Selective manipulation of steroid hydroxyl groups with boronate esters: efficient access to antigenic C-3 linked steroid-protein conjugates and steroid sulfate standards for drug detection

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Experimental

General experimental

Optical rotations were measured using a PolAAR 2001 polarimeter set at the 589.3 nm sodium D line, in a 0.25 dm cell, in the solvent indicated, and at the concentration (g / 100 mL) and temperature indicated. Optical rotations are quoted in 10^1 deg.cm^-2.g^-1. Infrared spectra were recorded on a Shimadzu FTIR-8400S Fourier transform infrared spectrometer. Compounds were prepared as thin films on a 0.5 cm NaCl plate, or as KBr disks, seated on a custom-made perch in the apparatus. Absorption maxima are expressed as wavenumbers (cm^-1).

1H Nuclear magnetic resonance spectra were recorded using a Bruker Avance 200 (200.13 MHz), a Bruker Avance 300 (300.13 MHz) or a Bruker DRX 400 (400.13 MHz) spectrometer. Spectra were recorded in CDCl3 or CD3OD and chemical shifts were arising from the solvent were used as internal standard (δ 7.26, or 63.30, respectively). Data are reported as chemical shift (δ), relative integral, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, m = multiplet), coupling constant (J in Hz) and assignment. All coupling constants and multiplicities reported are apparent values.

13C Nuclear magnetic resonance spectra were recorded using a Bruker Avance 200 (50.3 MHz), a Bruker Avance 300 (75.5 MHz) or a Bruker DRX 400 (100.62 MHz) spectrometer at ambient temperature, with complete proton decoupling. Spectra were recorded in CDCl3, CD3OD or in D2O-DMso and chemical shifts were recorded as δ values in parts per million (ppm). Signals arising from the solvent were used as internal standard (δ 77.0, δ 49.0 or δ 39.5 respectively).

Low resolution mass spectra were recorded by the Mass Spectrometry Unit, School of Chemistry, The University of Sydney. Major fragments are quoted as mass to charge ratio (assignment, percentage of base peak). Low resolution mass spectra were recorded on a Finnigan Polaris Q ion trap mass spectrometer, using electron impact (+EI) ionisation mode at 70 eV, or on a Finnigan LCQ ion trap mass spectrometer, using positive electrospray ionisation (+ESI), or negative electrospray ionisation (-ESI). High resolution mass spectra were recorded on a Kratos MS25 RFA mass spectrometer, using electron impact (+EI) ionisation, operating at 70 eV, in magnetic scan, with PFK as standard (The University of Queensland), or on a Spectrospin 7T FTICR, using positive or negative electrospray ionisation (The University of New South Wales).

Analytical thin layer chromatography (TLC) was performed using 0.2 mm thick, aluminium-backed, pre-coated silica gel plates (Merck Silica gel 60 F 254). Compounds were visualised by staining with Goofy’s Dip (15 g phosphomolybdic acid, 15 mL conc. sulfuric acid, 485 mL water, 2.5 g cerium sulfate) or an anisaldehyde solution (7.4 mL anisaldehyde, 383 mL ethanol 95%, 10 mL 35% sulfuric acid, 3 mL acetic acid). Flash chromatography was performed using Merck Silica gel 60 (230 – 400 mesh ASTM), under solvent indicated, and at the concentration (g / 100 mL) and temperature indicated. Optical rotations are quoted in 10^-1.deg.cm^-2.g^-1.

All solvents and reagents were purified according to standard procedures. Moisture sensitive reactions were carried out in oven-dried glassware under a dry, inert nitrogen atmosphere. Reaction temperatures were controlled using dry ice : acetone (-78 °C) or ice : water (0 – 5 °C) cooling baths. Concentration under reduced pressure refers to evaporation of solvent using a rotary evaporator connected to a water aspirator. Removal of residual solvent where desired, was achieved by evacuation (0.1 – 0.01 mmHg) with a high-stage, oil-sealed vacuum pump. 

Epiandrosterone (3β-hydroxy-5α-androstan-17-one) was obtained from Steraloids (Newport, RI, U.S.A.). 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), carboxymethoxylamine hemihydrochloride, N-hydroxysuccinimide and lithium acetylide-ethylenediamine complex, were purchased from Sigma-Aldrich (Castle Hill, NSW, Australia).

