ORGANOTIN SUBSTITUTED CHOLESTERYL ETHERS AND ESTERS

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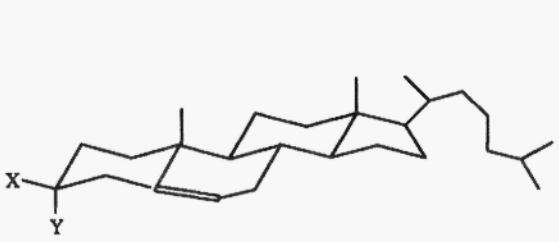
ABSTRACT

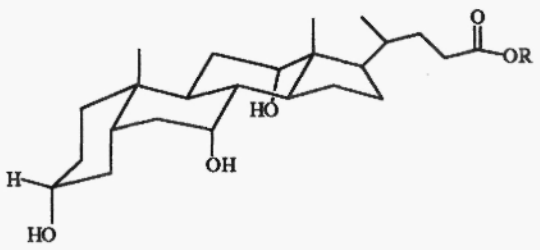
3β-[(Triphenylstannyl)methoxy]cholest-5-ene **7**, 3β-[3-(triphenylstannyl)propoxy]cholest-5-ene **8** and 3β-[3-(triphenylstannyl)propanoato]cholest-5-ene **9** have been synthesized. Characterisation of **7-9** and their iodophenylstannyl analogues has been generally carried out using ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. As shown by X-ray crystallography, **7** exists as discrete molecules with a distorted tetrahedral tin centre.

INTRODUCTION

Interest in organotin derivatives of natural products has been maintained over a long period of time for diverse reasons. Stannylated steroids have been studied with respect to biological activities (especially anti-tumour activities),[1-3] chemical reactivities[4] and structures.[3,5-7] The linking of stannyl moieties to steroid residues in these molecules has involved both Sn-O bonds [2,8,9] and Sn-C bonds.[3-7,10-12] Types of tin-oxygen bonded steroids include organotin alkoxides,[8,9] *e.g.*, **1** derived from cholesterol **2** and organotin carboxylates,[9] *e.g.*, **3** derived from cholic acid **4**. Reported tin-carbon linked triorganostannyl steroids include the non-functionalised saturated alkyl compounds, 3α- and 3β-triorganostannylcholest-5α-anes,[10] and their mono-ene analogues, 3α- and 3β-triphenylstannylcholest-5-enes (**5**: α-Ph_3Snchol; **6**: β-Ph_3Snchol)[10,12] and 3α-(triphenylstannyl)cholest-4-ene.[3] 7α-(Triphenylstannyl)cholest-5-en-3β-ol, 7α-(triorganostannyl)cholest-5-en-3-one (organo group = Ph or Bu), [[17(21)]-3-methoxy-19-norpregna-1,3,5(10),17(20)-pentaen-21-yl]triphenylstannane,[11] [(Z)-17-(2-triphenylstannyl)vinyl-4-estren-17β-ol [5] and (20Z)-3-methoxy-17-[2-(triphenyl-stannyl)vinyl]estra-1,3,5(10)-trien-17β-ol [7] illustrate well the diversity of functionalised derivatives. Iodoorganostannyl-steroids have also been obtained, including iodophenyl analogues of **5** and **6**, *i.e.* α- and β-I_nPh_{3-n}Snchol.

As a continuation of our studies on stannylated steroids, we have investigated compounds in which the organotin and cholesterol moieties are indirectly linked, *i.e.* R_3Sn-□-chol (□ = a linker group). Of particular interest were compounds, which could provide in good yields mono- and di-iodo-phenylstannyl-analogues, $X_nPh_{3-n}Sn$-□-(chol), suitable for further derivatisation. We now wish to report our findings on compounds **7-9**, in which the linker groups, □, are CH_2O, $CH_2CH_2CH_2O$ and $CH_2CH_2C(O)O$.





1: X = Ph_3SnO; Y = H
2: X = HO; Y = H
5: X = H; Y = Ph_3Sn
6: X = Ph_3Sn; Y = H
7: X = Ph_3SnCH_2O; Y = H
8: X = $Ph_3Sn(CH_2)_3O$; Y = H
9: X = $Ph_3SnCH_2CH_2C(O)O$; Y = H

3: R = Ph_3Sn
4: R = H

EXPERIMENTAL

Melting points were measured using a Kofler hot-plate microscope and are uncorrected. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were measured on a Bruker 250 MHz instrument; J values are in Hz. The numbering scheme used for the NMR data is shown in Figure 1. IR spectra were recorded on a Nicolet 205 Fourier-transform instrument. (Iodomethyl)triphenylstannane[13] and (3-chloropropyl)triphenylstannane[14] were prepared by published procedures.

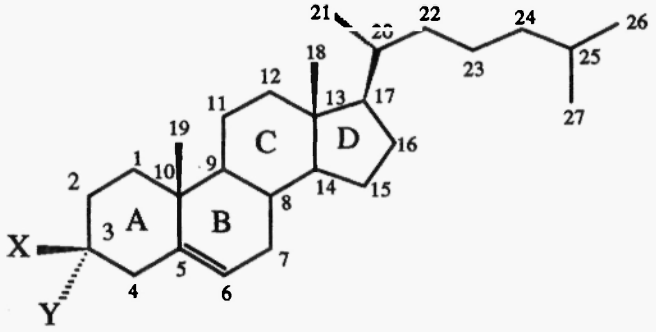


Figure 1. Numbering scheme for cholesteryl derivatives.

Allyl cholesteryl ether

Sodium hydride (55-60% suspension in mineral oil, 2.5g) was added to a stirred solution of cholesterol (7.00g, 0.018mol) and allyl bromide (6.56g, 0.054mol) in anhydrous DMF (25ml). The mixture was stirred under nitrogen at room temperature overnight. Methanol (30ml) was added to destroy the excess sodium hydride, and the mixture stirred for another 20 min before water (30ml) was added. The mixture was extracted with diethyl ether (3 x 30ml). The combined ethereal extracts were washed with water (3 x 30ml), dried over anhydrous magnesium sulfate and rotary evaporated to leave an oil, which was extracted with ethanol. The product crystallised on concentrating and cooling the EtOH extracts, m.p. 75-77°C, lit.[15] m.p. 78-79°C; yield 3.57g, 46.6%.

^{13}C NMR ($CDCl_3$) : δ 11.7 [C-18], 18.6 [C-21], 19.3 [C-19], 21.0 [C-11], 22.4 [C-26], 22.7 [C-27], 23.7 [C-23], 24.2 [C-15], 27.9 [C-2], 28.1 [C-25], 28.3 [C-12], 31.8 [C-8], 31.8 [C-7], 35.6 [C-20], 36.1 [C-22], 36.8 [C-1], 37.1 [C-4], 39.0 [C-10], 39.4 [C-24], 39.7 [C-16], 42.2 [C-13], 50.1 [C-9], 56.0 [C-17], 56.7 [C-14], 68.9 [CH_2O] 78.4 [C-3], 116.4 [CH_2=], 121.4 [C-6], 135.3 [CH=],140.8 [C-5].

