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Studies on the synthesis of cholane derivatives containing a mercapto group and their dimers with disulfide spacers. Part 1. 24-Mercapto-5β -cholane-3α,7α,12α-triol and its C(24)-C(24') disulfide dimer

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Studies on the synthesis of cholane derivatives containing a mercapto group and their dimers with disulfide spacers. Part 1. 24-Mercapto-5β-cholane-3α,7α,12α-triol and its C(24)–C(24′) disulfide dimer

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Two new sulfur-containing cholane derivatives were obtained from cholic acid: 24-mercapto-5β-cholane-3α,7α,12α-triol (**2**) and its C(24)–C(24′) disulfide dimer (**3**) as a potential supramolecular host.

Keywords: bile acids; cholane; disulfides; thiols; supramolecular chemistry

1. Introduction

Cholic acid (**1**) is widely used as a building block for synthesis of molecular receptors (*1*, *2*), enzyme models and transporters across phospholipid membranes (*3*, *4*). There are many kinds of acyclic structures based on cholic acid, among which the most interesting are: molecular "clefts" (*5*), "tweezers" (*6*) and "umbrellas" (*7*). In our previous papers (*8*, *9*), we described the syntheses of new acyclic and cyclic dimers of cholic acid with oxamide and hydrazide spacers. Now we report the synthesis of a new cholane derivative with mercapto group **2** and its dimer **3**, in which disulfide spacer binds steroidal subunits through positions 24 and 24′ (Scheme 1). The new concept is the usage of bile acids and their derivatives containing a thiol group in nanoscience. These molecules are very useful in the preparation of metal (especially gold) nanoparticles (*10*).

Reversible redox couples: $2\ \text{thiol} \rightleftarrows \text{disulfide} + 2\text{H}^+ + 2\text{e}^-$, *e.g.* cysteine–cystine, or glutathione–GSSG, play an important role in biological systems (*11*). Disulfide bridges were also used for binding other classes of chemical compounds, *e.g.* sugars (*12*) or glycopeptides (*13*). The use of disulfide spacers, which readily undergo reduction and decomposition, in the synthesis of supramolecular hosts should facilitate the release of the guest molecule from the supramolecule. Moreover, the conversion from hydrophobic disulfide moiety into

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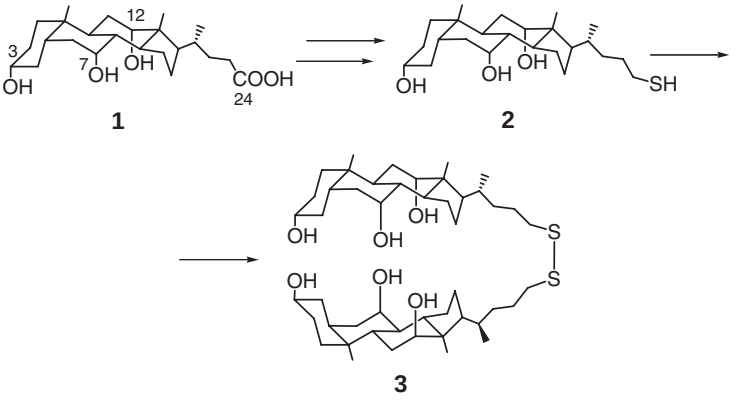


Scheme 1. Schematic representation of the formation of products **2** and **3**.

hydrophilic mercapto group would make easier the excretion of the host body from the organism in urine.

2. Results and discussion

Steroidal iodide **5** was prepared by iodination of alcohol **4** with iodine–triphenylphosphine complex in dry benzene/pyridine solution (*9*) with a high yield. Several attempts were undertaken to choose the best method for the synthesis of desired product **2**. In the first experiments, substrate **5** was subjected to reactions with $NaSH \cdot 2H_2O$ in various solvents (DMSO, NMP and absolute ethanol) under argon. The best result was achieved when the reaction was carried out in absolute ethanol. Lower yields of the product **6** were obtained when DMSO or NMP were used as the solvents. To deprotect the hydroxyl groups at C(3), C(7) and C(12), we applied the two-step procedure including AcOH hydrolysis of TBDMS ether at C(3) followed by reduction of C(7) and C(12) acetate groups with $LiAlH_4$. This way, the desired thiol **2** was obtained in an overall yield of 21%. When the sequence of reactions was reversed, the yield of the final compound was slightly lower.

