PART - I

RESULTS AND DISCUSSIONS
Ethers serve as excellent protecting groups for alcohols as they are stable under various reaction conditions. Recently methylthiomethyl (MTM) ethers have gained importance because of their easy preparations and their deprotection can be achieved under mild reaction conditions which is a prerequisite for a suitable protecting group. Although there are many other protecting groups for primary and secondary alcohols, there are only a few protecting groups for tert-alcohols. Pojer et al reported that MTM ethers of tert-alcohols can be easily prepared by reaction with dimethyl sulfoxide and acetic anhydride containing a catalytic amount of acetic acid. The deprotection of MTM ethers has been achieved with various reagents, viz., AgNO₃, HgCl₂/CdCO₃ & MeI/moist Me₂CO. It was reported by Sharma et al that methyl and methylthiomethyl ethers can be cleaved with chlorotrimethylsilane and acetic anhydride to furnish the corresponding acetates in excellent yields. In continuation of this study, the cleavage of tert-methylthiomethyl ethers was attempted with the above mentioned reagent combination. However, the corresponding acetates were not obtained, instead the corresponding acetoxyethyl
ethers were obtained in excellent yields. Obviously, the cleavage of carbon-sulphur bond is taking place in preference to the carbon-oxygen bond. Reactions were tried on various substrates as shown in Scheme 1 and the products were characterized primarily by NMR spectral data which displayed as sharp singlet integrating to two protons near $\delta 5.30$ ppm. The reaction products were further characterized by comparing with those obtained by cleavage with mercuric acetate as described below.

PREPARATION OF ACETOXYMETHYL ETHERS FROM MTM ETHERS THROUGH CLEAVAGE WITH MERCURIC ACETATE

It was reported that MTM ethers can be easily cleaved by reaction with mercuric chloride in CH$_3$CN-H$_2$O. It was, therefore, argued that the reaction of mercuric acetate with MTM ethers should provide the corresponding acetoxyethyl ethers in good yields according to the mechanism given below.

\[
\begin{align*}
\text{AcO}^- & \quad \text{Hg(OAc)} \\
\text{H}_3\text{C-S-Hg(OAc)} & \quad \text{C-0-CH$_2$S-CH$_3$} \\
\text{C-0-CH$_2$0Ac} & \quad \text{S}^+\text{-CH$_3$} \\
\text{AcO}^- & \quad \text{Hg(OAc)}
\end{align*}
\]
This surmise turned out to be true when the reaction of the substrates (1c), (2b), (3b), (4b) & (5b) furnished the corresponding acetoxyethyl ethers in 90-95% yields.

Acetoxyethyl ethers are extremely labile even to mild acid (0.01N HCl) and base (1% K₂CO₃ solution in EtOH) to furnish the corresponding alcohols quantitatively.
Scheme 1

(1) a, $R' = H$, $R = H$
b, $R' = Ac$, $R = H$
c, $R' = Ac$, $R = -CH_2 SCH_3$
d, $R' = Ac$, $R = -CH_2 OAc$

(2) a, $R = H$
b, $R = -CH_2 SCH_3$
c, $R = -CH_2 OAc$

(3) a, $R = H$
b, $R = -CH_2 SCH_3$
c, $R = -CH_2 OAc$

(4) a, $R = H$
b, $R = -CH_2 SCH_3$
c, $R = -CH_2 OAc$

(5) a, $R = H$
b, $R = -CH_2 SCH_3$
c, $R = -CH_2 OAc$
CONVERSION OF MTM ETHERS INTO MOM, EOM & MEM ETHERS:

As mentioned earlier, MTM ethers have been reported to be cleaved easily with mercuric chloride-cadmium carbonate in CH$_3$CN-H$_2$O. Mechanistically, it appeared that MTM ethers are first cleaved to furnish hydroxymethyl ethers or chloromethyl ethers, which being unstable under the reaction conditions, furnish the corresponding alcohols immediately as shown in Scheme 2 below.

Scheme 2

\[ R-O-\text{CH}_2 - S - \text{CH}_3 \]
\[ \xrightarrow{\text{Mercuric Chloride}} \]
\[ X \rightarrow \text{Hg}^+\text{Cl} \]
\[ \text{R-O-CH}_2\text{OH} \rightarrow \text{R-OH} \]

\[ X = \text{Cl}^- \text{ or } \text{OH}^- \]

It was argued that if this reaction is carried out in presence of methanol, ethanol and 2-methoxyethanol, the corresponding methoxymethyl (MOM), ethoxymethyl (EOM),
and methoxyethoxymethyl (MEM) ethers could be obtained in good yields. Indeed, when the substrates (6b), (7b), (2b) & (3b) given in Scheme 3 were treated with mercuric chloride in different solvents, the corresponding ethers (6c-e), (7c-e), (2d-f) & (3d-f) were obtained in 70-80% yields. The products were characterized by NMR and Mass spectroscopy.