Acrylyl chloride.

A mixture of acrylic acid (10.0g, 0.14mol), benzoyl chloride (39.1, 0.28mol), and hydroquinone (0.023g, $7x10^{-5}$mol) was distilled using a Vigreux column into a receiver containing hydroquinone (0.023g, $7x10^{-5}$mol) at -10°C. The fraction distilling below 85°C was initially collected and redistilled to give acrylyl chloride, b.p. 72-74°C, lit.[16] m.p. 74-77°C; yield 10.34g, 82%.

Cholesteryl 2-propenoate (cholesteryl acrylate).

A mixture of cholesterol (4.13g, 11mmol), acrylyl chloride (2.90g, 32mmol), *N,N*-dimethylaniline (2.58g, 21mmol) and hydroquinone (0.05g) was refluxed for 2 h. The solution was cooled and filtered. The filtrate was evaporated *in vacuo* to leave a green/yellow residue, which was crystallised from chloroform/acetone (1:3 v:v); m.p.125-127°C lit.[17] m.p. 125°C; yield 1.85g, 39.9%).

^{13}C NMR ($CDCl_3$) : δ 11.9 [C-18], 18.8 [C-21], 19.3 [C-19], 21.1 [C-11], 22.6 [C-26], 22.9 [C-27], 23.9 [C-23], 24.3 [C-15], 27.8 [C-2], 28.0 [C-25], 28.3 [C-12], 31.9 [C-8], 31.9 [C-7], 35.8 [C-20], 36.2 [C-22], 36.6 [C-1], 37.0 [C-4], 38.0 [C-10], 39.5 [C-24], 39.7 [C-16], 42.3 [C-13], 50.0 [C-9], 56.2 [C-17], 56.7 [C-14], 74.1 [C-3], 122.7 [C-6], 129.1 [CH=], 130.2 [CH_2=], 139.6 [C-5], 165.6 [CO_2].

Triphenyltin hydride

To a stirred suspension of lithium aluminium hydride (2.0g) in anhydrous diethyl ether (100ml) at 0°C, was added a solution of triphenyltin chloride (20.0g, 52mmol) in anhydrous diethyl ether (150ml) under a nitrogen atmosphere. The reaction mixture was refluxed for 3 h, cooled to -10°C, and water (100ml) added. The organic phase was collected: the aqueous phase was extracted with diethyl ether (2 x 50ml). The combined ethereal solutions were dried over anhydrous calcium chloride and rotary evaporated to leave Ph_3SnH as a colourless oily residue, which was used as such in subsequent syntheses.

3β-[(Triphenylstannyl)methoxy]cholest-5-ene (cholesteryl triphenylstannylmethyl ether) 7

To a stirred solution of cholesterol (3.87g, 10mmol) in anhydrous DMF (40ml) were successively added, under a nitrogen atmosphere, sodium hydride (55-60 % suspension in mineral oil, 1.82g) and (iodomethyl)triphenylstannane (4.90g, 10mmol). After maintaining the reaction mixture at room temperature for 56h, methanol (20ml) and water (50ml) were succcessively added. The reaction mixture was extracted with diethyl ether (4 x 30ml). The combined ether extracts were washed with water (3 x 30ml), dried over anhydrous magnesium sulfate and rotary evaporated. The residue was separated using thin layer chromatography (eluent 10% ethyl acetate / petroleum ether b.p. 60-80°C). The title compound was obtained as a colourless solid, which was recrystallised from ethanol, m.p. 111-114°C, yield 3.5g, 46.6%.
Analysis. Found: C, 73.3; H, 8.4. Calculated for $C_{46}H_{62}OSn$: C, 73.7; H, 8.3%.
^{1}H NMR ($CDCl_3$) : δ 0.67 [3H, s, Me-18], 0.86 [3H, d, Me-26, J 6.6], 0.86 [3H,d, Me-27, J 6.6], 0.91 [3H, d, Me-21, J 6.5], 0.97 [3H, s, Me-19], 1.0-2.4 [m, 28H], 3.08 [1H, m. H-3], 4.4

[2H, s, $SnCH_2$, J(^{119,117}Sn-^{1}H) 17.1], 5.25 [1H, d, H-6, J 5.2], 7.35 [9H, m, *m* + *p*-H], 7.58 [6H, m, J(^{119,117}Sn-^{1}H) 40, *o*-H].
^{13}C NMR ($CDCl_3$) : δ 11.7 [C-18], 18.6 [C-21], 19.3 [C-19], 21.0 [C-11], 22.4 [C-26], 22.7 [C-27], 23.7 [C-23], 24.2 [C-15], 27.8 [C-2], 27.9 [C-25], 28.1 [C-12], 31.8 [C-8], 31.8 [C-7], 35.7 [C-20], 36.1 [C-22], 36.8 [C-4], 37.1 [C-10], 38.4 [C-1], 39.4 [C-24], 39.7 [C-16], 42.2 [C-13], 50.0 [C-9], 56.0 [C-17], 56.7 [C-14], 60.0 [Sn-CH_2, J(^{119,117}Sn-^{13}C) 492, 470], 82.9 [C-3, J($^{119\,117}$Sn-^{13}C) 44], 121.4 [C-6], 128.3 [*m*-C, J($^{119\,117}$Sn-^{13}C) 49], 128.8 [*p*-C J($^{119\,117}$Sn-^{13}C) 11], 137.1 [*o*-C, J($^{119\,117}$Sn-^{13}C) 35], 138.5 [*i*-C, J($^{119\,117}$Sn-^{13}C) 491, 469], 140.8 [C-5].
^{119}Sn NMR ($CDCl_3$) : δ -144.6.