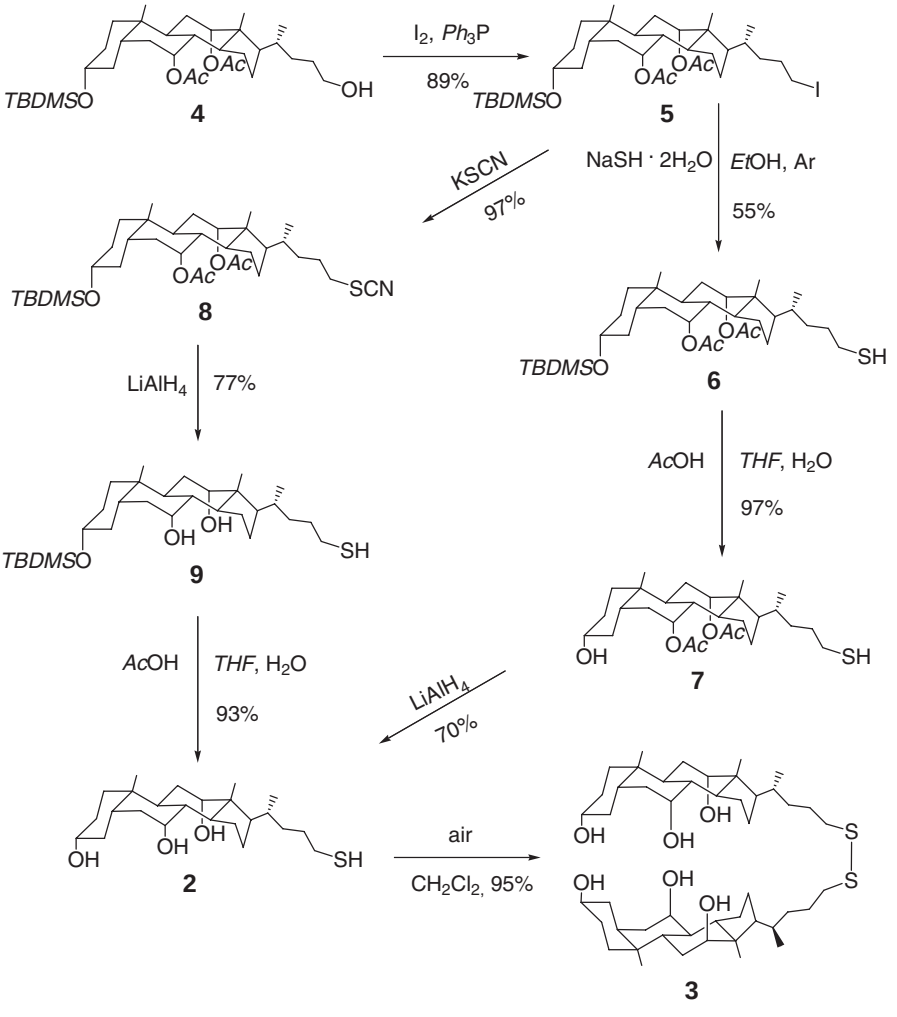
An attempt to produce thiol **2** in the reaction of iodide **5** with thiourea via S-alkylisothiuronium salt (*14*) was unsuccessful. A complex mixture of products was formed.

The last method tried out by us was the conversion of substrate **5** into thiocyanate **8** (*15*) followed by its reduction and hydrolysis to the final product **2**. In this case, the reduction of both thiocyanate and acetate groups was effected prior to the hydrolysis of silyl ether. This synthetic path appeared to be the most efficient: thiocyanate **8** formed with excellent yields (97%) and the overall yield of the final thiol **2** reached nearly 50%.

