Chapter II
EXPERIMENTAL

2.1 General Procedures

Melting points were determined with a Fisher-John melting point apparatus and are uncorrected. The FTIR spectra were recorded on Nicolet model Impact 140 spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained from Fourier Transformed Nuclear Magnetic Resonance Spectrometer of a Bruker, model AC-F 200 and a Joel, model JNM-A500, as solutions in deuterochloroform or DMSO-d_6 with tetramethylsilane (TMS) as an internal reference. Gas chromatograph analyses were carried out on a Shimudzu gas chromatograph GC-9A or on a Hewlett Packard gas chromatograph 5890 instrument equipped with flame ionization detector (FID) with N_2 or He as a carrier gas. Carbowax 20M column and DB-wax capillary column were used for chromatography. Elemental analysis (EA) was analyzed by CHNS/O Analyser of Perkin Elmer PE2400 series II. Mass spectrometry (MS) analysis was conducted on Fisson Instrument Model Trio 2000. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}). Flash column chromatography was proceeded on silica gel (Merck, Kieselgel 60, 230-400 mesh).

2.2 Chemicals

Solvents were used either as purchased or dried and purified by standard methods under dry nitrogen. Tetrahydrofuran was dried over sodium benzophenone in the presence of sodium metal, distilled and stored under nitrogen over molecular sieve.[30] Acetone was refluxed with phosphorus pentoxide (10g/L) for 2 hours and distillated at atmospheric pressure, to remove water: bp. 55-56°C / 760 mmHg. Distilled toluene may be stored over Na wire or left in the presence of a type 4A grade of molecular sieve, pure toluene has bp. 110.5°C / 760 mmHg.[31]

Other reference compounds and starting materials were obtained from Fluka Chemical Co., Inc. and Aldrich Chemical Co., Inc.

2.3 Typical Procedure for the Deoxygenation of Model Compounds

To a solution of the starting alcohol derivative (0.4 mmol) in dry toluene (4 mL), diphenylsilane (0.8 mmol, 147 μL) was added under nitrogen. Then the solution was brought to boil and treated with 50 μL portions of a solution of AIBN in toluene at 20 min intervals (262 mg AIBN was dissolved in 5.0 mL dry toluene). The reaction was monitored by TLC. When the reaction was complete, the mixture was work-up and the deoxygenated product was determined by gas chromatograph.

2.4 General Work-up Procedure

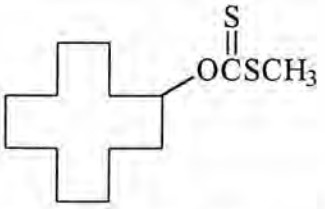
An aliquot of the reaction mixture 1.0 mL was acidified with 25% H_2SO_4. The mixture was then extracted with diethyl ether (2 × 2 mL). The ethereal extract was separated and successively washed with saturated sodium hydrogen carbonate 2.0 mL. Finally, the ethereal extract was dried over anhydrous sodium sulfate. The resulting solution was analyzed by gas chromatograph after addition of the exact amount of an appropriate internal standard.

2.5 Typical Procedure for the Deoxygenation of Natural Products

To a solution of the starting xanthate derivative (0.4 mmol) in dry toluene (3 mL), diphenylsilane (2 mmol, 367 μL) was added under nitrogen. Then the solution was brought to boil and treated with 200 μL portions of a solution of AIBN in toluene at 20 min intervals (13.1 mg AIBN was dissolved in 1.0 mL dry toluene). The reaction was monitored by TLC. When the reaction was complete, the solvent was evaporated in vacuum and the deoxygenated product was separated by silica gel column chromatography.