3β-[3-(Triphenylstannyl)propoxy]cholest-5-ene [cholesteryl 3-(triphenylstannyl)propyl] ether 8

Method 1. A solution of allyl cholesteryl ether (1.54g, 3.6mmol) in cyclohexane was added to triphenyltin hydride, prepared from lithium aluminium hydride (0.14g) and triphenyltin chloride (1.39g, 3.6mmol). A little azoisobutyronitrile (AIBN) was added and the mixture was gently heated for 20 min. After cooling to room temperature, the reaction mixture was rotary evaporated and the solid residue was recrystallised successively from petroleum ether (40-60°C) and chloroform / ethanol to give colourless crystals of **8**, m.p. 107-108°C, yield 0.78g, 28.5%.
Analysis. Found: C, 74.2; H, 8.4. Calculated for $C_{48}H_{66}OSn$: C, 74.1; H, 8.6%.
^{1}H NMR ($CDCl_3$) : δ 0.67 [3H, s, Me-18], 0.86 [3H, d, Me-26, J 6.6], 0.87 [3H,d, Me-27, J 6.6], 0.91 [3H, d, Me-21, J 6.4], 0.95 [3H, s, Me-19], 1.0-2.3 [m, 32H], 3.08 [1H, m. H-3], 3.45 [2H, t, CH_2 7], 5.25 [1H, d, H-6, J 5], 7.35 [9H, m, *m* + *p*-H], 7.55 [6H, m, *o*-H, J(^{119,117}Sn-^{1}H) 46].
^{13}C NMR ($CDCl_3$) : δ 7.0 [Sn-CH_2, J($^{119\,117}$Sn-^{13}C) 396, 378], 11.7 [C-18], 18.6 [C-21], 19.3 [C-19], 20.9 [C-11], 22.4 [C-26], 22.7 [C-27], 23.7 [C-23], 24.2 [C-15], 26.9 [SnCH_2*C*H_2, J(^{119,117}Sn-^{13}C) 20], 27.9 [C-2], 28.1 [C-25], 28.2 [C-12], 31.7 [C-8], 31.8 [C-7], 35.7 [C-20], 36.1 [C-22], 36.7 [C-1], 37.1 [C-4], 38.9 [C-10], 39.4 [C-24], 39.7 [C-16], 42.2 [C-13], 50.0 [C-9], 56.0 [C-17], 56.6 [C-14], 70.7 [CH_2O, J($^{119\,117}$Sn-^{13}C) 68], 78.9 [C-3], 121.3 [C-6], 128.3 [*m*-C, J(^{119,117}Sn-^{13}C) 48], 128.7 [*p*-C, J(^{119,117}Sn-^{13}C) 11], 136.9 [*o*-C, J(^{119,117}Sn-^{13}C) 35], 138.5 [*i*-C, J(^{119,117}Sn-^{13}C) 485, 464], 141.0 [C-5].
^{119}Sn NMR ($CDCl_3$) : δ -100.3.

Method 2. A solution of (3-chloropropyl)triphenylstannane (1.71g, 4mmol) and sodium iodide (3g) in acetone (20ml) was stirred overnight at room temperature. The reaction mixture was extracted with chloroform: the chloroform extract was, dried over magnesium sulfate and rotary evaporated. This procedure was repeated twice. The crude (iodopropyl)triphenyltin was used as such in subsequent reactions.

Sodium hydride (55-60 % suspension in mineral oil, 0.73g) and the crude (3-iodopropyl)triphenylstannane were successively added to a stirred solution of cholesterol (1.54g, 4.0mmol) in anhydrous DMF (40ml) under nitrogen. After stirring the reaction mixture under nitrogen at room temperature for 56 hours, methanol (20ml) was added to destroy the excess of sodium hydride. Water (50ml) was added and the mixture extracted with diethyl ether (4 x 30ml). The combined ethereal extracts were washed with water (3 x 30ml), dried over anhydrous magnesium sulfate and rotary evaporated. The resultant solid (2.92g) was chromatographed (TLC) using 10% ethyl acetate / petroleum ether b.p. 60-80°C as the eluent; further purification of 3β-[3-(triphenylstannyl)propoxy]cholest-5-ene was achieved by recrystallisation from ethanol / dichloromethane. The product was identical with that obtained by method 1.

3β-[3-(Iododiphenylstannyl)propoxy]cholest-5-ene

Solutions of **8** (0.049g, $6.3x10^{-5}$mol) in chloroform (0.5ml) and iodine (0.016g, $6.3x10^{-5}$mol) in chloroform (0.5ml) were mixed and left until decolourised. All volatiles were removed *in vacuo* to leave an oily product.

^{13}C NMR ($CDCl_3$) : Partial spectrum: δ 13.3 [Sn-CH_2, J(^{119,117}Sn-^{13}C) 410, 390], 26.8 [$SnCH_2CH_2$, J(^{119,117}Sn-^{13}C) 26], 70.4 [CH_2O, J($^{119\,117}$Sn-^{13}C) 70], 128.8 [*m*-C, J(^{119,117}Sn-^{13}C) 59], 129.0 [*p*-C, J($^{119\,117}$Sn-^{13}C) 13], 136.0 [*o*-C, J(^{119,117}Sn-^{13}C) 46], 137.5 [*i*-C, J($^{119\,117}$Sn-^{13}C) 498,478].

^{119}Sn NMR ($CDCl_3$) : δ -57.3.

3β-[3-(Triphenylstannyl)propanoato]cholest-5-ene: [cholesteryl 3-(triphenylstannyl)-propanoate] 9

Triphenyltin hydride (1.00g, 2.85mmol), 3β-(propen-2-oato)cholest-5-ene (1.26g, 2.85mmol) and AIBN (0.05g) were heated gently until evolution of gas ceased. After cooling, all volatiles were removed by evaporation. Dichloromethane was added, the reaction mixture filtered and the filtrate rotary evaporated. The residue was recrystallised from chloroform / ethanol; m.p. 102-103°C, yield 1.42g, 63%.

Analysis. Found: C, 72.9; H, 8.4. Calculated for $C_{49}H_{66}O_2Sn$: C, 72.8; H, 8.2%.

^{1}H NMR ($CDCl_3$) : δ 0.66 [3H, s, Me-18], 0.86 [3H, d, Me-26, J 6.7], 0.86 [3H,d, Me-27, J 6.7], 0.91 [3H, d, Me-21, J 6.4], 0.95 [3H, s, Me-19], 1.0-2.3 [m, 30H], 1.65 [2H, t, CH_2Sn, J 7.9], 2.69 [2H, t, CH_2CO_2, J 7.9, J($^{119\,117}$Sn-H) 66], 4.4-4-6 [1H, m, H-3], 5.3 [1H, d, H-6, J 4.9], 7.3-7.4[9H, m, *m* + *p*-H], 7.5-7.6[6H, m, J($^{119\,117}$Sn-^{1}H) 46 *o*-H].

^{13}C NMR ($CDCl_3$) : δ 5.5 [$SnCH_2$, J($^{119\,117}$Sn-^{13}C) 399, 383], 11.9 [C-18], 18.8 [C-21], 19.3 [C-19], 21.1 [C-11], 22.6 [C-26], 22.9 [C-27], 23.9 [C-23], 24.3 [C-15], 27.6 [C-2], 28.1 [C-25], 28.2 [C-12], 31.2 [$SnCH_2CH_2$, J(^{119,117}Sn-^{13}C) 35.2], 31.9 [C-8], 31.9 [C-7], 35.8 [C-20], 36.2 [C-22], 36.6 [C-1], 37.0 [C-4], 38.0 [C-10], 39.6 [C-24], 39.8 [C-16], 42.4 [C-13], 50.0 [C-9], 56.2 [C-17], 56.7 [C-14], 74.1 [C-3], 122.6 [C-6], 128.1 [*m*-C, J(^{119,117}Sn-^{13}C) 49], 128.9 [*p*-C, J(^{119,117}Sn-^{13}C) ~22], 136.9 [*o*-C, J(^{119,117}Sn-^{13}C) 36], 138.8 [*i*-C, J(^{119,117}Sn-^{13}C) 503, 481], 139.7 [C-5, J(^{119,117}Sn-^{13}C) 41], 174.4 [CO_2, J(^{119,117}Sn-^{13}C) 49].