The last step of the synthesis – oxidation of thiol **2** to disulfide dimer **3** – took place when **2** was kept in CH_2Cl_2 solution on air with a catalytic amount of triethylamine. The entire substrate was converted to the desired product in 5 h. (Scheme 2).

3. Conclusions

Steroidal thiol **2** and its dimer **3** with disulfide spacer were obtained from iodide **5** in good yield. Several methods of transformation of iodide to thiol were tested. The best yields were achieved in nucleophilic substitution of iodide by the thiocyanate ion followed by the reduction of the



Scheme 2. Synthetic route for products **2** and **3**.

intermediate **8** according to the procedures shown in Scheme 2. The desired dimer was formed from thiol **2** by a simple air oxidation procedure in almost quantitative yield. The disulfide **3** is expected to be a good supramolecular host for selected ions and small molecules. The physicochemical studies for guest ions and molecules complexation properties of this compound are underway.

4. Experimental

Melting points were determined on a *Kofler* apparatus of the *Boëtius* type. NMR spectra were taken with a Bruker Ultrashield Plus 400 spectrometer with TMS as the internal standard. Infrared spectra were recorded on a Nicolet series II Magna-IR 550 FT-IR spectrometer. Mass spectra were obtained with an AMD-604 spectrometer. The reaction products were isolated by column chromatography performed on 70-230 mesh silica gel (J.T. Baker). Thin-layer chromatograms were developed on aluminum TLC sheets precoated with silica gel F_{254} (Merck) and visualized with 50% H_2SO_4 after heating. All solvents were dried and freshly distilled prior to use. Cholic

acid (**1**) was purchased from ABCR GmbH & Co. KG and it was used without further purification. 3α-*t*-Butyldimethylsilyloxy-5β-cholane-7α,12α,24-triol 7,12-diacetate (**4**) was prepared according to the known procedure (*9*).

4.1. *3α-t-Butyldimethylsilyloxy-24-iodo-5β-cholane-7α,12α-diol 7,12-diacetate (5; $C_{34}H_{59}IO_5Si$)*

To a solution of 1.54 g of I_2 (6.06 mmol) in 18 ml anhydrous benzene, 1.6 g of triphenylphosphine (5.97 mmol) and 0.88 ml anhydrous pyridine (11 mmol) were added and the mixture was stirred at room temperature for 15 min. Then 1.2 g of **4** (2.02 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. After this time, benzene and pyridine were removed *in vacuo* and the residue was subjected to column chromatography. Pure iodide **5** was eluted with *n*-hexane/ethyl acetate 95:5 (1.27 g, 89% yield). Colorless crystals, mp 146–148 °C (*n*-heptane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.05$ (m, 1H, 12β-H), 4.86 (m, 1H, 7β-H), 3.41 (m, 1H, 3β-H), 3.13 (m, 2H, CH_2I), 2.13 (s, 3H, 12-CH_3CO), 2.06 (s, 3H, 7-CH_3CO), 0.87 (s, 3H, 19-CH_3 and s, 9H, *t*-Bu), 0.80 (d, $J = 6.4$ Hz, 3H, 21-CH_3), 0.71 (s, 3H, 18-CH_3), 0.07 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.74$ (C), 170.71 (C), 75.5 (CH), 73.0 (CH), 71.0 (CH), 47.5 (CH), 45.1 (C), 43.5 (CH), 41.3 (CH), 39.4 (CH_2), 37.8 (CH), 35.1 (CH_2), 34.7 (CH), 34.5 (CH_2), 34.4 (C), 31.4 (CH_2), 31.1 (CH_2), 29.1 (CH), 27.3 (CH_2), 25.9 (3 CH_3), 25.6 (CH_2), 25.0 (CH_2), 22.8 (CH_2), 22.6 (CH_3), 21.62 (CH_3), 21.56 (CH_3), 18.4 (C), 17.9 (CH_3), 12.2 (CH_3), −4.5 (2 CH_3), −7.4 (CH_2) ppm; IR ($CHCl_3$): $\bar{\nu} = 1721$, 1255, 1077 cm^{-1}; ESI MS: $m/z = 725.2$ ($M^+ + Na$; 100%).