Although a number of methods are available for protecting hydroxy functions, only a few are applicable to the tert-hydroxy group. Since MOM, EOM and MEM ethers of tert-alcohol are otherwise difficult to obtain, this method promises to be of value in organic synthesis. Recently Corey et al. have described a new method for conversion of (5-methoxyethoxymethyl (MEM) ethers into isopropylthiomethyl and cyanomethyl ethers.
Scheme 3

(6) a, R = H
   b, R = -CH$_2$SCH$_3$
   c, R = -CH$_2$OCH$_3$ (MOM)
   d, R = -CH$_2$OCH$_2$CH$_3$ (EOM)
   e, R = -CH$_2$OCH$_2$CH$_2$OCH$_3$ (MEM)

(7) a, R = H
   b, R = -CH$_2$SCH$_3$
   c, R = -CH$_2$OCH$_3$
   d, R = -CH$_2$OCH$_2$CH$_3$
   e, R = -CH$_2$OCH$_2$CH$_2$OCH$_3$

(2) d, R = -CH$_2$OCH$_3$
     e, R = -CH$_2$OCH$_2$CH$_3$
     f, R = -CH$_2$OCH$_2$CH$_2$OCH$_3$

(3) d, R = -CH$_2$OCH$_3$
     e, R = -CH$_2$OCH$_2$CH$_3$
     f, R' = -CH$_2$OCH$_2$CH$_2$OCH$_3$
CLEAVAGE OF MOM, BOM AND MEM ETHERS WITH TRITYL TETRAFLUOROBORATE (TTFB)

Sharma et al.\textsuperscript{12} have earlier described that MTM ethers can be easily cleaved with trityl tetrafluoroborate (TTFB) to obtain the corresponding alcohols. Since in MOM, BOM and MEM, the methylene group is attached to two oxygen atoms, it should be sufficiently basic to lose a hydride to trityl tetrafluoroborate and the resulting cation will collapse during aqueous work up to give the corresponding alcohol as shown in Scheme 4.

\textbf{Scheme 4}

\[ R\text{-}O\text{-}CH\text{-}OR' \xrightarrow{\text{H}} R\text{-}O\text{-}CH\text{-}OR' \xrightarrow{\text{BF}_4^-} R\text{-}O\text{-}CH\text{-}OR' \xrightarrow{\text{H}_2\text{O}} R\text{-}OH \]

\[ R'\text{=}\text{-}\text{CH}_3, \text{-}\text{C}_2\text{H}_5, \text{-}\text{CH}_2\text{OC}_2\text{H}_5 \]
When the ethers (6c-e), (7o-e), (2d-f) and (3d-f) were treated with TTPB according to the procedure described in Ref.\textsuperscript{12}, the corresponding alcohols (6a), (7a), (2a) & (3a) were obtained in 75-80\% yields in 10-15 min\textsuperscript{13, 14}.

After the completion of above studies, it was observed that the methyl ethers remained unaffected with chlorotrimethylsilane and acetic anhydride, when chlorotrimethylsilane was used from a different bottle. It was therefore concluded that the chlorotrimethylsilane originally used for carrying out the cleavage of methyl ethers\textsuperscript{15} was contaminated with some impurities which were responsible for the cleavage reactions. On searching for methods of preparation of chlorotrimethylsilane, it was found that it can be prepared from hexamethyldisiloxanes, ammonium chloride and concentrated sulphuric acid as shown in the equation (1)\textsuperscript{16}.

\begin{equation}
(\text{Me}_3\text{Si})_2\text{O} + 2\text{NH}_4\text{Cl} + H_2\text{SO}_4
\end{equation}

\[\rightarrow 2\text{Me}_3\text{SiCl} + (\text{NH}_4)_2\text{SO}_4 + H_2\text{O} \quad (1)\]

It was therefore suspected that original bottle of chlorotrimethylsilane might have been contaminated
with sulphuric acid. Therefore, when the cholesterol methyl ether (6f) was treated with chlorotrimethylsilane and acetic anhydride in presence of a trace amount of conc. \( \text{H}_2\text{SO}_4 \), the cholesteryl acetate (6h) was obtained in 90% yield. Reaction of cholesterol methyl ether (6f) with acetic anhydride and a trace amount of conc. \( \text{H}_2\text{SO}_4 \) led to decomposition of starting material and no cholesteryl acetate (6h) was obtained thus suggesting that chlorotrimethylsilane is also involved in the cleavage reaction. The mechanistic aspect of this reaction is difficult to predict at this stage.

Although methyl ethers remained unaffected on heating with chlorotrimethylsilane and acetic anhydride, benzyl ethers (6g) & (8a) were cleaved to yield the corresponding acetates (6h) & (8b) in 40-60% yields (Scheme 5).

**Scheme 5**

\[(\text{6}) \quad f, R = \text{CH}_3, \quad g, R = \text{CH}_2\text{C}_6\text{H}_5, \quad h, R = \text{Ac} \]

\[(\text{8}) \quad a, R = \text{CH}_2\text{C}_6\text{H}_5, \quad b, R = \text{Ac} \]
PART - I

EXPERIMENTAL

General procedure for the preparation of tert-methylthiomethyl ethers:

A solution of 0.5 m mol of the substrate in 2 ml of dimethylsulfoxide was treated with 1 ml of acetic anhydride and the reaction mixture was kept at room temperature for 12-36 hr monitoring by t.l.c. The reaction mixture was then diluted with excess water and extracted with chloroform (3 x 50 ml). The washed extract was dried over anhydrous sodium sulphate and distilled under reduced pressure. The crude residue so obtained was purified by preparative t.l.c.