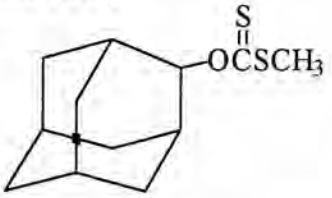
2.6 Synthesis of Starting Materials

_O_-Cyclododecyl _S_-methyl xanthate[32] (3a)



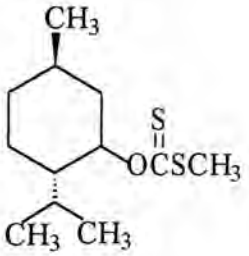
To a solution of cyclododecanol (3.68 g, 20 mmol) in THF (40 mL) was added *n*-butyllithium (12.5 mL, 1.6 M in THF, 20 mmol) at 0°C under N_2. The solution was stirred for 30 min at 0°C before the addition of CS_2 (1.24 mL, 21 mmol). The mixture was then stirred at room temperature for 4 h followed by the addition of MeI (1.3 mL, 21 mmol). The final solution was further stirred for 1 h at room temperature. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$ and brine sucessively. After drying over anhydrous $MgSO_4$ and evaporation of the solvent, the residue was crystallized from CH_2Cl_2-EtOH to give 1.87 g (70%) of the xanthate, m.p. 47-48°C (lit.[32] 48-48.5°C). IR (KBr) 2991, 2945, 2858, 1465, 1210 and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.20-1.45 (m, 18 H), 1.60-1.90 (m, 4H), 2.50 (s, 3H, SMe) and 5.85-5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 18.6, 20.9 (2 C), 23.2 (2 C), 23.4 (2 C), 23.7, 23.9, 28.7 (2 C), 82.8 and 215.3; MS *m/e* (relative intensity) 276 (M^+), 166, 111, 97, 83, 69, 55 and 41.

2-adamanthyl *S*-methyl xanthate (3b)



The general procedure was carriered out in the similar manner to the preparation of *O*-cyclododecyl *S*-methyl xanthate **(3a)**. 2-Adamanthyl *S*-methyl xanthate **(3b)** as white needle 76%, m.p.101-102°C was obtained from the recrystallization by EtOH-CH_2Cl_2. IR (KBr) 2911, 2879, 1218 and 1071 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.53-2.22 (m, 12H), 2.55 (s, 3H, SMe) and 5.67 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 18.6, 26.9, 27.1, 31.4, 32.1 (2C), 36.2 (2C), 37.2, 86.8 and 214.6.

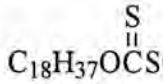
***O*-menthyl *S*-methyl xanthate (3c)**



Similar procedures as described above were used to carry out for the synthesis of *O*-menthyl *S*-methyl xanthate **(3c)**. Crystallized from EtOH-CH_2Cl_2 yielded methyl xanthate derivative as silkly yellow needles 63%, m.p. 38-39°C. IR (KBr) 2957, 2919, 2866, 1465, 1254, 1218 and 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.78-1.84 (m, 17H), 2.18 (s, 1H), 2.52-2.55 (m, 3H, SMe) and 5.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 14.8, 18.8, 20.6, 22.0, 23.8, 26.6, 31.3, 34.2, 39.6, 47.3, 84.5 and 215.4. Elemental analysis found %C 58.49 ; %H 9.06 ; calculated for $C_{12}H_{22}S_2O$: %C 58.49; %H 9.00.

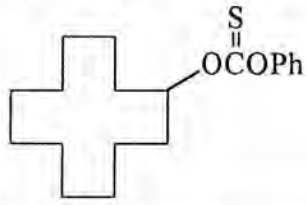
The FT-IR, ^1H NMR and ^{13}C NMR spectra are shown in Figs 1, 2 and 3.

***O*-octadecyl *S*-methyl xanthate (3d)**



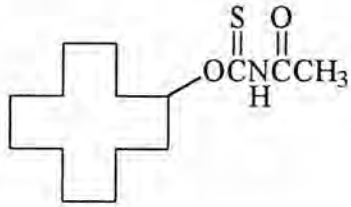
The foregoing procedure was followed; crystallized from hexane - CH_2Cl_2 gave methyl xanthate derivative as glossy orange plates 68%, m.p. 36-37°C. IR (KBr) 2962, 2919, 2845, 1481, 1234, 1068 and 721 cm^{-1} ; ^1H NMR ($CDCl_3$) δ (ppm) : 0.83-0.96 (m, 3H), 1.19-1.29 (m, 30H), 1.54-1.81 (m, 2H), 2.54 (s, 3H, SMe) and 4.54-4.60 (t, J = 6.65 Hz, 2H) ; ^{13}C NMR ($CDCl_3$) δ (ppm) : 6.9, 14.1, 18.9, 20.0, 22.7, 25.9, 28.2, 29.2, 29.4, 29.5 (2C), 29.6 (2C), 29.7 (2C), 30.1, 31.9, 36.7, 74.3 and 215.9.