Synthesis

5α,17α-pregn-20-yne-3β,16β,17β-triol (19). 3β,16β-Diacetoxy-5α-androstane-17-one 22 3 (0.973 g, 2.49 mmol) in THF (100 mL) was added drop-wise to a stirred suspension of lithium acetylide-ethylenediamine complex (2.76 g, 29.9 mmol) in THF (40 mL). After stirring for 20 hours, TLC (ethyl acetate/hexane, 1/1) analysis suggested an absence of diacetate 22 (Rf 0.8) and complete conversion to product. The reaction mixture was poured into saturated NH4Cl solution (600 mL) and extracted into ethyl acetate (4 x 100 mL). The combined ethyl acetate extracts were washed with pH 7 buffer (80 mL) and saturated NaCl solution (80 mL), then dried (Na2SO4) and concentrated. The resulting residue was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate/hexane, 1/3 then 1/2 then 1/1.2), which gave 17α-ethynyl triol 19 (0.592 g, 71%), as a
colourless, amorphous solid. \(R_t\) 0.3 (ethyl acetate/hexane, 1/1); \(m p\) 205-208 °C; [\(\text{a}\)]\(\text{D}\) \(22^\circ\) -26.4 (c 0.50, MeOH); \(\nu_{\text{max}}\) cm\(^{-1}\) (KBr disk) 3650-3000 (OH), 3275 (C=CH), 2920, 2851, 2110 (C=C), 1385, 1366, 1049; \(\delta_n\) (300 MHz, MeOD) 4.10 (1H, dd, \(J\) 7.9, 4.6, H16), 3.57-3.44 (1H, m, H3), 2.87 (1H, s, H21), 2.25-2.15 (1H, m), 1.82-0.80 (21H, m), 0.84 (3H, s, CH3), 0.82 (3H, s, CH3) 0.74-0.62 (1H, m); \(\delta_c\) (75 MHz, MeOD) 87.9, 77.8, 74.8, 71.8, 76.5, 55.8, 48.3, 47.3, 46.2, 38.9, 38.3, 37.0, 36.7, 35.7, 35.0, 33.1, 32.1, 29.8, 21.8, 13.5, 12.8; \(m/z\) (ESI+) 331.2281 (M−H, \(C_2H_5O\) requires 331.2273, 100%), 306 (M−C≡CH, 70%).

5α,17α-pregn-3β,16β,17β-triol (20). 17α-Ethynyl triol 19 (0.570 g, 1.72 mmol) was dissolved in MeOH (20 mL). 10% Pd/C (0.080 g) was added and the reaction mixture was stirred under an atmosphere of H₂ (balloon pressure) for 16 hours. The reaction mixture was diluted with ethyl acetate/MeOH (1/1) and filtered through celite, to afford 17α-ethynyl triol 20 (0.552 g, 96%), as a colourless, amorphous solid.

181°C; \(\nu_{\text{max}}\) cm\(^{-1}\) (film) 2943, 1709 (C=O), 1458, 1402, 1059, 1001, 989; \(\delta_n\) (300 MHz, CDCl3) 7.58-7.52 (2H, m, ArH), 7.40-7.33 (3H, m, ArH), 7.20-7.12 (1H, m, ArH), 6.70-6.63 (2H, m, ArH), 6.50-6.43 (2H, m, ArH), 6.00-5.93 (1H, m, ArH); \(\delta_c\) (75 MHz, CDCl3) 136.6, 129.3, 128.3, 126.9, 105.6, 90.7, 88.5, 71.3, 54.2, 53.3, 44.9, 44.7, 38.2, 37.0, 35.7, 35.6, 33.4, 32.0, 31.5, 31.0, 28.5, 21.0, 20.3, 15.8, 12.3; \(m/z\) (EI+) 410.2828 (M−H, \(C_2H_5O\) requires 410.2821, 10%); 409 (15), 367 (22), 243 (30), 231 (70), 216 (55), 135 (35), 107 (57), 91 (79), 84 (100), \(m/z\) (ESI−) 336.2336 (MH−, 30%), 271 (25), 243 (30), 231 (70), 216 (55), 135 (35), 107 (57), 91 (79), 84 (100), \(m/z\) (ESI−) 335.2560 (M−H, \(C_2H_5O\) requires 335.2592).