4.2. *3α-t-Butyldimethylsilyloxy-24-mercapto-5β-cholane-7α,12α-diol 7,12-diacetate (6; $C_{34}H_{60}O_5SSi$)*

One hundred milligrams (0.14 mmol) of **5** was dissolved in 10 ml of abs. ethanol and argon was passed through the solution for a minute. Next, 130 mg (1.4 mmol) of powdered $NaSH \cdot 2H_2O$ was added and the mixture was stirred at room temperature for 18 h under argon. The crude product was extracted with benzene/ethyl acetate 9:1 mixture, and combined organic layers were dried ($MgSO_4$) and evaporated to dryness. Purification with column chromatography gave pure **6** (48 mg) in 55% yield (elution with *n*-hexane/ethyl acetate 95:5). Colorless crystals, mp 164–167 °C (*n*-heptane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.08$ (m, 1H, 12β-H), 4.88 (m, 1H, 7β-H), 3.44 (m, 1H, 3β-H), 2.49 (m, 2H, C$\underline{H}_2$SH), 2.15 (s, 3H, 12-CH_3CO), 2.08 (s, 3H, 7-CH_3CO), 0.89 (s, 3H, 19-CH_3 and s, 9H *t*-Bu), 0.81 (d, $J = 6.6$ Hz, 3H, 21-CH_3), 0.73 (s, 3H, 18-CH_3), 0.07 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.74$ (C), 170.71 (C), 75.5 (CH), 73.0 (CH), 71.0 (CH), 47.5 (CH), 45.1 (C), 43.5 (CH), 41.3 (CH), 39.4 (CH_2), 37.8 (CH), 35.1 (CH_2), 34.7 (CH), 34.5 (CH_2), 34.4 (C), 31.4 (CH_2), 31.1 (CH_2), 30.5 (CH_2), 29.1 (CH), 27.3 (CH_2), 25.9 (3 CH_3), 25.6 (CH_2), 25.0 (CH_2), 22.8 (CH_2), 22.6 (CH_3), 21.63 (CH_3), 21.58 (CH_3), 18.4 (C), 17.9 (CH_3), 12.2 (CH_3), −4.5 (2 CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 2450$, 1721, 1255, 1076 cm^{-1}; ESI MS: $m/z = 631.3$ ($M^+ + Na$; 100%).

4.3. *24-Mercapto-5β-cholane-3α,7α,12α-triol 7,12-diacetate (7; $C_{28}H_{46}O_5S$)*

Compound **6** (48 mg; 0.08 mmol) was dissolved in a 5 ml mixture of acetic acid/water/THF (3:1:1) at room temperature under Ar. After 24 h, saturated $NaHCO_3$ solution was added dropwise to pH 8 and the crude product was extracted with CH_2Cl_2, the organic layer was dried ($MgSO_4$) and the solvent was evaporated. The residue was subjected to column chromatography. Pure product

7 was eluted with *n*-hexane/ethyl acetate 4:6 (38 mg, 97% yield). Colorless crystals, mp 157–160 °C (*n*-heptane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) : $\delta = 5.07$ (m, 1H, 12β-H), 4.89 (m, 1H, 7β-H), 3.49 (m, 1H, 3β-H), 2.47 (m, 2H, C$\underline{H}_2$SH), 2.12 (s, 3H, 12-CH_3CO), 2.08 (s, 3H, 7-CH_3CO), 0.90 (s, 3H, 19-CH_3), 0.80 (d, $J = 6.4$ Hz, 3H, 21-CH_3), 0.71 (s, 3H, 18-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.74$ (C), 170.71 (C), 75.5 (CH), 73.0 (CH), 71.0 (CH), 47.5 (CH), 45.1 (C), 43.5 (CH), 41.3 (CH), 39.4 (CH_2), 37.8 (CH), 35.1 (CH_2), 34.7 (CH), 34.5 (CH_2), 34.4 (C), 31.4 (CH_2), 31.1 (CH_2), 30.5 (CH_2), 29.1 (CH), 27.3 (CH_2), 25.6 (CH_2), 25.0 (CH_2), 22.8 (CH_2), 22.7 (CH_3), 21.62 (CH_3), 21.58 (CH_3), 17.9 (CH_3), 12.2 (CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 2452$, 1720, 1253, 1076 cm^{-1}; ESI MS: $m/z = 494.3$ ($M^+ + Na$; 100%).