***O*-Cyclododecyl *O'*-phenylthioxocarbonate[32] (6a)**



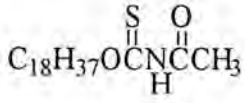
To a solution of cyclododecanol (0.92 g, 5 mmol) and dry pyridine (15 mL, 19 mmol) in dry CH_2Cl_2 (30 mL) was added phenyl chlorothionoformate (1.0 mL, 5.5 mmol) under N_2. Then the solution was stirred for 2 h at room temperature. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. After filtration and concentration in vacuum the residue was crystallized from EtOH to give 1.20 g (75 %) of the thionocarbonate: m.p. 60-62°C (lit.[32] 60-62°C). IR (KBr) 2937, 2863, 1488, 1253 and 1189 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.25-1.60 (m, 18 H), 1.64-2.00 (m, 4H), 5.45-5.58 (m, 1H), 7.04-7.18 (m, 2H), 7.20-7.30 (m, 1H) and 7.32-7.45 (m, 2H); ^{13}C NMR($CDCl_3$) δ (ppm) : 20.9 (2C), 23.2 (2C), 23.4 (2C), 23.6, 23.9 (2C), 28.5 (2C), 83.9, 122.1 (2C), 126.4, 129.3 (2C), 153.4 and 194.4.

***O*-Cyclododecyl *N*-Acetylthioxocarbamate[33] (4a)**



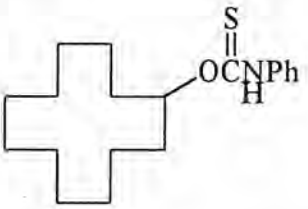
A mixture of dried KSCN (0.58 g, 6 mmol) and acetyl chloride (0.39 g, 5 mmol) in anhydrous acetone (5 mL) was stirred for 10 min, followed by the addition of cyclododecanol (0.92 g, 5 mmol), and the mixture was then refluxed overnight. After evaporation of acetone in *vacuo*, the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL), and the organic phase separated and dried ($MgSO_4$). After removal of solvent, the residue was chromatographed on silica gel. Elution with hexane/EtOAc (9:1) gave white crystal 1.13 g (66%) of the acetylthiocarbamate: m.p. 111-112°C (lit[33] 108-109°C). IR (KBr) 3211, 2929, 1710, 1523, 1298 and 1201 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.33-1.88 (m, 22 H), 2.30 (s, 3H), 5.58-5.64 (m, 1H) and 8.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 20.9, 21.0, 23.1, 23.3 (2C), 23.8, 24.0, 24.2, 25.6, 28.6, 32.5, 69.2, 83.0, 168.7 and 188.1.

***O*-Octadecyl *N*-acetylthioxocarbamate (4d)**



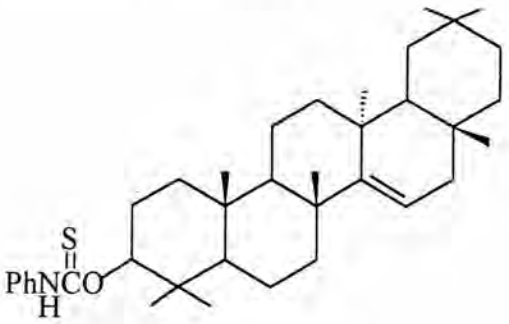
The method described in the foregoing preparation was followed, the cyclododecanol being replaced by 1-octadecanol. Chromatographed on silica gel, elution with hexane/ethyl acetate (9:1) gave thioxocarbamate derivative 63 %, m.p.66-67°C (lit.[3] 64-65 °C). IR (KBr) 3223, 2935, 1704, 1543, 1478 and 1219 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.88-1.80 (m, 23H), 2.39 (s, 3H), 4.52 (t, J = 6.7 Hz, 2H), and 8.54 (s, 1H) ^{13}C NMR ($CDCl_3$) δ (ppm) : 14.1, 22.7, 23.3, 25.7, 28.1, 28.5, 29.2 (2C), 29.3, 29.4, 29.7, 30.4, 31.9, 32.8, 33.9, 63.1, 64.7, 72.1, 73.5, 168.6 and 188.6.