^{119}Sn NMR ($CDCl_3$) : δ -100.2

3β-[3-(Iododiphenylstannyl)propanoato]cholest-5-ene

Solutions of **9** (0.050g, $6.3x10^{-5}$mol) in chloroform (0.5ml) and iodine (0.016g, $6.3x10^{-5}$mol) in chloroform (0.5ml) were mixed and left until decolourised. All volatiles were removed *in vacuo* to leave an oily product.

^{1}H NMR ($CDCl_3$) : δ 0.67 [3H, s, Me-18], 0.86 [3H, d, Me-26, J 6.7], 0.86 [3H,d, Me-27, J 6.7], 0.91 [3H, d, Me-21, J 6.7], 0.99 [3H, s, Me-19], 1.0-2.3 [m, 30H], 1.96 [2H, t, CH_2Sn J(H-H) 7.3], 2.77 [2H, t, CH_2CO_2, J(H-H) 7.3, J(^{119,117}Sn-^{1}H) 110], 4.7 [1H, m, H-3], 5.37 [1H, d, H-6, J 5.2], 7.3-7.5 [6H, m, *m* + *p*-H], 7.8-7.9 [4H, m, J(^{119,117}Sn-^{1}H) 63, *o*-H].

^{13}C NMR ($CDCl_3$) : δ 11.9 [C-18], 17.0 [$SnCH_2$, J($^{119\,117}$Sn-^{13}C) 486.3, 464.9], 18.8 [C-21], 19.3 [C-19], 21.1 [C-11], 22.6 [C-26], 22.9 [C-27], 23.9 [C-23], 24.3 [C-15], 27.5 [C-2], 28.1 [C-25], 28.3 [C-12], 30.7 [$SnCH_2CH_2$, J(^{119,117}Sn-^{13}C) 35.2], 31.8 [C-8], 31.9 [C-7], 35.8 [C-20], 36.2 [C-22], 36.6 [C-1], 36.8 [C-4], 37.9 [C-10], 39.6 [C-24], 39.7 [C-16], 42.3 [C-13], 50.0 [C-9], 56.1 [C-17], 56.7 [C-14], 77.3 [C-3], 123.3 [C-6], 128.6 [*m*-C, J(^{119,117}Sn-^{13}C) 65], 129.4 [*p*-C, J(^{119,117}Sn-^{13}C) 14], 136.5 [*o*-C, J(^{119,117}Sn-^{13}C) 48], 138.8 [C-5, J(^{119,117}Sn-^{13}C) 53], 139.7 [*i*-C, J(^{119,117}Sn-^{13}C) 656, 626], 180.0 [CO_2, J(^{119,117}Sn-^{13}C) 41].

^{19}Sn NMR ($CDCl_3$) : δ -97.2.

3β-[3-(Diiodophenylstannyl)propanoato]cholest-5-ene

Solutions of **9** (0.041g, $5.1x10^{-5}$mol) in chloroform (0.5ml) and iodine (0.026g, $10.2x10^{-5}$mol) in chloroform (0.5ml) were mixed and left until decolourised. All volatiles were removed *in vacuo* to leave an oily product.

^{1}H NMR ($CDCl_3$) : δ 0.67 [3H, s, Me-18], 0.86 [3H, d, Me-26, J 6.4], 0.87 [3H,d, Me-27, J 6.7z], 0.91 [3H, d, Me-21, J 6.4], 1.01 [3H, s, Me-19], 1.0-2.3 [m, 30H], 2.16 [2H, t, CH_2Sn, J 7.3], 2.8 [2H, t, CH_2CO_2, J 7.3, J($^{119\,117}$Sn-H) 141, 134] 4.7 [1H, m, H-3], 5.4 [1H, d, H-6, J 4.9], 7.4-7.5 [3H, m, *m* + *p*-H], 7.8-7.9 [2H, m, J(^{119,117}Sn-^{1}H) 87, *o*-H].

^{13}C NMR ($CDCl_3$) : δ 11.9 [C-18], 18.8 [C-21], 19.3 [C-19], 21.1 [C-11], 22.6 [C-26], 22.9 [C-27], 23.4 [$SnCH_2$], 23.9 [C-23], 24.3 [C-15], 27.6 [C-2], 28.1 [C-25], 28.3 [C-12], 31.2 [$SnCH_2CH_2$], 31.8 [C-8], 31.9 [C-7], 35.8 [C-20], 36.1 [C-22], 36.6 [C-1], 36.8 [C-4], 37.9 [C-10], 39.5 [C-24], 39.7 [C-16], 42.3 [C-13], 50.0 [C-9], 56.1 [C-17], 56.7 [C-14], 77.6 [C-3], 123.4 [C-6], 128.6 [*m*-C, J($^{119\,117}$Sn-^{13}C) 84], 130.5 [*p*-C, J(^{119,117}Sn-^{13}C) 18], 135.2 [*o*-C, J(^{119,117}Sn-^{13}C) 59], 138.9 [*i*-C], 139.0 [C-5], 178.7 [CO_2, J(^{119,117}Sn-^{13}C) 55].

^{119}Sn NMR ($CDCl_3$) : δ -227.8.