4.4. *24-Mercapto-5β-cholane-3α,7α,12α-triol (2; $C_{24}H_{42}O_3S$)*

To a solution of 38 mg of **7** (0.09 mmol) in 5 ml of anhydrous THF, 20 mg of $LiAlH_4$ (6.67 mmol) was added under Ar and the mixture was stirred at room temperature for 16 h. Then several drops of water were added and the precipitate was filtered off. Purification with column chromatography gave pure **2** (22 mg) in 70% yield (elution with ethyl acetate). Colorless crystals, mp 173–174 °C (*n*-heptane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.97$ (m, 1H, 12β-H), 3.84 (m, 1H, 7β-H), 3.43 (m, 1H, 3β-H), 2.51 (m, 2H, C$\underline{H}_2$SH), 0.98 (d, $J = 6.6$ Hz, 3H, 21-CH_3), 0.89 (s, 3H, 19-CH_3), 0.69 (s, 3H, 18-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 73.1$ (CH), 71.9 (CH), 68.4 (CH), 47.3 (CH), 46.4 (C), 41.7 (CH), 41.5 (CH), 39.6 (CH_2), 39.5 (CH), 35.284 (CH_2), 35.280 (CH), 34.7 (C), 34.65 (CH_2), 34.61 (CH_2), 30.8 (CH_2), 30.4 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 26.4 (CH), 25.1 (CH_2), 23.2 (CH_2), 22.5 (CH_3), 17.7 (CH_3), 12.5 (CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 3610$, 3417, 2458, 1077, 1041 cm^{-1}; HRMS: calc. mass for $C_{24}H_{42}NaO_3S$: 433.2752, found: 433.2751.

4.5. *3α-t-Butyldimethylsilyloxy-5β-cholane-7α,12α-diol 7,12-diacetate 24-thiocyanate (8; $C_{35}H_{59}NO_5SSi$)*

Compound **5** (274 mg; 0.39 mmol) was dissolved in 20 ml of dry acetone and 380 mg (3.92 mmol) of powdered KSCN was added to the flask. The reaction mixture was stirred at room temperature for 18 h. After this time, the solvent was evaporated and the crude product was subjected to column chromatography. Pure thiocyanate **8** was eluted with *n*-hexane/ethyl acetate 85:15 (240 mg, 97% yield). Colorless crystals, mp 210–212 °C (*n*-hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.08$ (m, 1H, 12β-H), 4.88 (m, 1H, 7β-H), 3.44 (m, 1H, 3β-H), 2.91 (m, 2H, CH_2SCN), 2.16 (s, 3H, 12-CH_3CO), 2.09 (s, 3H, 7-CH_3CO), 0.89 (s, 3H, 19-CH_3 and s, 9H *t*-Bu), 0.84 (d, $J = 6.5$ Hz, 3H, 21-CH_3), 0.73 (s, 3H, 18-CH_3), 0.07 (s, 6H, Si(CH_3)$_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.7$ (2 C), 112.3 (C), 75.4 (CH), 72.9 (CH), 70.9 (CH), 47.4 (CH), 45.1 (C), 43.4 (CH), 41.3 (CH), 39.3 (CH_2), 37.8 (CH), 35.1 (CH_2), 34.7 (CH), 34.5 (CH_2), 34.4 (C), 34.1 (CH_2), 31.4 (CH_2), 31.1 (CH_2), 29.1 (CH), 27.3 (CH_2), 26.6 (CH_2), 25.9 (3 CH_3), 25.6 (CH_2), 22.9 (CH_2), 22.6 (CH_3), 21.64 (CH_3), 21.58 (CH_3), 18.4 (C), 17.8 (CH_3), 12.2 (CH_3), −4.5 (2 CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 2157$, 1721, 1254, 1076 cm^{-1}; ESI MS: $m/z = 656.5$ (M^+ + Na; 100%).