_O_-Cyclododecyl _N_-phenylthioxocarbamate[34] (5a)



To a solution of cyclododecanol (1.84 g, 11 mmol) and phenyl isothiocyanate (1.49 g, 11 mmol) in anhydrous THF (10 mL) was added NaH (60% in oil, 0.44 g, 11 mmol) and the reaction was monitored by TLC. When the reaction was complete, the solvent was removed in *vacuo* and the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with hexane/EtOAc (9/1) gave cyclododecyl *N*-phenylthioxocarbamate (2.47 g, 75%) as a colorless solid plate, m.p.116-117°C (lit.[34] 115-116°C). IR (KBr) 3186, 3037, 2936, 2850, 1598, 1544, 1400, 1299, 1202, 1018, 760 and 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.35-1.87 (m, 22 H), 5.64-5.72 (m, 1H) 7.28-7.35 (m, 5H aromatic) and 8.22 (br, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 20.9, 21.0, 23.1, 23.2, 23.4 (2C), 23.8, 23.9, 24.0, 24.2, 28.8, 29.4, 82.5, 118.6, 121.5, 123.2, 125.2, 129.0, 137.3 and 188.2.

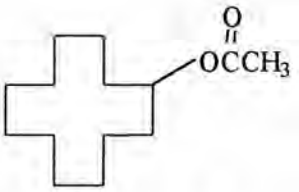
Taraxeryl *N*-phenylthioxocarbamate (4h)



The method described in the foregoing preparation was followed, the cyclododeccanol being replaced by taraxerol (**1h**). Recrystallization from ethanol gave taraxeryl *N*-phenylthioxocarbamate (**4h**) 76% as white solid plates, m.p. 249-250°C. IR (KBr) 3385, 2940, 1609, 1531, 1388, 1168, 769 and 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm) : 0.80-1.99 (m, 46 H), 5.11-5.19 (dd, J = 4.94, 4.03 Hz, 1H), 5.48-5.54 (dd, J = 2.95, 2.95 Hz, 1H) and 7.24-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 15.5, 17.5 (2 C), 18.6, 18.8, 21.3, 23.0, 25.9, 27.1, 27.9, 28.0, 28.8, 29.8, 29.9, 33.1, 33.3, 33.7, 35.1, 35.8, 36.7, 37.3, 37.5, 37.7, 37.9, 38.3, 39.0, 41.2, 48.8, 49.1, 55.6, 116.9, 117.0, 125.3, 125.5, 129.0, 129.6 and 157.9.

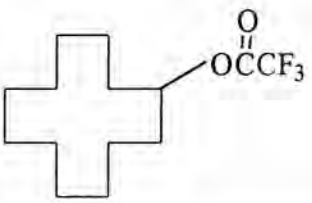
The FT-IR, ^{1}H NMR and ^{13}C NMR spectra are shown in Figs 4, 5 and 6.

***O*-Cyclododecyl acetate (7a)**



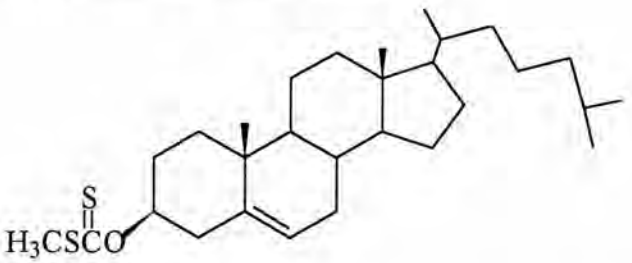
To a solution of cyclododecanol (1.84 g, 10 mmol) in dry pyridine 2 mL was added acetic anhydride (1.89 g, 20 mmol) under N_2. Then the solution was stirred for 3 h at reflux temperature. The reaction mixture was partitioned between CH_2Cl_2 (20 mL) and H_2O (20 mL), then the organic layer was washed with 1M HCl, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. After filtration and concentration in vacuum, the residue was obtained as light yellow oil (60%). IR (neat) 2942, 2877, 1723, 1502 and 1243 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.30-1.71 (m, 22 H), 1.97 (s, 3H) and 4.89-4.99 (m, 1H); ^{13}C NMR δ (ppm) : 20.9 (2C), 21.3, 23.2 (2C), 23.3 (2C), 23.8 (2C), 24.1 (2C), 29.0, 73.6 and 172.3.