General procedure for the cleavage of tert-MTH ethers with CTMS-Ac₂O:

A solution of 0.5 m mol of the substrate in 2 ml of acetic anhydride (a few drops of dry CH₂Cl₂ was added in case the ether was insoluble in Ac₂O) was treated with 1 ml of CTMS and the reaction mixture was stirred at room temperature for 10-12 hr monitoring by t.l.c. The reaction mixture was diluted with excess water and extracted with chloroform (3 x 100 ml). The
washed and dried extract was evaporated under reduced pressure. The crude residue was then purified by preparative t.l.c.

**General procedure for the cleavage of tert-MTM ethers with Hg(OAc)$_2$ in CH$_3$CN:**

A solution of 1 m mol of the tert-MTM ether in 4 ml of dry CH$_3$CN was treated with 1 m mol of mercuric acetate and the reaction mixture was stirred at room temperature monitoring by t.l.c. After 2 hr the reaction mixture was quenched with water and extracted with chloroform (3 x 100 ml). The washed and dried extract was evaporated under reduced pressure. The crude residue so obtained was purified by preparative t.l.c.

**General procedure for hydrolysis of tert-MTM ethers with base:**

A solution of 0.5 m mol of the substrate in 4 ml of ethanol was treated with 10 drops of 5% K$_2$CO$_3$ in H$_2$O under nitrogen atmosphere while stirring at room temperature. The reaction was monitored on t.l.c. and after half an hour the reaction mixture was quenched with water.
and extracted with chloroform. The washed and dried extract was then evaporated under reduced pressure. The residue so obtained was then purified on preparative t.l.c.

**General procedure for conversion of MTM ethers into MOM, EOM and MEM ethers:**

A solution of 0.5 m mol of the MTM ether in 4 ml of methanol (few drops of THF was added when the substrate was not soluble in the solvent) was stirred with 1 m mol of mercuric chloride at room temperature monitoring the reaction on t.l.c. After 2-3 hr the reaction mixture was quenched with water and extracted with chloroform (3 x 100 ml). The extract after drying over anhydrous Na₂SO₄ was evaporated under reduced pressure. The crude residue was then purified by preparative t.l.c. which furnished pure MOM ether.

The above reaction was then carried out in 4 ml of ethanol and 4 ml of 2-methoxyethanol separately in the same way, corresponding EOM ethers and MEM ethers were obtained.
General procedure for cleavage of MOM, EOM and MEM ethers with trityl tetrafluoroborate:

A solution of 1.0 mol of the substrate in 4 ml of dry dichloromethane was treated with 1.25 mol of trityl tetrafluoroborate and the reaction mixture was stirred under nitrogen atmosphere at room temperature for 10-15 min monitoring by t.l.c. When the t.l.c. indicated that no more starting material was left, it was quenched with water and extracted with chloroform (3 x 150 ml). The washed and dried extract was then evaporated under reduced pressure. The residue so obtained was then purified on preparative t.l.c. to obtain the pure alcohol.

General procedure for the preparation of methyl ethers:

To a stirring solution of 0.5 mol of the substrate in 5 ml N,N-dimethylacetamide at room temperature was added 2 mol of sodium hydride (50% dispersion in oil) after washing with dry hexane. After 2 hr of stirring, 1 mol of CH₃I was added to the reaction mixture and the stirring continued until t.l.c. indicated the disappearance of the starting material (6 to 8 hr).
Excess water was added to the reaction mixture, extracted with chloroform (3 x 100 ml) and washed with water. The extract was dried over anhydrous sodium sulfate and distilled under reduced pressure to obtain a crude residue which was purified by preparative t.l.c.

**General procedure for the preparation of benzyl ethers:**

A solution of 0.5 m mol of the substrate in 4 ml of dry N,N-dimethylacetamide was stirred with 2 m mol of NaH (50% dispersion in oil, washed with dry hexane) at room temperature under N₂. After half an hour 1 m mol of benzyl chloride was added and stirring continued for 12-15 hr monitoring the reaction on t.l.c. The reaction mixture was then worked up as described in the procedure for the preparation of methyl ethers and the crude residue so obtained was purified by preparative t.l.c.

**General procedure for the cleavage of benzyl ethers with CTMS–Ac₂O:**

A solution of 0.5 m mol of the benzyl ether in 2 ml of acetic anhydride (a drop of dry CH₂Cl₂ was added...
in case the ether was not soluble in Ac$_2$O) was treated with 1 ml of CTMS and the reaction mixture was heated for 3-12 hr on an oil bath at 110°C monitoring by t.l.c. The reaction mixture was worked up by diluting with excess water followed by extraction with chloroform (3 x 100 ml). The washed and dried extract was evaporated under reduced pressure to obtain a crude residue which was purified by preparative t.l.c.