Table 1. Crystal data and structure refinement

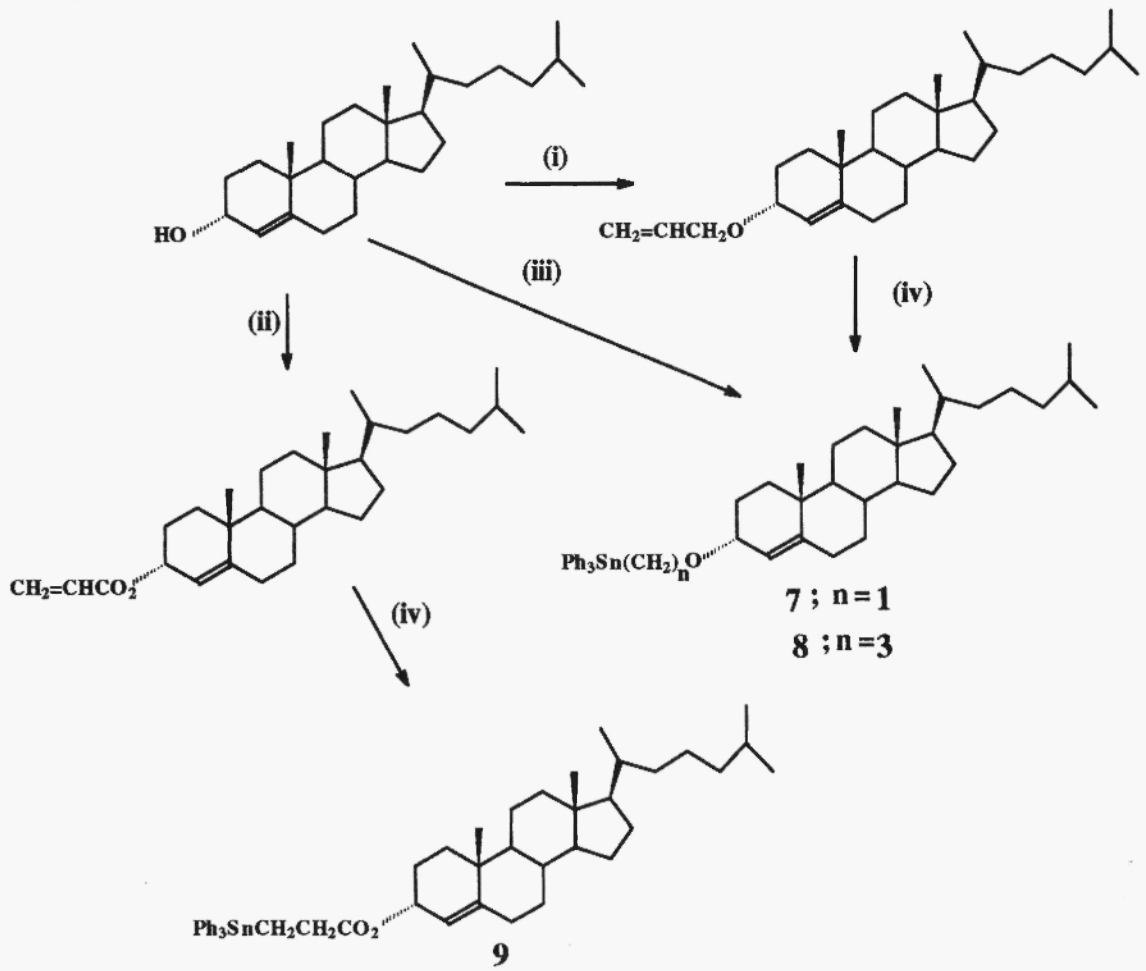
Empirical Formula	$C_{46}H_{66}OSn$
Formula weight	749.65
Temperature	150(2) K
Wavelength	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.114(3) Å; b = 11.480(4) Å; c = 57.064(10) Å
Volume	4005(3) Å^3
Z	4
Density (calculated0	1.243 Mg/m^3
Absorption coefficient	0.670 mm^{-1}
F(000)	1584
Crystal size	0.30 x 0.28 x 0.18 mm
Theta range for data collection	1.81 to 25.07^0
Index ranges	$-6 \le h \le 6$; $0 \le k \le 12$; $0 \le 1 \le 64$
Independent reflections	5417
Observed reflections [(I)2σ(I)]	3842
Max. and min. transmission	0.8889 and 0.8243
Refinement method	Full-matrix l.s. on F^2
Number of parameters	240
Goodness-of-fit on F^2(S)	1.154
Final R indices [(I)2σ(I)]	R1 = 0.0992, wR2 = 0.2331
R indices (all data)	R1 = 0.1229, wR2 = 0.2399
Final weighting scheme	calc $w=1/[\sigma^2Fo^2) + (0.0943P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$
Absolute structure parameter	0.01(7)
Residual diffraction max.	1.585 e/Å^3 at Sn position
Residual diffraction min.	-1.177 e/Å^3

Crystal structure determination of 7.

The X-ray data were collected on a Delft Instruments FAST diffractometer and corrected for Lorentz and polarisation effects. Following structure elucidation with SHELX86,[18] an absorption correction was made with XABS2.[19] Details of the crystal structure and refinement[20] with SHELXL-93 are shown in Table 1. Tin and side-chain atoms, [C20-C27], were refined with anisotropic temperature factors but due to the poor data set resulting from difficulty in finding a suitable crystal, other atoms were refined with isotropic temperature factors. The hydrogen atoms were included in calculated positions in riding mode with one or two isotropic temperature factors (methyl or non-methyl). The molecular plot was obtained with ZORTEP.[21]

RESULTS AND DISCUSSION

General. From considerations of the ease of formation and reactivities, the following R_3Sn-□-(chol) type compounds were prepared:- 3β-(triphenylstannylmethoxy)-cholest-5-ene **7**, 3β-(3-triphenylstannylpropoxy)cholest-5-ene **8** and 3β-cholest-5-enyl (3-triphenylstannyl)-prop-2-enoate **9**. Triphenylstannyl derivatives were prepared (Scheme 1) due to the generally greater reactivity of Ph-Sn bonds compared to alkyl-tin bonds towards electrophiles and hence greater potential to form $X_nR_{3-n}Sn$-□-(chol) (X = halide) on reaction with halogen containing electrophiles.



Scheme 1. Reagents:. (*i*) CH_2=$CHCH_2Br$, NaH, DMF; (*ii*) CH_2=CHCOCl, $PhNMe_2$; (*iii*) $Ph_3Sn(CH_2)_nI$ (n = 1 or 3), NaH, DMF; (*iv*) Ph_3SnH, AIBN.

Compound **7** was obtained by the alkylation of cholesterol by (iodomethyl)triphenylstannane in the presence of sodium hydride. Two routes were used for **8**. One involved alkylation of cholesterol with (3-chloropropyl)triphenylstannane while the other utilised the free radical addition of triphenyltin hydride to allyl cholesteryl ether; in neither case was the yield particularly good. Triphenyltin hydride addition to cholesteryl acrylate was employed for the formation of **9**. Only a single addduct was obtained in each of the Ph_3SnH reactions.

The complete assignment of the ^{13}C NMR spectra of 3α-(triphenylstannyl)cholest-5-ene has been reported[12] from HMQC and HMBC NMR spectra, obtained at 599.9 MHz and the known ^{13}C NMR chemical shifts for cholesterol. By analogy and use of chemical shift increment tables, complete ^{13}C NMR spectra assignments, obtained at 62.9MHz, were achieved for **7-9**. The only significant changes from the cholesterol chemical shifts occurred in the A ring.