***O*-Cyclododecyl trifluoroacetate (8a)**



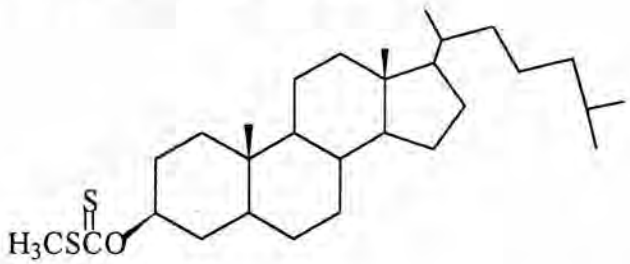
To a solution of cyclododecanol (1.84 g, 10 mmol) in dry pyridine 2 mL was added trifluoroacetic anhydride (2.82 mL, 20 mmol) under N_2. Then the solution was stirred for 3 h at reflux temperature. The reaction mixture was partitioned between CH_2Cl_2 (20 mL) and H_2O (20 mL), then the organic layer was washed with 1M HCl, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. After filtration and concentration in vacuum, the residue was attained as orange oil (79%). IR (neat) 2945, 2889, 1777, 1475, 1227 and 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 1.54-1.88 (m, 22H) and 5.11-5.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 20.5 (2 C), 20.8, 23.0, 23.2, 23.8, 23.9 (2 C), 24.1, 28.6 (2 C), 32.1, 77.9 and 157.6.

Cholesteryl *S*-methyl dithiocarbonate[35] (3e)



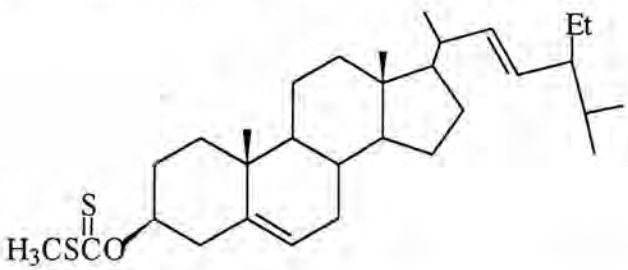
To a solution of cholesterol (3.9 g, 10 mmol), potassium *t*-butoxide (12.5 mL), *n*-butyllithium (12.5 mmol, 1.6 M solution in THF), and imidazol (18 mg, 0.3 mmol) in anhydrous THF 100 mL under N_2 was added CS_2 (1.8 mL, 30 mmol) at 0 °C. The reaction mixture was stirred for 4 h at room temperature, and then cooled to 0°C, and methyl iodide (1.9 mL, 30 mmol) was added. After a further stirring for 4 h at room temperature, the reaction mixture was washed with 1M HCl, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was crystallized from EtOH-CH_2Cl_2 to give 4.79 g (68%), m.p. 129-130°C. IR (KBr) 2945, 2835, 2156, 1458, 1210 and 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.86-1.35 (m, 41 H), 1.54 (s, 1 H), 2.54 (s, 3 H) and 5.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 11.8, 18.7, 18.9, 19.3, 21.1, 22.6, 22.8, 23.8, 24.3, 27.2, 28.0, 28.2, 31.9, 35.8, 36.2, 36.7, 36.9, 37.4, 39.5, 39.7, 42.3, 50.0, 56.1, 56.7, 83.6, 123.2, 139.2 and 215.1.