**Preparation of (1b):**

100 mg of cholesterol in 4 ml of chloroform was epoxidized by treating with 100 mg of MCPBA keeping the reaction mixture at room temperature for overnight. The reaction mixture was diluted with chloroform, excess MCPBA was destroyed by treating with a solution of KI and liberated iodine was removed by washing with sodium thiosulfate solution. The extract was washed with a solution of NaHCO$_3$ followed by water and distillation at reduced pressure left a residue which on purification by preparative t.l.c. (EtOAc:Hexane, 1:7) yielded 70 mg of 5,6$\alpha$-epoxy-5$\alpha$-cholestan-3$\beta$-ol m.p. 141°C (MeOH), reported$^{13}$ m.p. 141°C.

100 mg of 5,6$\alpha$-epoxy-5$\alpha$-cholestan-3$\beta$-ol was reduced with LiAlH$_4$ in the usual way to give 5$\alpha$-cholestan-3$\beta$. 
5-diol (1a). This diol, without further purification, was acetylated with Ac$_2$O-Py, affording 100 mg of 5α,7α-cholestane-3β,5-diol 3-acetate (1b) which was recrystallized from acetone m.p. 185°C, reported$^{18}$ m.p. 185°C.

**Preparation of (1c):**

The reaction of 100 mg of (1b) with DMSO-Ac$_2$O for 36 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:16) 65 mg of (1c) 135-136°C (EtOAc-MeOH); IR bands at 2900, 1730, 1460, 1375 and 1250 cm$^{-1}$; NMR: 4.45 (O-CH$_3$-S), 4.35 (H-3), 2.00 (S-CH$_3$) and 1.95 (OAc); Mass spectrum peaks were at m/z 506 (M$^+$), 463, 448, 445, 429 & 71 (as base peak).

**Reaction of (1c) with CTMS-Ac$_2$O:**

The reaction of 50 mg of (1c) with CTMS-Ac$_2$O for 12 hr as described under general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:12) 45 mg of (1d) as a gum. It showed IR bands at 2900, 1725 (double intensity), 1460, 1375, 1250 and 1120 cm$^{-1}$; NMR: 5.30 (-O-CH$_2$-O-), 2.00 (-O-CH$_2$-OAc) & 1.95 (OAc); MS m/z at 518 (M$^+$), 445, 432, 430, 402 and 71.
Reaction of (1c) with Hg(OAc)$_2$:

The reaction of 50 mg of (1c) with mercuric acetate in dry acetonitrile for 2 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc-Hexane, 1:12) 47 mg of (1d) which was found to be identical with the product obtained from the reaction of (1c) with CTMS-Ac$_2$O (t.l.c., IR, NMR and Mass spectral data).

Preparation of (2b):

The reaction of 100 mg of parthenin (2a) with DMSO-Ac$_2$O for 36 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:2) 60 mg of (2b) as a gum. It exhibited IR bands at 2900, 1760, 1725, 1600, 1500, 1100 and 1000 cm$^{-1}$; NMR: 7.75 d (J=6 Hz, H-2), 6.20 d (J=6 Hz, H-3), 6.05 d (J=2 Hz, H-13b), 5.45 d (J=2 Hz, H-13a), 4.75 d (J=8 Hz, H-6), 4.45 s (O-CH$_2$-S-), 3.30 m (H-7), 2.00 s (S-CH$_3$), 1.20 s (H-15), 1.05 d (J=7 Hz, H-14); MS m/z 322 (M$^+$), 275, 261, 260, 245, 230 & 77; Anal. calcd. for C$_{17}$H$_{22}$O$_4$S: C, 63.34; H, 6.88; Found: C, 63.47; H, 6.71.
Reaction of (2b) with CTMS-Ac$_2$O:

The reaction of 50 mg of (2b) with CTMS-Ac$_2$O for 10 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:2) 46 mg of (2c) as a gum. It showed IR bands at 2900, 1760, 1735, 1180, 1080, 1000 cm$^{-1}$; NMR: 7.72 d (J=6 Hz, H-2), 6.40 d (J=6 Hz, H-3), 6.20 d (J=2 Hz, H-13b), 5.58 d (J=2 Hz, H-13a), 5.20 s (O-CH$_2$-O-), 4.80 d (J=8 Hz, H-6), 3.30 m (H-7), 1.98 s (OAc), 1.20 s (H-15), 1.05 d (J=7 Hz, H-14); MS m/z 334 (M$^+$), 291, 276, 246 & 71 (base peak); Anal. calcd. for C$_{18}$H$_{22}$O$_6$: C, 66.66; H, 6.63; Found: C, 64.71, H, 6.51.

Reaction of (2b) with Hg(OAc)$_2$:

The reaction of 50 mg of (2b) with mercuric acetate in 4 ml of dry acetonitrile for 2 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:2) 48 mg of (2c) which was found to be identical with the product obtained from the reaction of (2b) with CTMS-Ac$_2$O (t.l.c., IR, NMR and Mass spectral data).
Preparation of (3a):

The compound (3a) was prepared as discussed in the literature.\(^\text{19}\)

Preparation of (3b):

