# *Chapter Four*

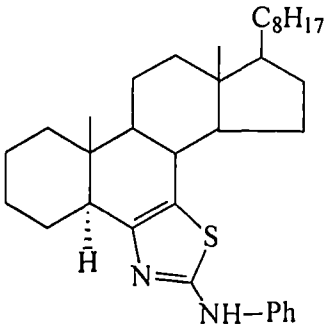
# *Mass spectral studies of Thiazoles*

# *Discussion*

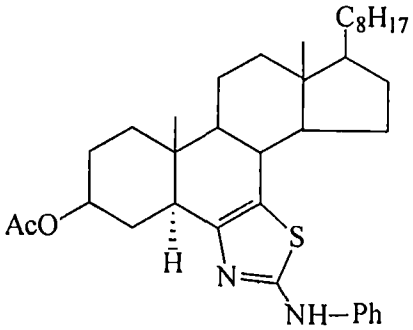
A survey of literature revealed that no systematic mass spectral study of steroidal thiazoles has been reported and many such compounds being synthesized recently[1]. In the previous chapter we have described the combined with the fact that our laboratories has reported the mass spectral studies of several class of steroidal compounds in the recent past[2-5], prompted us to examine the mass spectra of some steroidal thiazoles as an attempt to establish spectra structure relationship. The compounds included in the study are 2′-N-phenylamino-5α-cholest-6-eno[6,7-d] thiazole (I) 3β-acetoxy-2′-N-phenylamino-5α-cholest-6-eno[6,7-d] thiazole (II), 3β-proponoxy-2′-N-phenlyamino-5α-cholest-6-eno[6,7-d] thiazole (III), 2′-amino-5α-cholest-6-eno[6,7-d] thiazole (IV), 3β-acetoxy-2′-amino-5α-cholest-6-eno[6,7-d] thiazole (V) and 3β-proponoxy-2′-amino-5α-cholest-6-eno[6,7-d] thiazole (VI). These compounds are structurally very close to each other, it was anticipated that they will follow similar fragmentation patterns thus offering a simple and effective method of their characterization by mass spectrometry. It is indeed observed that they show close resemblances and hence can be used for characterisation of such compounds.

The suggested fragmentation pathways get support from the composition of the important ions. In the absence of mass spectra of appropriate deuterated analogues the suggested mechanism of fragmentations remains tentative, though substitutes in some cases compensate this deficiency to some extent.

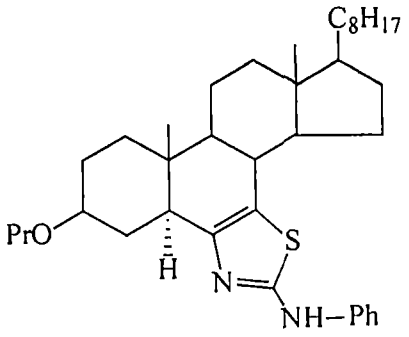
In this Chapter, the mass spectrum of 2′-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (I) has been discussed in detail and this may be considered as the representative of model for other compounds (II and III)[7-9].



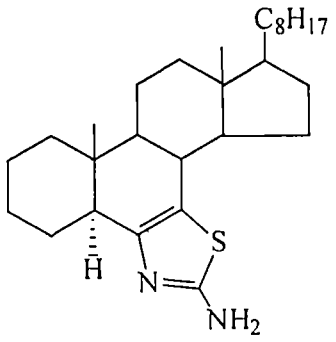

(I)



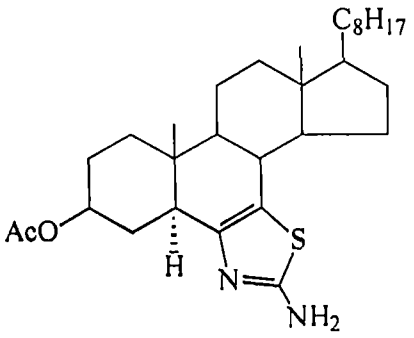

(II)



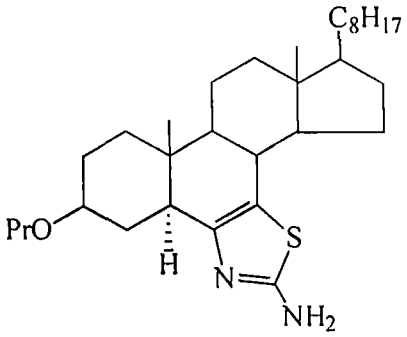

(III)