[(S)-16β,17β-benzylidenedioxy]-17α-methyl-5α-androstan-3β-ol. 17α-Methyl triol 18 (0.50 g, 1.55 mmol) was stirred (the triol was partially insoluble) in a mixture of DMF/DCM (1/1, 12 mL). Benzaldehyde dimethyl acetal (0.35 mL, 0.354 g, 2.33 mmol) was added, followed by conc. H₂SO₄ (10 drops). After 2 hours, a homogenous solution resulted. After 4 hours, TLC (ethyl acetate / hexane, 1/2) showed an absence of starting material (\(R_f\) 0.1) and complete conversion to product. The reaction mixture was poured into H₂O (150 mL) and extracted with ethyl acetate (5 x 80 mL). The organic extracts were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated. The resulting mixture was dissolved in MeOH (20 mL), then washed with pH 7 buffer (80 mL) and saturated NaCl solution (80 mL), then dried (Na₂SO₄) and concentrated. The resulting

\(\nu_{\text{max}}\) cm\(^{-1}\) (film) 2943, 1709 (C=O), 1458, 1402, 1059, 1001, \(\delta_n\) (300 MHz, MeOD) 4.10 (1H, dd, \(J\) 7.9, 4.6, H16), 3.65-3.52 (1H, m), 3.09 (3H, t, \(J\) 7.2, H21), 0.84 (3H, s, CH₃), 0.81 (3H, s, CH₃) 0.68-0.57 (1H, m); \(\delta_c\) (75 MHz, MeOD) 81.2, 73.4, 71.8, 55.9, 48.0, 47.1, 46.2, 38.9, 38.2, 37.1, 36.7, 36.3, 33.8, 33.3, 32.1, 29.9, 28.2, 21.9, 15.0, 12.7, 7.5; \(m/z\) (ESI+) 336 (MH+, 30%), 271 (25), 243 (30), 231 (70), 216 (55), 135 (35), 107 (57), 91 (79), 84 (100), \(m/z\) (ESI−) 335.2560 (M−H, \(C_2H_5O\) requires 335.2592).
residue was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate/hexane, 1/2 then 1/1), which gave diol 32 (1.659 g, 94%), as a colourless solid. Rf 0.4 (ethyl acetate / hexane, 1/1); mp 265-267°C (lit., 4 260-261°C); [α]D 25 -42.8 (c 0.43, CHCl₃ / MeOH, 5/1); v(CHCl₃) cm⁻¹ 316.2406 (M+). α-Carboxymethoxylamine hemihydrochloride (2 mmol) in pyridine (10 mL). The reaction mixture was heated to 80 °C and stirred under an atmosphere of H₂ (balloon pressure) for 16 hours. The reaction mixture was filtered through celite and the latter procedure afforded 17α-hydroxy-5β-pregnan-3-one (30) (0.050 g, 75%). Rf 0.06 (ethyl acetate / hexane, 1/1); mp 145-148°C; [α]D 25 +12.6 (c 0.70, CHCl₃); v(CHCl₃) cm⁻¹ 316.2402 (M+H+, C₂₁H₃₂O₂ requires 316.2402, 8%). 17α-hydroxy-5α-pregnan-3-one (31). 17α-Ethynyl ketone 30 (0.110 g, 0.33 mmol) was treated as per the general procedure. The residue obtained was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate/MeOH/H₂O, 50/2/1 then 20/2/1 then 10/2/1) which afforded a mixture of α,β-unsaturated ketones (30%); m/z (ESi+) 845 (2M+K⁺, 35%), 829 (2M+Na⁺, 45), 426 (M+Na⁺, 80), 404.2421 (M+H⁺, C₂₁H₂₂O₂ requires 404.2421, 100%). General procedure for preparation of (carboxymethyl)oximes 33-36. Carboxymethoxylamine hemihydrochloride (2 mmol) was added to a solution of 16, 17, 30 or 31 (1 mmol) in pyridine (10 mL). The reaction mixture was heated to 80 °C and stirred under an atmosphere for 4-5 hours. The reaction mixture was partially concentrated in vacuo, and then poured into distilled water (100 mL) and extracted into ethyl acetate (3 x 60 mL). The combined organic layers were washed with pH 7 buffer (1 x 60 mL) and saturated sodium chloride solution (1 x 60 mL), and then dried (Na₂SO₄) and concentrated to give the product 33, 34, 35, 36.