Cholestanyl *S*-methyl dithiocarbonate (3f)



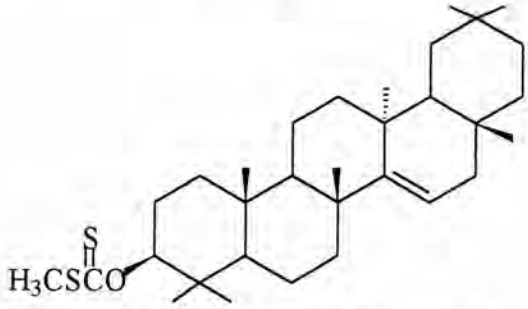
The method described in the foregoing preparation was followed, the cholesterol (**1e**) being replaced by cholestanol (**1f**). Recrystallization from EtOH-CH_2Cl_2 yielded cholestanyl *S*-methyl dithiocarbonate (**3f**) 66%, m.p. 89°C. IR (KBr) 2945, 2847, 1467, 1219 and 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.67-2.55 (m, 47 H), 2.55 (s, 3 H) and 5.50 (1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 12.1, 12.3, 18.7 (2 C), 18.8, 21.2, 22.6, 22.8, 23.8, 24.2, 26.8, 28.0, 28.2, 28.6, 32.0, 33.3, 35.5, 35.8, 36.2, 36.7, 39.5, 40.0, 42.6, 44.6, 54.2, 56.3, 56.4, 83.7 and 215.3.

Stigmasteryl *S*-methyl dithiocarbonate (3g)



The foregoing procedure was followed; the cholesterol (**1e**) being replaced by stigmasterol (**1g**). Crystallized from EtOH-CH_2Cl_2 gave stigmasteryl *S*-methyl dithiocarbonate (**3g**) 70%, m.p. 91-92°C. IR (KBr) 2962, 2832, 1465, 1216 and 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.66-1.05 (m, 46 H), 1.58 (s, 1H), 2.57 (s, 3H) and 5.45 (s, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 11.9, 12.0, 18.8, 18.9, 19.0, 19.3, 19.8, 20.2, 21.1, 23.1, 24.3, 26.1, 27.2, 28.2, 29.2, 31.9 (2C), 33.9, 36.1, 36.7, 36.9, 37.4, 39.7, 42.3, 45.8, 50.0, 56.0, 56.7, 83.6, 123.2, 139.2 and 215.1.

Taraxeryl *S*-methyl dithiocarbonate (3h)



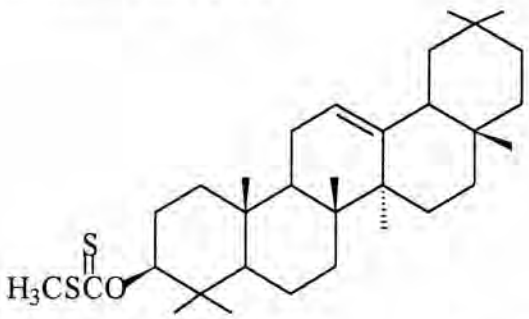
The procedure described above was followed; the cholesterol (**1e**) being replaced by taraxerol (**1h**). Crystallized from EtOH-CH_2Cl_2 furnished taraxeryl *S*-methyl dithiocarbonate (**3h**) 78%, m.p. 241-242°C. IR (KBr) 2939, 2850, 1467, 1221, 1217 and 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.80-1.72 (m, 44 H), 1.88-1.93 (m, 2H), 2.04-2.06 (dd, J = 6.5, 12.5 Hz, 1H), 2.53 (s, 3H), 5.29-5.33 (dd, J = 4.5, 5.0 Hz, 1H) and 5.53-5.56 (dd, J = 3.5, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) 15.5, 17.3, 17.5, 18.6, 18.8, 21.3, 22.4, 25.9, 27.9, 28.8, 29.8, 29.9, 33.1 (2C), 33.3, 33.6, 35.1, 35.7, 36.7, 37.2, 37.5, 37.7, 37.9, 38.6, 39.0, 41.2, 48.8, 49.1, 55.7, 91.4, 117.0, 157.8 and 215.6. Elemental analysis found %C 74.37; %H 10.15; calculated for $C_{32}H_{52}S_2O$: %C 74.36; %H 10.14.

The FT-IR, ^1H NMR and ^{13}NMR spectra are displayed in Figs 7, 8 and 9.

