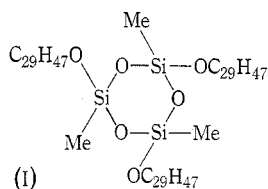


POLYSTIGMASTEROXYSILANES AND TRISTIGMASTEROXYTRIMETHYLCYCLOSILOXANE*

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The first steroxysilane was reported by Liu and Wang;¹ polycholesteroxysilanes have been reported more recently.² It is interesting that no significant steric hindrance was observed even in tetracholesteroxysilane. A particular infrared peak has been observed at 905 cm⁻¹; this is due to the stretching vibration of the Si-O-C bond between steroid group and silicon atom.

To ascertain, for comparison purposes, the properties of the corresponding stigmasteroxy compounds, the present authors synthesized distigmasteroxydimethylsilane [Me₂Si(OC₂₉H₄₇)₂], tristigmasteroxymethylsilane, and tetrasteroxysilane, by treating anhydrous stigmasterol with the appropriate chlorosilane in toluene. Structures of the new compounds were deduced from elementary analysis and infrared absorption spectra; results of molecular weight determination agreed with all the theoretical values. The infrared peak at 900–910 cm⁻¹ mentioned above also appeared in this series. No peak was found at 3330 cm⁻¹ (absence of O-H), but peaks were observed at 1055–1100 (Si-O-C) and 1250–1259 cm⁻¹ (Si-Me₁₋₃).



On adding an excess of pyridine and an excess of methyltrichlorosilane to the toluene solution of stigmasterol, a cyclic siloxane was obtained. Analysis and molecular weight determination indicated that this compound was tristigmasteroxytrimethylcyclotrisiloxane (I). The infrared spectrum showed broad absorption in the 1020–1140 cm⁻¹ zone—a combination of Si-O-C and Si-O-Si peaks. The Me-Si peak at 1259 cm⁻¹ was also clearly observed.

Experimental

Stigmasterol having m.p. 164–165° was used. Molecular weights were determined by cryoscopy in benzene.

Distigmasteroxydimethylsilane

Stigmasterol (9.1 g, 0.022 mole) was dissolved in 80 ml of toluene which contained 2 g of pyridine (0.025 mole) in a flask fitted with stirrer and reflux condenser. Under constant stirring a solution of 0.8 g of dimethylchlorosilane (0.013 mole) in 20 ml of toluene was added at 110°. Heating and stirring were continued for 12 hr to complete the reaction. After cooling, the precipitate of pyridine hydrochloride was filtered off, the filtrate was evaporated to 40 ml, and 40 ml of dry acetone was added to precipitate the reaction product. A white solid (5 g) melting at 140–145° was obtained. This was then extracted with acetone in a Soxhlet apparatus until the melting

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¹ Liu, S. L., and Wang, T. T., *J. Chin. Chem. Soc., Taipei*, 1963, **10**(ser. II), 166.

² Liu, S. L., Wang, T. T., and Lin, H. L., *J. Chin. Chem. Soc., Taipei*, 1964, **11**(ser. II), 62 (*Chem. Abstr.*, 1964, **61**, 8365a).

point had risen to 157°, when the *product* weighed 4 g (40·6% yield). A mixed melting point with stigmasterol gave a depression to 130–136° (Found: C, 81·2; H, 11·2; Si, 3·2; mol. wt., 877. $C_{60}H_{102}O_3Si$ requires C, 81·4; H, 11·4; Si, 3·2%; mol. wt., 881). Peaks at 1252 (SiMe₂), 1080, 900 cm⁻¹ (Si–O–C); there was no peak at 3330 cm⁻¹ (absence of O–H).

Tristigmasteroxymethylsilane

Stigmasterol (5 g, 0·012 mole) in 40 ml of toluene containing 2 g (0·025 mole) of pyridine was treated as above with trichloromethylsilane (0·6 g, 0·004 mole) in 40 ml of toluene at 102°. The pyridine salt was removed as described and the filtrate concentrated to 50 ml; 200 ml of acetone was added. The glue-like precipitate was extracted with acetone until 0·5 g (17·5% yield) of white *solid*, m.p. 160–162°, remained. Admixture of this with the starting material depressed the melting point to 130–140° (Found: C, 82·4; H, 11·1; Si, 2·3; mol. wt., 1280. $C_{88}H_{144}O_3Si$ requires C, 82·6; H, 11·3; Si, 2·2%; mol. wt., 1278). Peaks at 1255 (SiMe), 1080, 907 cm⁻¹ (Si–O–C).

Tetrastigmasteroxysilane

The reaction was carried out as above [5 g (0·012 mole) of stigmasterol in 25 ml of toluene and 1 g (0·012 mole) of pyridine; 0·5 g (0·003 mole) of silicon tetrachloride in 25 ml of toluene]. After filtering off pyridine hydrochloride, an equal volume of dry acetone was added; overnight precipitation gave crystals, m.p. 170–180°. Further purification was carried out by reprecipitating from 5 ml of toluene by addition of 15 ml of acetone. A glassy fluid (1·5 g) was obtained. Prolonged extraction of this with acetone in a Soxhlet apparatus gave a brittle *solid*, m.p. 161–162°. Admixture with stigmasterol or tristigmasteroxymethylsilane depressed the melting point to 145–152° and 148–160° respectively. The product weighed 1·2 g (yield 24%) (Found: C, 83·0; H, 11·0; Si, 1·6; mol. wt., 1672. $C_{116}H_{188}O_4Si$ requires: C, 83·2; H, 11·3; Si, 1·7%; mol. wt., 1671). Peaks at 1060–1100 and 900 cm⁻¹ (Si–O–C); there were no peaks corresponding to O–H (3330) and SiMe (1259 cm⁻¹).

1,3,5-Tristigmasteroxy-1,3,5-trimethylcyclotrisiloxane

Stigmasterol (5 g, 0·012 mole) was dissolved in 30 ml of toluene; 2 g (0·025 mole) of pyridine and 1·3 g (0·009 mole) of trichloromethylsilane were added. The mixture was heated to 102° for 1 hr, then cooled to room temperature and stirred for 8 hr more. After removal of the pyridine salt the filtrate was evaporated to 40 ml and 50 ml of dry acetone was added. A glassy semi-solid was precipitated, from which prolonged acetone extraction in a Soxhlet apparatus produced a white *solid*. This melted at 154–156° and weighed 3 g (yield 53·5%) (Found: C, 76·5; H, 10·9; Si, 5·8; mol. wt., 1415. $C_{90}H_{150}O_6Si_3$ requires C, 76·6; H, 10·6; Si, 6·0; mol. wt., 1412). Peaks at 1259 (SiMe), 1090, 900 cm⁻¹ (Si–O–C); the peak of the trisiloxane bond at 1020 cm⁻¹ combined with that of Si–O–C to give a very wide band.

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