3-(Carboxymethoxymino)-5α,17α-pregn-20-ene-16β,17β-diol (33). 17α-Ethynyl ketone 16 (0.063 g, 0.19 mmol) was treated as per the general procedure. The residue obtained was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate / MeOH / H₂O, 50/2/1 then 20/2/1 then 10/2/1) which afforded a mixture of E and Z isomers of 33 (0.058 g, 75%), as colourless crystals. Rf 0.3 (ethyl acetate/MeOH/H₂O, 50/2/1); mp 138-140°C; [α]D 25 +29.1 (c 0.22, MeOH); v(CHCl₃) cm⁻¹ 3700-3100 (OH), 3271 (C=O), 2935, 1713 (C=O), 1447, 1000, 980; δH (300 MHz, CDCl₃) 2.45-2.16 (3H, m), 2.12-1.88 (3H, m), 1.76-0.78 (18H, m), 1.02 (3H, s, CH₃); δC (75 MHz, CDCl₃) 173.2, 145.4, 138.3, 105.2, 103.2, 79.7, 78.8, 73.8, 53.3, 50.3, 47.1, 46.4, 44.5, 39.6, 38.3, 37.9, 35.9, 35.5, 33.1, 28.6, 23.2, 21.1, 13.1, 10.9; m/z (ESi+) 314.2255 (M⁻, C₂₁H₂₂O₂ requires 314.2246, 5%), 289 (17%), 229 (17), 155 (25), 145 (26), 124 (100).
3-(Carboxymethoxyimino)-5α,17α-pregn-20-yn-17β-ol (35). 17α-Ethynyl ketone 30 (0.092 g, 0.29 mmol) was treated as per the general procedure. The residue obtained was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate / MeOH / H2O, 80/2/1) which afforded a mixture of E and Z isomers of 35 (0.105 g, 86%), as colourless crystals. Rf 0.3 (ethyl acetate/MeOH/H2O, 100/2/1) then 80/2/1 then 60/2/1 which afforded a mixture of E and Z isomers of 35 (0.069 g, 0.17 mmol) was treated as per the general procedure. Preparation of the resulting solid from ethyl acetate/hexane gave 37 (0.058 g, 84%) as a 1:1 mixture of isomers. Rf 0.8 (ethyl acetate); mp 119-121°C; [α]23D -10.0 (c 0.02, CH2Cl2); νmax/cm-1 (film) 3600-3200 (OH), 3302 (C=O), 2937, 2854, 1740 (C=O), 1737, 1724, 1690, 1674, 1400, 1076; δ6 (300 MHz, CDCl3) 4.88 (4H, s, CH2OH), 4.20 (2H, dd, J 8.0, 4.1, H16), 3.97-3.15 (1H, m), 3.26-1.34 (1H, m), 2.84 (8H, s, COCH2CH2CO), 2.56 (2H, s, CH2OH), 2.36-0.83 (40H, m), 0.90 (6H, s, CH3), 0.86 (6H, s, CH3), 0.81-0.68 (2H, m); δc (75 MHz, CDCl3) 168.7, 165.8, 163.1, 162.8, 85.8, 78.8, 77.4, 74.8, 67.8, 53.6, 53.5, 46.8, 46.4, 46.2, 45.2, 38.2, 37.3, 36.2, 35.4, 34.6, 33.9, 33.6, 31.4, 28.5, 28.4, 28.2, 27.4, 25.6, 21.5, 20.6, 12.7, 11.5, 11.3 (21C overlapping); m/z (ESI+) 559 (55%), 523.2410 (M+N+, C27H55N2O4Na requires 523.2415, 30%), 501 (M+H+, 30%), 488 (100).