A solution of 100 mg (3a) in 1 ml of DMSO was treated with 2 ml of \(\text{Ac}_2\text{O}\) for 18 hr as described earlier in the general method of making MTM ether. After usual work up followed by purification by preparative t.l.c. (EtOAc:Bz, 1:7) yielded 90 mg of (3b) m.p. 153-154°C (EtOAc); IR bands at 2900, 1775, 1730, 1700, 1645, 1140, 1080, 1000 & 960 cm\(^{-1}\); NMR: 6.10 d (\(J=3.5\) Hz, H-13b), 5.70 m (H-8), 5.50 d (\(J=3.5\) Hz, H-13a), 5.20 d (\(J=10\) Hz, H-6), 4.40 s (-O-CH\(_2\)-S), 3.20 m (H-7), 2.00 s (-S-CH\(_3\)), 1.80 br (H-15), 1.05 s (H-14), 1.10 d (\(J=7\) Hz, H-3', & H-4'); MS m/z 408 (M\(^{+}\)), 348, 331, 278, 260, 242, 217, 200 and 71 (base peak); Anal. calcd. for C\(_{21}\)H\(_{28}\)O\(_5\)S: C, 61.75; H, 6.91; Found: C, 61.83; H, 6.99.

Reaction of (3b) with CTMS-\(\text{Ac}_2\text{O}\):

The reaction of 50 mg of (3b) with CTMS-\(\text{Ac}_2\text{O}\) for 10 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:5) 47 mg of (3c) m.p.
156-158°C (EtOAc); It showed IR bands at 2950, 1775, 1730, 1715, 1650, 1150, 1115, 1015 and 960 cm\(^{-1}\); NMR: 6.10 d (J=3.5 Hz, H-13b), 5.70 m (H-8), 5.58 d (J=3.5 Hz, H-13a), 5.30 s (-O-CH\(_2\)-O-), 5.15 m (H-6), 3.40 m (H-7), 1.92 s (OAc), 1.81 br (H-15), 1.05 s (H-14), 1.12 d (J=7 Hz, H-3' & H-4'); MS m/z 420 (M\(^+\)), 377, 362, 332, 278, 242 & 71; Anal. calcd. for C\(_{22}\)H\(_{28}\)O\(_8\): C, 62.85; H, 6.71; Found: C, 62.98; H, 6.82.

Reaction of (3b) with Hg(OAc)\(_2\):

The reaction of 50 mg of (3b) in 4 ml of dry acetonitrile with mercuric acetate for 2 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:5) 40 mg of (3c) which was found to be identical with the compound obtained from the reaction of (3b) with CTMS-Ac\(_2\)O (t.l.c., m.p., IR, NMR and Mass spectral data).

Preparation of (4a):

Discussed in the experimental section of Part-II A

(Page No 109)
Preparation of (4b)

The reaction of 100 mg of (4a) with DMSO-\(\text{Ac}_2\text{O}\) for 24 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:3) 75 mg of MTM ether (4b) as a gum. It showed IR bands at 3050, 1765, 1210, 1120, 1060 & 980cm\(^{-1}\); NMR: 6.85 d (J=17 Hz, H-1), 6.35 d (J=17 Hz, H-2), 6.25 br (H-13a), 5.69 br (H-13b), 5.20 m (H-8), 4.70 m (H-6), 4.40 s (-O-CH\(_2\)-OAc), 3.23 m (H-7), 2.00 s (-\(\text{CH}_3\)), 1.45 s (H-14), 1.10 d (J=7 Hz, H-15) and 1.05 d (J=7 Hz, H-3' & H-4'); MS m/z 410 (M\(^+\)), 349, 333, 322, 279, 262, 229 and 71.

Reaction of (4b) with CTMS-\(\text{Ac}_2\text{O}\)

The reaction of 50 mg of (4b) with CTMS-\(\text{Ac}_2\text{O}\) for 12 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:4) 45 mg of (4c) as a gum. It showed IR bands at 2990, 2910, 1770, 1740, 1685, 1375, 1225, 1145, 1125, 1020 cm\(^{-1}\); NMR: 6.85 d (J=17 Hz, H-1), 6.35 d (J=17 Hz, H-2), 6.25 s br (H-13a), 5.69 s br (H-13b), 5.30 s (-O-CH\(_2\)-OAc), 5.20 m (H-8), 4.70 m (H-6), 3.23 m (H-7), 2.00 (OAc), 1.45 s (H-14), 1.10 d (J=7 Hz, H-15), and 1.05 d (J=7 Hz, H-3' and H-4'); MS m/z 422 (M\(^+\)), 379, 364, 349, 334, 322, 262, 229, 200 and 71.
**Reaction of (4b) with Hg(OAc)$_2$**

The reaction of 50 mg of (4b) with mercuric acetate in 4 ml of dry acetonitrile for 2 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:4) 42 mg of a compound which was found to be identical with (4c) obtained from the cleavage of MTM ether (4b) with CTMS–Ac$_2$O (t.l.c., IR, NMR and MS).

**Preparation of (5b)**

The reaction of 100 mg of $\beta$-terpineol (5a) with DM$_2$SO–Ac$_2$O for 24 hr as described under the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:9) 70 mg of (5b) as an oil. It showed IR bands at 2990, 2970, 1665, 1450, 1375, 1210 and 750 cm$^{-1}$; NMR: 5.30 s br (H-9a & H-9b), 4.40 s (–O–CH$_2$–S), 2.00 s (–S–CH$_3$), 1.80 s br (H-10), 1.20 s (H-7); MS m/z 214 (M$^+$), 153, 137 and 71.