4.6. *3α-t-Butyldimethylsilyloxy-24-mercapto-5β-cholane-7α,12α-diol (9; $C_{30}H_{56}O_3SSi$)*

To a solution of 200 mg of **8** (0.32 mmol) in 16 ml of anhydrous THF, 54 mg of $LiAlH_4$ (1.42 mmol) was added under Ar and the mixture was stirred at room temperature for 16 h. Then several drops of water were added and the precipitate was filtered off. Purification with column chromatography gave pure **9** (128 mg) in 77% yield (elution with *n*-hexane/ethyl acetate 87:13). Colorless crystals, mp 104–106 °C (*n*-hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.98$ (m, 1H,

12β-H), 3.84 (m, 1H, 7β-H), 3.43 (m, 1H, 3β-H), 2.51 (m, 2H, C$\underline{H}_2$SH), 0.98 (d, $J = 6.4$ Hz, 3H, 21-CH_3), 0.88 (s, 3H, 19-CH_3 and s, 9H *t*-Bu), 0.69 (s, 3H, 18-CH_3), 0.07 (s, 6H, Si$(CH_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 72.91$ (CH), 72.88 (CH), 68.3 (CH), 47.3 (CH), 46.5 (C), 42.1 (CH), 41.6 (CH), 40.0 (CH_2), 39.6 (CH), 35.4 (CH_2), 35.2 (CH), 34.7 (C), 34.6 (CH_2), 31.0 (CH_2), 30.7 (CH_2), 29.7 (CH_2), 28.4 (CH_2), 27.6 (CH_2), 26.8 (CH), 25.9 (3 CH_3), 25.1 (CH_2), 23.1 (CH_2), 22.6 (CH_3), 18.3 (C), 17.7 (CH_3), 12.5 (CH_3), -4.58 (CH_3), -4.64 (CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 3614$, 3467, 1254, 1091, 837 cm^{-1}; ESI MS: $m/z = 547.4$ ($M^+ + Na$; 100%). The removal of the *TBDMS* protecting group was carried out according to the procedure described for **7**.

4.7. *Di(3α,7α,12α-trihydroxy-5β-cholan-24-yl) disulfide (3; $C_{48}H_{82}O_6S_2$)*

Compound **2** (20 mg; 0.05 mmol) was dissolved in 2 ml of CH_2Cl_2 containing 5 µl of triethylamine and allowed to stay for 5 h at room temperature. After this time, the solvent was evaporated and the product was crystallized from *n*-heptane/ethyl acetate mixture giving 19 mg (95% yield) of **3**. Colorless crystals, mp 148–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.01$ (m, 2H, 12β-H), 3.87 (m, 2H, 7β-H), 3.47 (m, 2H, 3β-H), 2.51 (m, 4H, CH_2S), 1.00 (d, $J = 6.6$ Hz, 6H, 21-CH_3), 0.91 (s, 6H, 19-CH_3), 0.71 (s, 6H, 18-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 73.1$ (2 CH), 71.8 (2 CH), 68.4 (2 CH), 47.2 (2 CH), 46.3 (2 C), 41.5 (2 CH), 41.4 (2 CH), 39.44 (2 CH), 39.42 (2 CH_2), 35.30 (2 CH_2), 35.28 (2 CH), 34.7 (2 C), 34.63 (2 CH_2), 34.60 (2 CH_2), 30.8 (2 CH_2), 30.3 (2 CH_2), 28.1 (2 CH_2), 27.6 (2 CH_2), 26.3 (2 CH), 25.1 (2 CH_2), 23.2 (2 CH_2), 22.4 (2 CH_3), 17.7 (2 CH_3), 12.4 (2 CH_3) ppm; IR ($CHCl_3$): $\bar{\nu} = 3611$, 3416, 1076, 1041 cm^{-1}; HRMS: calc. mass for $C_{48}H_{82}NaO_6S_2$: 841.5451, found: 841.5450.

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