Hydrolysis of β-amyrin palmitate (1i)[36]

A solution of 10% ethanolic KOH (40 mL) was added to β-amyrin palmitate (2.4 g, 3.64 mmol) and a mixture was heated under refluxing on a water bath for 4 h (check whether the reaction was complete or not by TLC). Evaporation of ethanol gave a solid which was further extracted with diethyl ether, 150 mL, three times. The combined diethyl ether was dried over anhydrous $CaCl_2$. Evaporation of the solvent furnished a solid with pale yellow oil. After recrystallization this solid with a mixture of chloroform and CH_3OH, bright white needle designated as β-amyrin (1.17 g., 76%) m.p. 196-198°C (lit.[36] 196-198°C), was obtained. IR (KBr) 3290, 2950, 2923, 2857, 1645, 1467, 1380, 1361, 1040, 1021 and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.84 (s, 3H), 0.88 (m, 12H), 0.96-0.98 (m, 6H), 1.14 (s, 3H), 3.23 (t, J = 7.69 Hz, 1H) and 5.19 (t, J = 3.18 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ (ppm) : 15.5 (2 C), 16.8, 18.4, 23.5, 23.7, 25.9, 26.2, 26.9, 28.1, 28.4, 31.0, 32.5, 32.7, 33.3, 34.7, 36.9, 37.1, 38.6, 38.7, 39.6, 41.7, 46.9, 47.2, 47.6, 55.1, 79.0, 121.7 and 145.1.

β-amyryl *S*-methyl dithiocarbonate (3i)



The general procedure was carriered out in the similar manner to the preparation of cholesteryl *S*-methyl dithiocarbonate (**3e**), the cholesterol (**1e**) being replaced by β-amyrin (**1i**). Crystallized from EtOH-CH_2Cl_2 yielded β-amyryl *S*-methyl dithiocarbonate (**3i**) 67%, m.p. 175-176°C. IR (KBr) 2950, 1482, 1235 and 1059 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.78-0.97 (m, 41H), 1.10 (s,1H), 1.38 (s, 1H), 1.58 (s, 2H), 1.81-1.93 (m, 2H), 2.51 (s, 3H), 5.15 (s, 1H) and 5.25-5.37 (dd, J = 15.00, 13.33 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 16.1, 17.1, 17.8, 18.2, 19.0, 22.9, 23.8, 24.2, 25.9, 26.3, 27.2, 28.7, 29.1, 31.0, 33.0, 34.2, 35.1, 36.9, 37.2, 38.3, 38.9, 40.0, 41.5, 46.4, 47.1, 47.8, 55.5, 91.9, 121.8, 146.7 and 216.3.

Deoxygenation of Cholesteryl *S*-methyl dithiocarbonate (2e)

The method of deoxygenation of natural products was described in the foregoing preparation. Crystallized from absolute ethanol yielded 5-cholestene (**2e**) 62% m.p. 89-90°C (lit.[37] 89-90°C). IR (KBr) 2934, 1470, 1230 and 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm) : 0.66-2.38(m, 45H) and 5.23 (s, 1H) ; ^{13}C NMR ($CDCl_3$) δ (ppm) : 11.9, 18.7, 19.5, 20.8, 22.6 (2 C), 22.8, 23.8, 24.3, 28.0, 28.1, 28.3, 31.8, 31.9, 32.9, 35.8, 36.2, 37.5, 39.5, 39.9 (2 C), 42.3, 50.6, 56.2, 56.9, 119.0 and 143.7.

Deoxygenation of Cholestanyl *S*-methyl dithiocarbonate (2f)

The foregoing procedure was followed; the cholesteryl *S*-methyl dithiocarbonate (**3e**) being replaced by cholestanyl *S*-methyl dithiocarbonate (**3f**). Crystallized from absolute ethanol provided 5α-cholestane (**2f**) 55% m.p. 78-80°C (lit.[37] 80-80.5°C). IR (KBr) 2934, 1472, 1388 and 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm) : 0.62-1.97 (m, 48 H) ; ^{13}C NMR ($CDCl_3$) δ (ppm) : 12.1, 12.2, 18.7, 20.8, 22.2, 22.6, 22.8, 23.8, 24.2, 26.9, 28.0, 28.2, 29.1, 32.2, 35.5 (2C), 35.8, 36.2, 38.7, 39.5, 40.0, 40.1, 47.0, 54.8, 56.3, 56.6 and 75.8.