Compound 7

Solution NMR study. The $\delta^{119}Sn$ (-144.6 ppm) and $\delta^{13}C_\alpha$ (60.0 ppm) values for **7** occur in the regions previously reported for Ph_3SnCH_2OR (R = alkyl or aryl),[22-25] see Table 2. The values of $\delta^{13}C_\alpha$ and $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ for **7** are closest to the values for $Ph_3SnCH_2O^iPr$ -another compound with a non-functionalised secondary-R group. As shown by the values for Ph_3SnCH_2OR (R = acyclic alkyl group), $\delta^{119}Sn$, $\delta^{13}C_\alpha$ and $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ vary with the R group, *e.g.*, $\delta^{13}C_\alpha$ and $\delta^{119}Sn$, to a lesser degree, occur at progressively lower field in the sequence R = Me, Et, Pr^i and Bu^t. The $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ values increase in the same sequence. The NMR spectral data are also influenced by the presence of additional funtional groups within the R unit.

Table 2. Selected NMR values for Ph_3SnCH_2OR in $CDCl_3$ solution.

Compound	$\delta^{13}C_\alpha$	$\delta^{119}Sn$	$J(^{119}Sn\text{-}^{13}C_i)/J(^{119}Sn\text{-}^{13}C_\alpha)$	Ref.
Ph_3SnCH_2OMe	65.8	−145.1	496/481	22
Ph_3SnCH_2OEt	63.2	−145.1	491/485	22
$Ph_3SnCH_2OPr^i$	60.1	−145.3	493/497	22
$Ph_3SnCH_2OBu^t$	52.8	−146.5	496/521	22
$Ph_3SnCH_2OCH_2CH_2OH$	63.7	−142.3	501/476	22
$Ph_3SnCH_2O(CH_2)_3OCH_2Ph$	63.5	−144.0	494/485	22
$Ph_3SnCH_2OC_6H_4Me$-p	60.1	−140.8	492/467	23
$Ph_3SnCH_2OC_6H_3Br_2$-2,4	61.6	−142.9	527/472	23
10	62.5	−144.3	512/480	24
11	64.2	−143.8	510/480	24
Ph_3SnCH_2O-chol[a] **7**	60.0	−144.6	492/491	b

[a] chol = cholesteryl, $C_{27}H_{45}$. [b] This study.

Crystal structure of 7. A crystal structure determination of **7** was undertaken, but as a result of the poor crystal quality, the structure could only be refined to a relatively high R value (0.099). However, it is clear that the compound exists as discrete molecules, with a distorted tetrahedral geometry at tin. The atom arrangement and numbering system are shown in Figure 2. Atom coordinates are listed in Table 3 and selected bond lengths and angles are in Table 4. The Sn-C bond lengths range from 2.12(2)-2.163(14) Å and the valency angles about tin are between 105.8(6) and 112.1(7)°. Although the tin -oxygen separation in **7** is <3.0 Å and is well within the

Table 3. Atom coordinates (x 10^4) and equivalent isotropic displacment parameters (Å x 10^3). U(eq) is defined as one third of the trace of the orthogonal Uij tensor.

Atom	x	y	z	U(eq)
Sn	7901(2)	1815(1)	1971(1)	21(1)
O	9384(15)	1930(10)	1493(2)	27(2)
C(1)	9150(2)	1522(14)	847(3)	29(4)
C(2)	8750(2)	2065(13)	1088(3)	27(4)
C(3)	9760(2)	1320(13)	1273(3)	23(4)
C(4)	12240(2)	1130(12)	1224(3)	23(3)
C(5)	12580(2)	623(11)	980(2)	17(3)
C(6)	13760(2)	-336(12)	945(3)	13(3)
C(7)	14300(2)	-853(13)	715(3)	21(4)
C(8)	13870(2)	4(12)	511(3)	18(3)
C(9)	11620(2)	587(12)	552(3)	17(3)
C(10)	11550(2)	1316(11)	782(2)	13(3)
C(11)	10910(3)	1312(13)	336(3)	24(4)
C(12)	11110(2)	692(13)	98(3)	21(4)
C(13)	13420(2)	188(12)	71(3)	17(3)
C(14)	13890(2)	-616(13)	280(3)	20(4)
C(15)	15860(2)	-1318(13)	212(3)	23(4)
C(16)	15640(3)	-1442(14)	-62(3)	32(4)
C(17)	13660(2)	-705(12)	-142(3)	15(3)
C(18)	15100(2)	1173(12)	43(3)	22(4)
C(19)	12730(2)	2494(12)	758(3)	26(4)
C(20)	13950(3)	-208(13)	-394(3)	26(4)
C(21)	12100(3)	593(14)	-463(3)	39(4)
C(22)	14090(3)	-1237(14)	-570(3)	38(5)
C(23)	14730(4)	-893(18)	-813(3)	61(6)
C(24)	14240(3)	-1893(17)	-998(3)	58(6)
C(25)	14600(3)	-1653(19)	-1237(4)	54(5)
C(26)	13040(5)	-720(2)	-1323(5)	101(10)
C(27)	14360(4)	-2764(18)	-1378(4)	69(7)
C(28)	10140(3)	1367(14)	1693(3)	30(4)
C(29)	6080(2)	3328(14)	1880(3)	26(4)
C(30)	4810(2)	3351(16)	1682(3)	34(4)
C(31)	3420(3)	4270(15)	1627(3)	43(5)
C(32)	3240(3)	5210(15)	1791(3)	40(5)
C(33)	4560(2)	5237(15)	1985(4)	41(4)
C(34)	5970(2)	4295(14)	2042(3)	29(4)
C(35)	5620(2)	381(12)	1994(3)	25(4)
C(36)	5650(2	-400(13)	1799(3)	27(4)
C(37)	4130(3)	-1327(15)	1791(4)	38(5)
C(38)	2630(2)	-1434(12)	1961(3)	33(4)
C(39)	2580(2)	-684(12)	2151(3)	27(4)
C(40)	4090(2)	248(14)	2158(3)	29(4)
C(41)	9580(2)	2100(13)	2292(3)	24(4)
C(42)	9260(2)	1428(13)	2491(3)	28(4)
C(43)	10560(3)	1585(15)	2689(3)	37(5)
C(44)	12160(3)	2454(14)	2690(3)	41(4)
C(45)	12480(2)	3139(15)	2500(3)	35(4)
C(46)	11180(2)	2978(14)	2292(3)	32(4)

sum of the van der Waals radii of tin and oxygen [3.70 Å][26], no significant tin-oxygen interaction is indicated by the C-Sn-C angles. Similar Sn-O separations have been established in other R_3SnCH_2OR' compounds.[23,24,27]

