300 MHz): 0.71 (3 H, s, 18-Me), 0.99 (3 H, d, *J* = 6.3, 21-Me), 1.28 (3 H, s, 19-Me), 1.20-2.90 (24 H, m, steroid protons), 3.60 (3 H, s, OMe), 4.02-4.08 (1 H, m, 12β-H). ^{13}C NMR (75 MHz): 12.99, 17.62, 22.28, 24.32, 27.66, 29.70, 31.00, 31.20, 34.99, 35.46, 36.16, 36.75, 37.56, 40.82, 43.05, 45.01, 46.76, 47.71, 48.27, 49.71, 51.65, 72.10, 174.61, 210.22, 210.61.

Methyl 12α-hydroxy-3,7-bis(oximino)-5β-cholan-24-oate **10**: $[\alpha]_D^{20}$ -35 (*c* 1, $CHCl_3$–CH_3OH (6:1)). Found (%): C 65.54; H 9.40; N 6.33. Calc. for $C_{25}H_{40}N_2O_5 \times ½\ H_2O$ (%): C 65.62; H 9.03; N, 6.12. ^1H NMR (400 MHz): 0.63 (3 H, s, 18-Me), 0.91 (3 H, d, *J* = 5.8, 21-Me), 0.99 (3 H, s, 19-Me), 1.02-2.35 (22 H, m, steroid protons), 2.91-3.11 (2 H, m, steroid protons), 3.59 (3 H, s, OMe), 3.94-4.00 (1 H, m, 12β-H). ^{13}C NMR (100 MHz): 13.07, 17.61, 19.53, 22.71, 25.04, 25.43, 26.19, 27.46, 27.54, 28.89, 29.84, 31.11, 31.22, 31.27, 32.50, 35.06, 35.18, 35.85, 36.03, 36.22, 41.03, 42.29, 42.36, 44.72, 46.01, 46.46, 46.58, 46.68, 46.78, 51.65, 72.67, 159.49, 160.46, 174.99.