3-(Carboxymethoxyimino)-5α,17α-pregn-17β-ol (36). 17α-Ethyl ketone 31 (0.099 g, 0.31 mmol) was treated as per the general procedure. The residue obtained was pre-adsorbed onto silica from DCM/MeOH and subjected to flash chromatography (ethyl acetate / MeOH / H2O, 80/2/1) which afforded a mixture of E and Z isomers of 36 (0.105 g, 86%), as colourless crystals. Rf 0.3 (ethyl acetate/MeOH/H2O, 100/2/1) then 80/2/1 then 60/2/1 which afforded a mixture of E and Z isomers of 36 (0.099 g, 0.31 mmol) was treated as per the general procedure. Preparation of the resulting solid from ethyl acetate/hexane gave 37 (0.058 g, 84%) as a 1:1 mixture of isomers. Rf 0.8 (ethyl acetate); mp 119-121°C; [α]23D -10.0 (c 0.02, CH2Cl2); νmax/cm-1 (film) 3600-3200 (OH), 3302 (C=O), 2937, 2854, 1740 (C=O), 1737, 1724, 1690, 1674, 1400, 1076; δ6 (300 MHz, CDCl3) 4.88 (4H, s, CH2OH), 4.20 (2H, dd, J 8.0, 4.1, H16), 3.97-3.15 (1H, m), 3.26-1.34 (1H, m), 2.84 (8H, s, COCH2CH2CO), 2.56 (2H, s, CH2OH), 2.36-0.83 (40H, m), 0.90 (6H, s, CH3), 0.86 (6H, s, CH3), 0.81-0.68 (2H, m); δc (75 MHz, CDCl3) 168.7, 165.8, 163.1, 162.8, 85.8, 78.8, 77.4, 74.8, 67.8, 53.6, 53.5, 46.8, 46.4, 46.2, 45.2, 38.2, 37.3, 36.2, 35.4, 34.6, 33.9, 33.6, 31.4, 28.5, 28.4, 28.2, 27.4, 25.6, 21.5, 20.6, 12.7, 11.5, 11.3 (21C overlapping); m/z (ESI+) 559 (55%), 523.2410 (M+N+, C27H55N2O4Na requires 523.2415, 30%), 501 (M+H+, 30%), 488 (100).
3-(Carboxymethoxyimino)-5α,17α-pregn-17β-ol N-hydroxysuccinimide ester (40). Compound 36 (0.048 g, 0.12 mmol) was treated as per the general procedure. Precipitation of the resulting solid from ethyl acetate/hexane gave 40 (0.058 g, 97%) as a 1:1 mixture of isomers. \( R_f \) 0.7 (ethyl acetate); \( [\alpha]_D^{23} \) -8.0 (c 0.20, CHCl₃); \( \nu_{\max} / \text{cm}^{-1} \) (film) 3600-3200 (OH), 2937, 2351, 1823, 1784, 1740 (C=O), 1630, 1580, 1464, 1377, 1252 (C=O), 1090, 1011; \( \delta_{\text{H}} \) (300 MHz, CDCl₃) 4.88 (4H, s, OCH₂CO₂), 3.26-3.14 (1H, m), 3.02-2.93 (1H, m), 2.84 (8H, s, COCH₂CH₂CO), 2.35-0.78 (46H, m), 0.97 (6H, t, \( J = 7.3 \), C₂₁-H₃), 0.90 (6H, s, CH₃), 0.87 (6H, s, CH₃), 0.71-0.59 (2H, m); \( \delta_{\text{C}} \) (75 MHz, CDCl₃) 168.7, 165.8, 163.1, 163.0, 83.5, 67.9, 53.9, 53.8, 50.4, 46.6, 46.4, 45.4, 38.3, 37.4, 36.3, 36.2, 34.0, 33.6, 31.5, 28.8, 28.7, 28.5, 28.2, 27.5, 25.6, 23.6, 21.5, 20.8, 14.5, 11.5, 11.4, 7.8 (21C overlapping); \( m/z \) (ESI+) 547 (100%), 511 (M+Na⁺, 25), 489 (M+H⁺, C₂₇H₄₁N₂O₆ requires 489.2959, 65%).