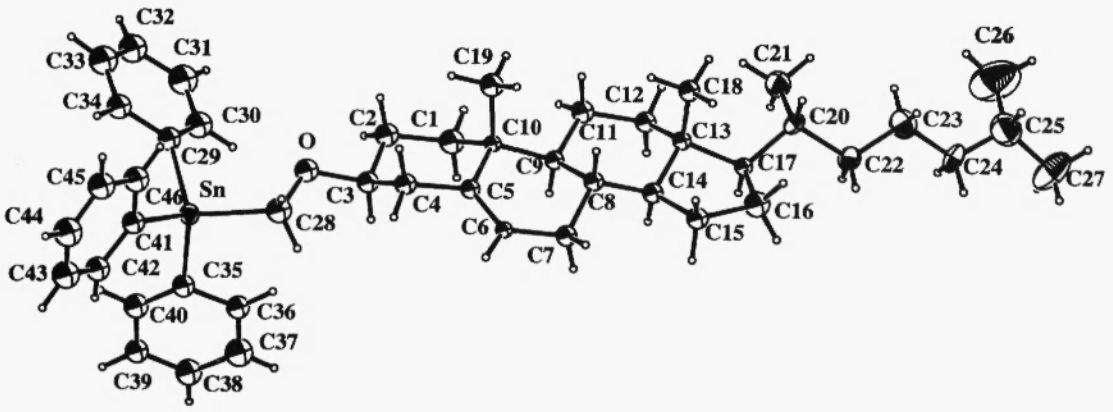


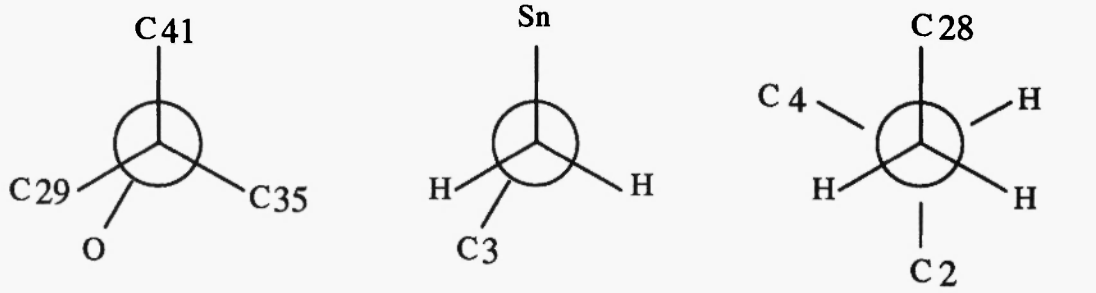
Figure 2. Atom arrangement for 7

The angles the tin substituent makes to the C(29)-C(34) phenyl ring in **7** are close to the ideal value of 120°, being 120.8(13)° [Sn-C(29)-C(30)], and 119.4(12)° [Sn-C(29)-C(34)]. In contrast, the angles tin makes to the other phenyl rings are significantly different from 120°, being 114.8(12)° [Sn-C(35)-C(36)] and 125.3(13)° [Sn-C(35)-C(40)] for ring C(35)-C(40) and 116.6(12)° [Sn-C(41)-C(46)] and 123.7(12)° [Sn-C(41)-C(42)] for ring C(41)-C(46).

Table 4. Selected bond lengths [Å] and angles [°] for 7

Sn-C29	2.13(2)	Sn-C41	2.12(2)	Sn-C35	2.163(14)
Sn-C28	2.16(2)	O-C3	1.46(2)	O-C28	1.38(2)
C29-Sn-C28	110.2(6)	C29-Sn-C35	107.5(6)	C35-Sn-C28	105.8(6)
C28-Sn-C41	111.5(6)	C29-Sn-C41	109.7(7)	C35-Sn-C41	112.1(7)
C30-C29-Sn	120.8(13)	C36-C35-Sn	114.8(12)	C46-C41-Sn	116.6(12)
C34-C29-Sn	119.4(12)	C40-C35-Sn	125.3(13)	C42-C41-Sn	123.7(12)
O-C3-C2	105.9(13)	O-C3-C4	111.9(120	C28-O-C3	115.5(13)
O-C28-Sn	106.2(10)				

The arrangements of the groups about the bonds in the linking unit, Sn-C28, C28-O and O-C3 bonds, are shown in Figure 3. As can be seen, atoms about the Sn-C28 bond are in a near eclipsed arrangement: a similar situation exists for a hydrogen and the C3 atom about the C28-O bond. An ideal straggered arrangement is found about the O-C3 bond.

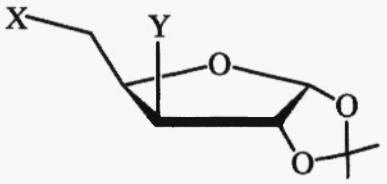


(a) C29-Sn-C28-O = -18.8(13)° (b) Sn-C28-O-C3 = -147.2(10)° (c) C28-O-C3-C2 = 178.2(13)°
C41-Sn-C28-O = -140.9(10)° C28-O-C3-C4 = -61.2(2)°
C35-Sn-C28-O = 97.1(11)°

Figure 3. (a) Arrangement of atoms looking down the Sn-C28 bond, (b) the C28-O bond and (c) the O-C3 bond.

Rings A and C in **7** adopt chair conformations, ring D a near envelope conformation with a flap at C13, while in ring B, C8 and C9 are on opposite sides of the plane through C5, C6, C7 and C10. Disorder among the atoms in the side chain at C17 is indicated by their large thermal parameters.

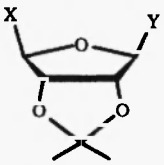
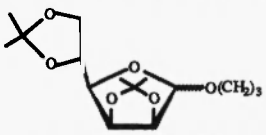
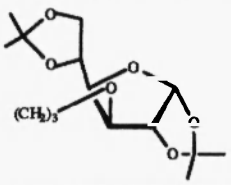
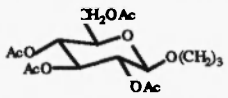
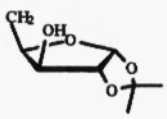
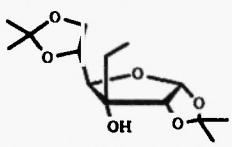
Reaction of 7 with iodine. Generally, a Ph-Sn bond is very much more reactive than a simple alkyl-tin bond, as found in $Ph_{3-n}Me_nSn$, towards electrophiles and is hence preferentially cleaved. In contrast, the relative reactivities of Ph-Sn and CH_2-Sn bonds in Ph_3SnCH_2OR (R = alkyl or aryl) towards electrophiles, are dependent on the R group, *e.g.*, (*i*) the reaction of equimolar I_2 with either $Ph_3SnCH_2OC_6H_4Me$-*p* [28] or 2,3-*O*-isopropylidene-3-*O*-(triphenylstannylmethyl)-5-*O*-trityl-α-D-xylofuranose **10** [24] resulted predominately in Ph-Sn cleavage (>95%), (*ii*) significant amounts of both types of Sn-C bond cleavage were detected for Ph_3SnCH_2OMe [29] as were also secondary products, *e.g.*, Ph_2SnI_2 and (*iii*) the major reaction (>95%) of 2,3-*O*-isopropylidene-3-*O*-benzyl-*O*-(triphenylstannylmethyl)-α-D-xylofuranose (**11**) occurred by Sn-CH_2 cleavage.[24]



(**10**: X = Ph_3CO; Y = Ph_3SnCH_2O)
(**11**: X = Ph_3SnCH_2O; Y = $PhCH_2O$)
(**12**; X = $I_nPh_{3-n}Sn$; Y = HO)

The reaction of **7** with equimolar iodine was far from regioselective and gave several tin containing products, all in significant amounts, with δ^{119}Sn values of -242.9 [Ph_2SnI_2; lit.[30] value - 243.8ppm] -122.8, -100 and +185 ppm. The primary tin containing-products would be Ph_3SnI (lit.[31] value of δ^{119}Sn -114.6 ppm) and IPh_2SnCH_2O-chol (*ca* -120-130ppm, from values obtained in previous studies for related compounds).[24] The compound, IPh_2SnCH_2O-chol [δ^{119}Sn -122.8?] is probably present, but not Ph_3SnI. However it is clear that Ph_3SnCH_2O-chol is not an efficient precursor of halo-Ph_2SnCH_2O-chol compounds.