**Reaction of (5b) with CTMS–Ac$_2$O**

The reaction of 70 mg of (5b) with CTMS–Ac$_2$O for 12 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:9) 64 mg of (5c) as
an oil; IR bands at 2990, 2970, 1735, 1665, 1450, 1375, 1210 and 750 cm\(^{-1}\); NMR: 5.30 (overlapping signals of H-9a, H-9b and -O-CH\(_2\)-O-), 2.00 s (OAc), 1.80 s br (H-10), 1.20 s (H-7); MS m/z 226 (M\(^+\)), 183, 168, 153 and 71.

**Reaction of (5b) with Hg(OAc)\(_2\):**

The reaction of 50 mg of (5b) with mercuric acetate in 4 ml of dry acetonitrile for 2 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:9) 45 mg of a compound which was identical with (5c) obtained from the reaction of (5b) with CINS-Ac\(_2\)O (t.l.c., IR, NMR & Mass spectral data).

**Preparation of (6b):**

The reaction of 100 mg of cholesterol (6a) with DMSO-Ac\(_2\)O for overnight as described in the general procedure for making MTM ether, furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:16) 85 mg of (6b) m.p. 115°C (EtOAc); IR bands at 2900, 1455, 1370 and 1150 cm\(^{-1}\); NMR: 5.25 s br (H-6), 4.40 s (-O-CH\(_2\)-S-), 2.00 (-S-CH\(_3\)); Mass spectrum peaks were at m/z 446 (M\(^+\)), 369 and 71; Anal. calcd. for C\(_{29}\)H\(_{50}\)O\(_8\): C, 77.97; H, 11.28; Found: C, 78.28; H, 11.01.
Reaction of (6b) with HgCl$_2$ in CH$_3$OH:

The reaction of 50 mg of (6b) in 4 ml of methanol (a few drops of THF was used) with HgCl$_2$ for 2 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:12) 40 mg of (6c) m.p. 78°C (MeOH), reported$^{20}$ m.p. 78.8°C; IR bands at 2900, 1450, 1370 and 1060 cm$^{-1}$; NMR: 5.25 s br (H-6), 4.60 (-OCH$_2$O-), 3.30 s (OCH$_3$); Mass spectrum peaks were at 4.30 (M$^+$), 399, 285 and 269.

Reaction of (6b) with HgCl$_2$ in C$_2$H$_5$OH:

The reaction of 50 mg of (6b) in 4 ml of dry ethanol (a few drops of THF was added) with HgCl$_2$ for 2 hr as described in the general procedure for making EOM ether, furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:12) 38 mg of (6d) m.p. 92°C (MeOH); IR bands at 2900, 1450, 1370, 1150 and 1000 cm$^{-1}$; NMR: 5.25 br (H-6), 4.60 (-OCH$_2$O-), 3.50 q (J=7 Hz, -OCH$_2$CH$_3$); MS m/z 444 (M$^+$), 399, 385, 369 and 71 (base peak)
**Reaction of (6b) with HgCl₂ in 2-methoxyethanol:**

The reaction of 50 mg of (6b) in 4 ml of dry 2-methoxyethanol (few drops of dry THF was added) with HgCl₂ for 3 hr as described in the general procedure for making MEM ether, furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:16) 36 mg of (6e) as a gum. It exhibited IR bands at 2900, 1715, 1450, 1300 and 1060 cm⁻¹; NMR: 5.25 br (H-6), 4.60 s (-O-CH₂-O-), 3.50 m (-OCH₂CH₂-), 3.20 s (-OCH₃); Mass spectrum peaks at m/z 474 (M⁺), 443, 399, 385, 369.

**Preparation of (7b):**

The reaction of 100 mg of C₁₆-cetyl alcohol (7a) with DMSO-Ac₂O for 18 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:3) 90 mg of (7b) as a gum. It exhibited IR bands at 2800, 1715, 1450, 1300 and 1060 cm⁻¹; NMR: 4.48 s (-O-CH₂-S-), 3.34 t (J=4 Hz, -CH₂-CH₂-OCH₂-S-), 1.98 s (S-CH₃), 1.10 s (28H), 0.70 t (J=6.5 Hz, end CH₃); Mass spectrum peaks at m/z 302 (M⁺), 241, 225 and 71 (as base peak).
Reaction of (7b) with HgCl₂ in MeOH:

The reaction of 50 mg of (7b) in 4 ml of MeOH with mercuric chloride for 2 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:2) 35 mg of (7c) as a gum. It showed IR bands at 2800, 1720, 1450, 1300 and 1060 cm⁻¹; NMR: 4.50 s (O-CH₂-O⁻), 3.40 (O-CH₃), 3.34 t (J=4 Hz, -CH₂-O-CH₂-O⁻), 1.10 s (28H), 0.70 t (J=6.5 Hz, end CH₃); MS m/z at 286 (M⁺), 255, 225 and 71.

Reaction of (7b) with HgCl₂ in ethanol:

The reaction of 50 mg of (7b) in 4 ml of dry ethanol with HgCl₂ for 2.5 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:2) 40 mg of (7d) as a gum. It showed IR bands at 2800, 1715, 1450, 1300 and 1060 cm⁻¹; NMR: 4.50 s (O-CH₂-O⁻), 3.50 (overlapping signals of -C-CH₂-O-CH₂-O-CH₂-CH₃), 1.10 s (28H), 0.70 t (J=6.5 Hz, end CH₃); MS m/z at 300 (M⁺), 255 and 71.