Deoxygenation of Stigmasteryl *S*-methyl dithiocarbonate (2g)

The procedure as previously described was followed ; the cholesteryl *S*-methyl dithiocarbonate (**3e**) being replaced by stigmasteryl *S*-methyl dithiocarbonate (**3g**). Crystallized from absolute ethanol gave stigmastane or sitostane (**2g**) 51% m.p. 84-85°C (lit.[37] 85.4-85.7°C). IR (KBr) 2934, 2960, 2878, 1460 and 1388 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm) : 0.67-1.56 (m, 51 H) and 4.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 11.9, 12.0, 18.8, 19.0, 19.5, 19.8, 20.8, 22.6, 23.1, 24.3, 26.1, 28.1, 28.3, 29.2, 31.9 (2C), 32.9, 34.0, 36.2, 37.5, 39.9 (2C), 42.3, 45.9, 50.6, 56.1, 56.9, 128.1, 135.7 and 143.7.

Deoxygenation of Taraxeryl *S*-methyl dithiocarbonate and Taraxeryl-*N*-phenylthioxocarbamate (2h)

Followed the foregoing procedure, taraxeryl *S*-methyl dithiocarbonate (**3h**) and taraxeryl *N*-phenylthioxocarbamate (**4h**) were reduced with Ph_2SiH_2 in toluene. Crystallized from absolute ethanol yielded taraxerene (**2h**) 94 and 93%, respectively m.p.197-198°C. IR (KBr) 3052, 2935, 2115, 1480, 1388, 1265, 1065 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.82-1.94 (m, 29H), 5.45 and 5.49 (d, J = 7.86 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ (ppm) : 15.4, 17.5, 18.4, 19.1, 21.3, 21.6, 25.9, 28.8, 29.8, 33.1, 33.3, 33.7, 35.1, 35.8, 36.7, 37.7, 39.4, 41.3, 42.1, 48.7, 49.3, 56.6, 116.6, 127.9, 130.5 and 134.5.

The FT-IR, ^1H NMR and ^{13}C NMR spectra are exhibited in Figs 10,11 and 12.

Deoxygenation of β-amyryl-*S*-methyl dithiocarbonate (2i)

Similar procedures as previously described were used to carry out the deoxygenation reaction. Crystallized from absolute ethanol furnished β-amyrane (**2i**) 68% m.p. 139-140°C. IR (KBr) 3293, 2945, 1472, 1380 and 1022 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) : 0.73-1.89 (m, 48 H), 4.91 (s, 1H) and 5.17 (t, J = 13.33 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 15.5, 16.9, 18.5, 18.7, 21.8, 23.5, 23.7, 26.0, 26.1, 27.0, 28.4, 31.1, 32.5, 32.6, 33.4 (2C), 34.7, 37.2, 40.2, 42.0, 46.8, 47.2, 47.7, 56.1, 122.0, 128.1, 129.9, 135.7 and 145.2.

Deoxygenation of *O*-menthyl *S*-methyl xanthate (2c)

The general procedure was carried out in the similar manner to the preparation of 5-cholestene (**2e**); the cholesteryl *S*-methyl dithiocarbonate (**3e**) being replaced by *O*-menthyl *S*-methyl xanthate (**2c**). Separated a pure product *via* column chromatography obtained *trans*-1-methyl-4-isopropylcyclohexane (**2c**) as clear liquid which was quantified by gas chromatograph : 75% yield. ^1H NMR ($CDCl_3$) δ (ppm) : 0.84 (s, 3H), 0.87 (s, 4H), 1.24 (s, 6H) and 1.55 (s, 7H); ^{13}C NMR ($CDCl_3$) δ (ppm) : 14.1, 22.7, 26.6, 27.6, 28.8, 29.7 and 31.6.

The ^1H NMR and ^{13}C NMR spectra are shown in Figs 13 and 14.