Table 5. δ^{119}Sn NMR values for $I_nPh_{3-n}SnR$ in $CDCl_3$ solution at 25°C.

R	Ph_3SnR	IPh_2SnR	I_2PhSnR	Ref
	δ^{119}Sn [J(Sn-C_i),J(Sn-C_α)]	δ^{119}Sn [J(Sn-C_i),J(Sn-C_α)]	δ^{119}Sn [J(Sn-C_i),J(Sn-C_α)]	
Me	-92.5 [510, 377]	-68.7 [536, 381]	-209.3 [614, 405]	32
Et	-97.3 [481, 405]	-47.1 [499, 408]		32
Pr	-101.0 [480, 398]	-54.1 [498, 399]		32
$CH_2CH_2CH_2CH_2SnPh_{3-n}I_n$	-100.1 [483, 393][a]	-55.1 [505, 391][b]	-162.4 [549, 411][c]	33
$CH_2CH_2CH_2OH$	-100.0 [491, 398]	-113.1 [605, 493]		34
$CH_2CH_2CH_2O$-chol[d]	-100.3 [485, nd]	-57.3 [501, nd]		e
 X = $HOCH_2$, Y = $O(CH_2)_3$	-100.3 [494, 388]	-61.5 [554, 401]		35
X = CH_2, Y = OMe	-109.6 [509, 361]	- 82.4 [nd, 392]	-195.1 [nd, 436]	32
	α -100.1 [491, 396] β -99.5 [491, 392]	α -79.2 [nd, nd] β -63.9 [nd, 410]		35 35
	-99.7 [490, 393]	-58.3 [nd, 402]		35
	-99.6 [nd, nd]	-61.9 [nd, 410]	-172.6[nd, 445]	35
	-107.3 [515, 371]	-119.4 [nd, 531]	-224.0 [744, 548]	29
	-111.3 [518, 377]	-96.7 [nd, 423]		37
$CH_2CH_2CO_2Me$	-99.8 [504, 396]	-94.4 [635, 491]		38
$CH_2CH_2CO_2$-chol[d]	-100.2 [503, 399]	-97.2 [656, 486]	-227.8 [nd, nd]	e

[a] n=0; [b] n = 1; [c] n = 2; [d] chol = cholesteryl, $C_{27}H_{45}$; [e] This study.

Compound 8.

The solution δ^{119}Sn, $^1J(^{119}Sn\text{-}^{13}C_i)$ and $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ data for **8** can be compared with those for a number of unsubstituted - as well as β- and γ-oxygen-substituted-primary-alkyl-triphenylstannanes[32-38] in Table 5; the similar NMR parameters indicate all are tetetrahedral structures compounds with 4-coordinate tin centres in solution.

Reaction with iodine. Compound **8** undergoes ready iododephenylation to give $IPh_2SnCH_2CH_2CH_2O$-chol on reaction with equimolar I_2. The compound, $IPh_2SnCH_2CH_2CH_2O$-chol, was formed very cleanly and will be used in futher derivatisations. Selected NMR parameters of $IPh_2SnCH_2CH_2CH_2O$-chol in Table 5 can be compared with values for other $I(RCH_2)Ph_2Sn$ compounds. 4-Coordinate $I(RCH_2)Ph_2Sn$ compounds in solution have $\delta^{119}Sn$, $^1J(^{119}Sn\text{-}^{13}C_i)$ and $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ values of -55±10 ppm, *ca* 500 Hz and *ca* 400 Hz, respectively. Compounds with 5-coordinate tin centres, *i.e.* compounds in which an intramolecular donor centre is coordinated to tin, have $\delta^{119}Sn$, $^1J(^{119}Sn\text{-}^{13}C_i)$ and $^1J(^{119}Sn\text{-}^{13}C_\alpha)$ values in solution of *ca.* -105±15 ppm, 630±30 Hz and 510±30Hz, respectively. Intermediate values are suggestive of rapid equilibria between 4- and 5-coordinate species. It appears that $IPh_2SnCH_2CH_2CH_2O$-chol is four coordinate in solution, in contrast to $IPh_2SnCH_2CH_2CH_2OH$; this suggests the greater donor ability of a hydroxyl group compared to a secondary alkoxy unit.

Compound 9.

Compound **9** undergoes ready iododephenylation to give $IPh_2SnCH_2CH_2CO_2$-chol on reaction with equimolar I_2: further iodo-de-phenylation to $I_2PhSnCH_2CH_2CO_2$-chol also readily occurs. Use of $I_nPh_{3-n}SnCH_2CH_2CO_2$-chol (n = 1 or 2) will provide ready routes to further derivatives. Similar NMR arguments, as used for **8**, indicate that **9** is 4-coordinate in solution, while $IPh_2SnCH_2CH_2CO_2$-chol is 5-coordinate in solution. Compound, $I_2PhSnCH_2CH_2CO_2$-chol, also contains a 5-coordinate tin atom, as shown by the comparison with the NMR data for 5-deoxy-5-*C*-diiodophenylstannyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**12,** n = 2) (5-coordinate)[32] and $I_2PhSn(CH_2)_4SnPhI_2$ (4-coordinate).[33] Further support for the coordination at the tin centres in **8** and $I_nPh_{3-n}SnCH_2CH_2CO_2$-chol (n = 1 or 2) is provided by IR data. Values of ν(CO) for **8**, $IPh_2SnCH_2CH_2CO_2$-chol and $I_2PhSnCH_2CH_2CO_2$-chol are 1740, 1684 and 1680cm^{-1}, respectively: coordination of the carbonyl group with the tin centre in $I_nPh_{3-n}SnCH_2CH_2CO_2$-chol (n = 1 or 2) leads to a reduction of a free ν(CO) value, *e.g.*, 1740 cm^{-1} as found in simple organic esters, *e.g.*, $MeCO_2Me$. Similar findings have ben established for $I_nPh_{3-n}SnCH_2CH_2CO_2Me$ (n = 0 or 1).

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