Reaction of (7b) with HgCl₂ in 2-methoxyethanol:

The reaction of 50 mg of (7b) in 4 ml of dry 2-methoxyethanol with HgCl₂ for 2 hr as described earlier furnished after purification by preparative t.l.c.
(EtOAc:Hexane, 1:2) 36 mg of (7e) as a gum. It showed IR bands at 2900, 1715, 1450, 1300 and 1060 cm\(^{-1}\); NMR: 4.50 s (-O-CH\(_2\)-O-), 3.34 t (J=4 Hz, -CH\(_2\)-O-CH\(_2\)-), 3.20 s (-OCH\(_3\)), 1.10 s (2SH), 0.70 t (J=6.5 Hz, end CH\(_3\)) ; Mass spectrum peaks at m/z 330 (M\(^+\)) 299, 255, 225 and 71 (base peak).

**Reaction of (2b) with HgCl\(_2\) in MeOH:**

The reaction of 50 mg of (2b) in 4 ml methanol with mercuric chloride for 3 hr as described earlier furnished after purification by preparative t.L.C. (EtOAc:Hexane, 1:1) 42 mg of (2d) as a gum. It showed IR bands at 2900, 1760, 1725, 1600, 1475, 1100 cm\(^{-1}\); NMR: 7.75 d (J=6 Hz, H-2), 6.20 d (J=6 Hz, H-3), 6.05 d (J=2 Hz, H-13b), 5.45 d (J=2 Hz, H-13a), 4.75 d (J=8 Hz, H-6), 4.60 s (O-CH\(_2\)-O-), 3.30 m (H-7), 3.20 s (O-CH\(_3\)), 1.20 s (H-15), 1.05 d (J=7 Hz, H-14); MS m/z 306 (M\(^+\)), 275, 245, 235, 201 and 71.

**Reaction of (2b) with HgCl\(_2\) in ethanol:**

The reaction of 50 mg of (2b) in 4 ml of dry ethanol with mercuric chloride for 3 hr as described earlier furnished after purification by preparative...
t.l.c. (EtOAc:Hexane, 1:1) 40 mg of (2e) as a gum. It exhibited IR bands at 2900, 1760, 1725, 1600, 1475, 1150 cm\(^{-1}\); NMR: 7.75 d (J=6 Hz, H-2), 6.20 d (J=6 Hz, H-3), 6.05 d (J=2 Hz, H-13b), 5.45 d (J=2 Hz, H-13a), 4.75 d (J=8 Hz, H-6), 4.60 (−O−CH\(_2\)−O−), 3.05 to 3.50 (overlapping signals of H-7 and −OCH\(_2\)CH\(_3\)), 1.20 s (H-15), 1.05 d (J=7 Hz, H-14); Mass spectrum peaks were at m/z 320 (M\(^+\)), 275, 261, 245 and 71 (base peak).

**Reaction of (2b) with HgCl\(_2\) in 2-methoxyethanol:**

The reaction of 50 mg of (2b) in 4 ml of dry 2-methoxyethanol with mercuric chloride for 3 hr as described earlier furnished 36 mg of (2f) as a gum. It showed IR bands at 2900, 1760, 1725, 1600, 1475 and 1150 cm\(^{-1}\); NMR: 7.75 d (J=6 Hz, H-2), 6.20 d (J=6 Hz, H-3), 6.05 d (J=2 Hz, H-13b), 5.45 d (J=2 Hz, H-13a), 4.75 d (J=8 Hz, H-6), 4.60 (−O−CH\(_2\)−O−), 3.45 m (−O−CH\(_2\)−CH\(_2\)−O−), 3.30 m (H-7), 3.20 s (−OCH\(_3\)), 1.20 (H-15), 1.05 d (J=7 Hz, H-14); Mass spectrum peaks were at m/z 350 (M\(^+\)), 319, 291, 275, 261 and 245.

**Reaction of (3b) with HgCl\(_2\) in MeOH:**

A solution of 50 mg of (3b) in 4 ml of dry methanol was treated with mercuric chloride as described earlier.
Usual work up after 2 hr followed by purification on preparative t.l.c. (EtOAc:Bz, 1:2) furnished 36 mg of MOM ether (3d) as a gum. It showed IR bands at 2900, 1775, 1730, 1700, 1645, 1460, 1140, 1060, 1000 and 960 cm\(^{-1}\); NMR: 6.10 d (J=3.5 Hz, H-13b), 5.70 m (H-8), 5.50 d (J=3.5 Hz, H-13a), 5.20 d (J=10 Hz, H-6), 4.60 s (-O-CH\(_2\)-O-), 3.30 s (O-CH\(_3\)), 3.15 m (H-7), 1.80 br (H-15), 1.05 (H-14), 1.10 d (J=7 Hz, H-3' and H-4'); MS m/z 392 (M\(^+\)), 361, 347, 331, 304 and 71.