Sodium 3β-(tert-butyldimethylsilyloxy)-16β,17β-dihydroxy-17α-methyl-5α-androstane 16-sulfate (47). Diol 46 (0.061 g, 0.14 mmol) was dissolved in DMF (4.5 mL). Pyridine (0.225 mL, 0.220 g, 2.78 mmol) and 4Å molecular sieves (20) were added and the mixture was stirred overnight. Sulfur trioxide-pyridine complex (0.156 g, 0.98 mmol) was added and the reaction mixture was stirred for 50 minutes at 45ºC. TLC (ethyl acetate / hexane, 1/1) analysis showed an absence of starting material. The molecular sieves were removed and the reaction mixture was poured into saturated NaHCO₃ solution (50 mL), which was extracted with ethyl acetate (5 x 20 mL). The organic extracts were dried (Na₂SO₄) and concentrated to give a residue which was triturated with Et₂O (2 mL) to give silyl protected 16-sulfate 47 (0.046 g, 61%). \( R_f \) 0.5 (MeOH / DCM, 1/4); \( mp \) 200-202°C; \( [\alpha]_D^{22} \) -55.2 (c 0.21, CHCl₃ / MeOH, 1/1); \( \nu_{\max} / \text{cm}^{-1} \) (film) 3700-3200 (OH), 2928, 1377, 1252 (O-SO₂), 1090, 1011; \( \delta_{\text{H}} \) (400 MHz, CDCl₃ / MeOD, 1/1) 4.30 (1H, dd, \( J = 8.2, 5.8 \), H₁₆), 3.58-3.48 (1H, m, H₃), 2.26-2.16 (1H, m), 1.69-0.78 (18H, m), 1.16 (3H, s, CH₃), 0.85 (9H, s, (CH₃)₃CSi), 0.82 (3H, s, CH₃), 0.80 (3H, s, CH₃), 0.64-0.55 (1H, m), 0.03 (6H, s, (CH₃)₂Si); \( \delta_{\text{C}} \) (100 MHz, CDCl₃ / MeOD, 1/1) 84.4, 80.2, 73.0, 55.1, 47.8, 45.6, 39.0, 37.7, 36.3, 36.1, 33.7, 32.8, 32.5, 32.3, 29.1, 26.2, 24.4, 21.2, 18.7, 14.1, 12.6 (1C overlapping); \( m/z \) (ESI+) 561.2666 (MNa⁺, C₂₆H₄₇Na₂O₆SSi requires 561.2656, 100%).

Sodium 3β,16β,17β-trihydroxy-17α-methyl-5α-androstane 16-sulfate (44). Silyl protected 16-sulfate 47 (0.020 g, 0.037 mmol) was dissolved in acetic acid / H₂O (4/1, 1.1 mL) and stirred for 1 hour. TLC (MeOH / DCM, 1/4) showed complete conversion to product (\( R_f \) 0.2). The mixture was poured into saturated NaHCO₃ solution (60 mL) and extracted into ethyl acetate (3 x 20 mL) and then into CHCl₃/iPrOH (3/1, 5 x 15 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo. The residue was dissolved in DCM/MeOH and pre-adsorbed onto silica for flash chromatography (DCM/MeOH/H₂O, 60/15/1), which afforded 16-sulfate 44 (0.011 g, 69%). \( R_f \) 0.4 (DCM/MeOH/H₂O, 60/15/1); \( mp \) 279-280 °C (decomp.); \( [\alpha]_D^{23} \) -28.6 (c 0.21, MeOH); \( \nu_{\max} / \text{cm}^{-1} \) (film) 3700-3100 (OH), 2922, 1379, 1248 (O-SO₂); \( \delta_{\text{H}} \) (300 MHz, CDCl₃ / MeOD, 1/1) 4.30 (1H, dd, J 8.3, 5.6, H₁₆), 3.56-3.42 (1H, m, H₃), 2.28-2.15 (1H, m), 1.78-0.78 (18H, m), 1.16 (3H, s, CH₃), 0.83 (3H, s, CH₃), 0.80 (3H, s, CH₃), 0.66-0.55 (1H, m); \( \delta_{\text{C}} \) (100 MHz, CDCl₃ / MeOD, 1/1) 84.4, 80.2, 71.3, 55.1, 47.9, 45.6, 38.2, 37.6, 36.4, 36.2, 33.8, 32.8, 32.5, 31.5, 29.2, 24.5, 21.2, 14.1, 12.6; \( m/z \) (ESI-) 401.1987 (C₂₀H₃₃O₆S requires 401.1998, 100%).

Notes and references