**Reaction of (3b) with HgCl\(_2\) in EtOH**

The reaction of 50 mg of (3b) with mercuric chloride in 4 ml of dry ethanol for 3 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:2) 38 mg of (3e) as a gum; IR bands at 2900, 1775, 1730, 1700, 1445, 1460, 1140, 1060, 1000 and 970 cm\(^{-1}\); NMR: 6.10 d (J=3.5 Hz, H-13b), 5.70 m (H-8), 5.50 d (J=3.5 Hz, H-13a), 5.20 d (J=10 Hz, H-6), 4.60 s (-O-CH\(_2\)-O-), 3.10-3.40 (overlapping signals of H-7 and -OCH\(_2\)CH\(_3\)), 1.80 br (H-15), 1.05 s (H-14), 1.10 d (J=7 Hz, H-3' and H-4'); MS m/z 406 (M\(^+\)), 361, 347, 331, 318, 260, 242, 200 and 71.
Reaction of (3b) with HgCl$_2$ in 2-methoxyethanol:

The reaction of 50 mg of (3b) with HgCl$_2$ in 4 ml of dry 2-methoxyethanol for 3 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:1) 36 mg of MEM ether (3f) as a gum; IR bands at 2900, 1775, 1730, 1700, 1645, 1460, 1140, 1060 and 900 cm$^{-1}$; NMR: 6.10 d (J=3.5 Hz, H-13b), 5.70 m (H-8), 5.50 d (J=3.5 Hz, H-13a), 5.20 d (J=10 Hz, H-6), 4.60 s (O-CH$_2$O$^-$), 3.30-3.40 (overlapping signals of H-7 and -O-CH$_2$-CH$_2$O$^-$), 3.20 s (-OCH$_3$), 1.80 br (H-15), 1.05 s (H-14), 1.10 d (J=7 Hz, H-3' and H-4'); MS m/z 436 (M$^+$), 405, 377, 361, 348, 331, 242, 200 and 71.

Hydrolysis of (2b):

Hydrolysis of 100 mg of (2b) in ethanol with K$_2$CO$_3$ for 30 min as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:2) 95 mg of (2a) as a gum which was identical with authentic parthenin (2a) (t.l.c., NMR, IR and Mass).

Hydrolysis of (3b):

A solution of 100 mg of (3b) in ethanol was treated with K$_2$CO$_3$ for 30 min as described earlier. After usual
work up and purification by preparative t.l.c. (EtOAc:Bz, 1:7) 97 mg of (3a) was obtained as a gum which was crystallized from methanol. Compound (3a) was found to be identical with its authentic sample (t.l.c., m.p., NMR, IR and MS) (3a).

Preparation of (6f):

The reaction of 100 mg of cholesterol (6a) with CH₃I in presence of sodium hydride in N,N-dimethylacetamide for 8 hr as described in the general procedure for making methyl ethers, furnished 80 mg of (6f) as a crystalline solid m.p. 84°C (MeOH) reported m.p. 84.5°C.

Reaction of (6f) with CTMS-Ac₂O in presence of conc. H₂SO₄:

A solution of 40 mg of (6f) in 1 ml of acetic anhydride was treated with 0.5 ml of CTMS and two drops of concentrated H₂SO₄ was added to the mixture. The reaction mixture was kept at room temperature. After 16 hr it was quenched with water and extracted with chloroform (3x100 ml). The washed and dried extract was evaporated under reduced pressure and the crude residue on purification by preparative t.l.c. (EtOAc:Hexane, 1:9).
furnished 36 mg of cholesteryl acetate (6h) as a crystalline solid m.p. 115°C (EtOAc), reported21 m.p. 114-115°C.

Reaction of (6f) with CTMS-H₂SO₄:

To a solution of 40 mg of (6f) in 1 ml of dichloromethane was added 0.5 ml of CTMS followed by one drop of concentrated H₂SO₄. The reaction mixture was kept at room temperature for 16 hr monitoring by t.l.c. which indicated decomposition only.

Preparation of (6g):

The reaction of 100 mg of cholesterol (6a) with benzyl chloride and sodium hydride in N,N-dimethylacetamide for 12 hr as described in the general procedure for preparation of benzyl ether yielded after purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 40 mg of (6g) m.p. 118°C (acetone), reported21 m.p. 118.5°C.

Reaction of (6g) with CTMS-AC₂O:

The reaction of 60 mg of (6g) with CTMS-AC₂O for 12 hr as described in the general procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:16) 30 mg of (6h) m.p. 115°C (EtOAc), reported21 m.p. 114-115°C.
Preparation of (8a):

The reaction of 100 mg of cholestan-3β-ol with benzyl chloride and sodium hydride in 4 ml of N,N-dimethylacetamide for 10 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 40 mg of (8a) m.p. 80°C (EtOAc); IR bands at 2990, 1450, 1350 and 1060 cm⁻¹; HMR: 7.16 br (five aromatic protons), 4.35 s (O-CH₂-Ph); MS m/z 478 (M⁺), 387, 371 and 71 (base peak).

Reaction of (8a) with CTMS-Ac₂O:

Reaction of 50 mg of (8a) with CTMS-Ac₂O for 12 hr as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:16) 25 mg of (8b) m.p. 110°C (EtOAc-MeOH), reported m.p. 110-111°C.
REFERENCES

22. See reference 21, p. 700.