(IV)




(V)




(VI)

The mass spectrum of 2′-N-phenylamino-5α-cholest-6-eno[6,7-d] thiazole (I) (Fig.I) gave a prominent molecular ion at m/z 518 ($C_{34}H_{50}N_2S$). Other significant ion peaks were observed at m/z 517 (M–H), 503 (M–$CH_3$), 462 (M–$C_4H_8$), 441 (M–Ph), 426 (M–$C_6H_6N$), 411 (426–$CH_3$), 405 (M–$C_8H_{17}$), 400 (M–118), 387 (M–140), 349 (462–$C_8H_{17}$), 301 (441–$C_8H_{17}$ CH=$CH_2$), 296 (M–222), 281(296–$CH_3$), 311 (M–207), 309 (M–209), 240 ($C_{14}H_{12}N_2S$), (122, $C_7H_7S$) and lower mass.

The formations of the more interesting and important fragments have been suggested in the following schemes.

**m/z 517 (M–H)**

The ion m/z 517 obviously arises by the loss of one hydrogen from molecular ion. The loss of hydrogen may involve one hydrogen form $C_5$ or $C_8$ position or from NHPh as shown in Scheme-I. As pointed out earlier this suggestion does not have the support of mass spectrum of appropriate deuterated analogues.

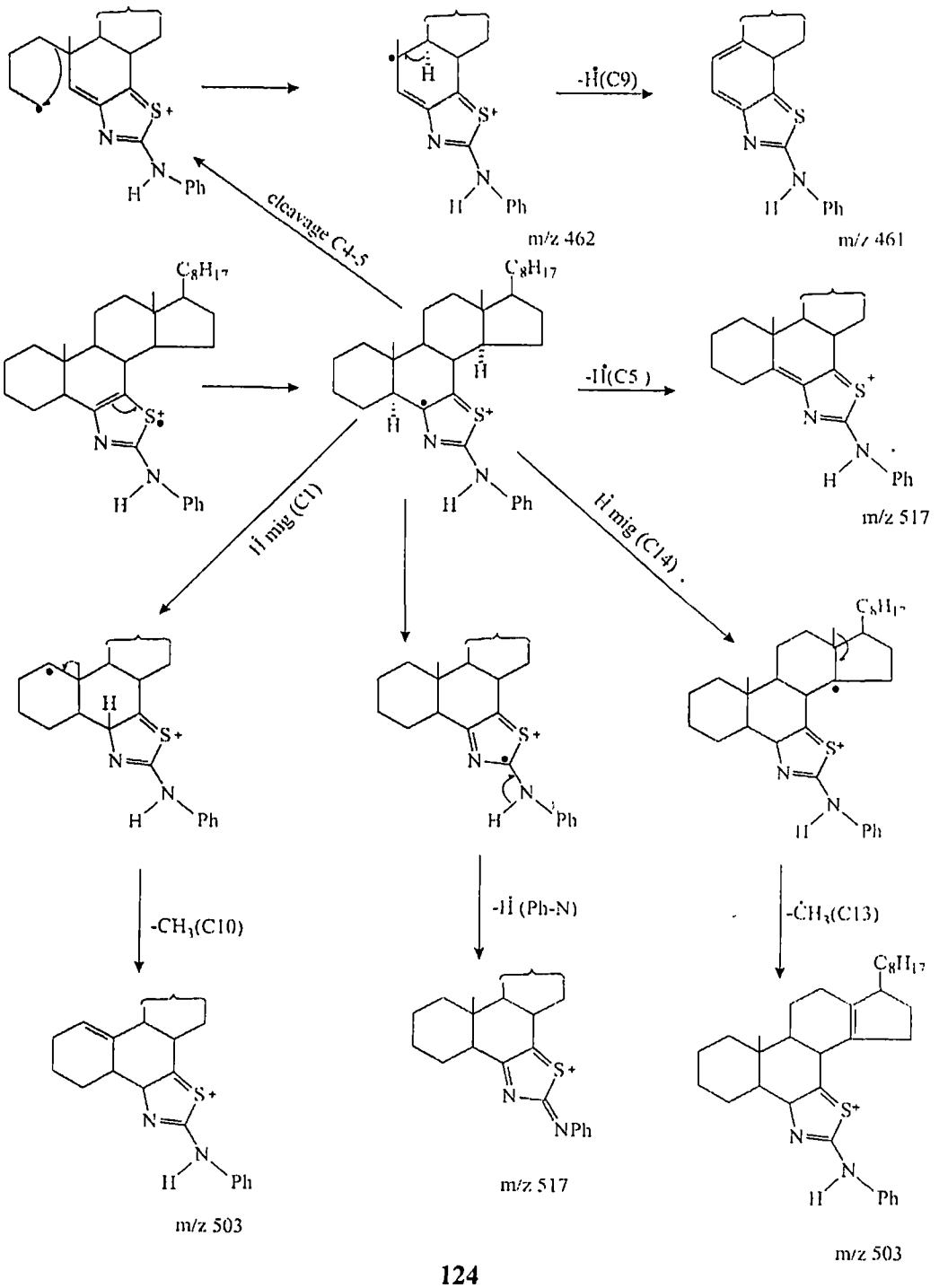
**m/z 503 (M–$CH_3$)**

The loss of methyl group form the molecular ion can occur in several ways, the most preferred loss is likely to involve $C_{13}$ or $C_{10}$-methyl (Scheme-I).

**m/z 462/461**

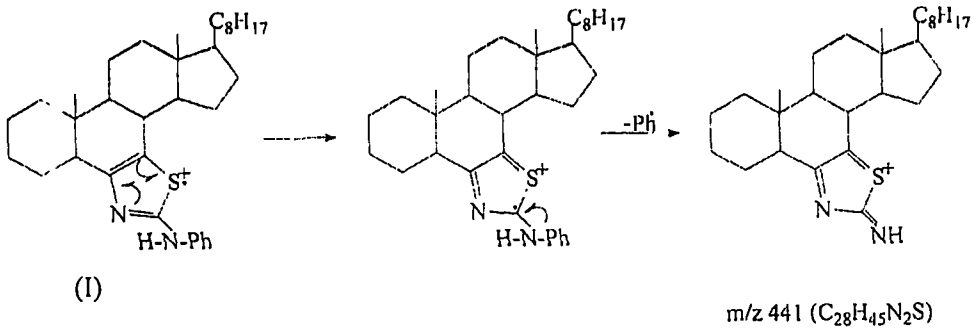
This ion most probably arises by the loss of a ring A from molecular ion as shown (Scheme-I).

**SCHEME – I**



**m/z 441 (M–Ph)**

The formation of the ion m/z 441 can be shown to arise by the loss of phenyl group from the molecular ion m/z 578.

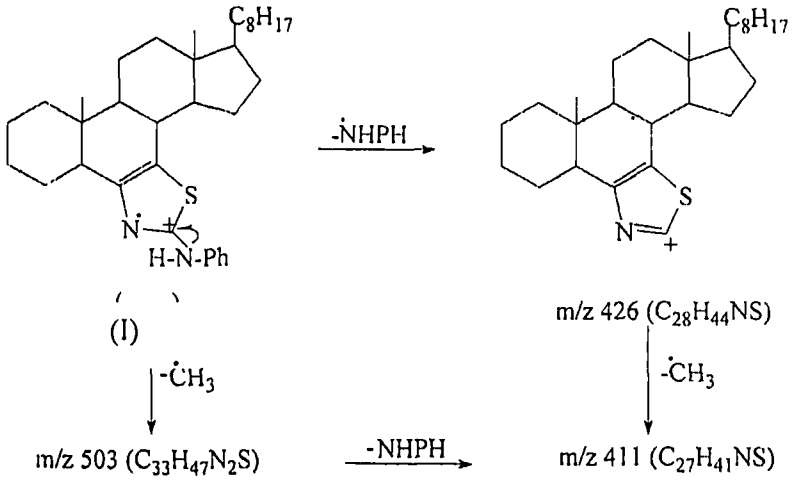



(I)

m/z 441 ($C_{28}H_{45}N_2S$)

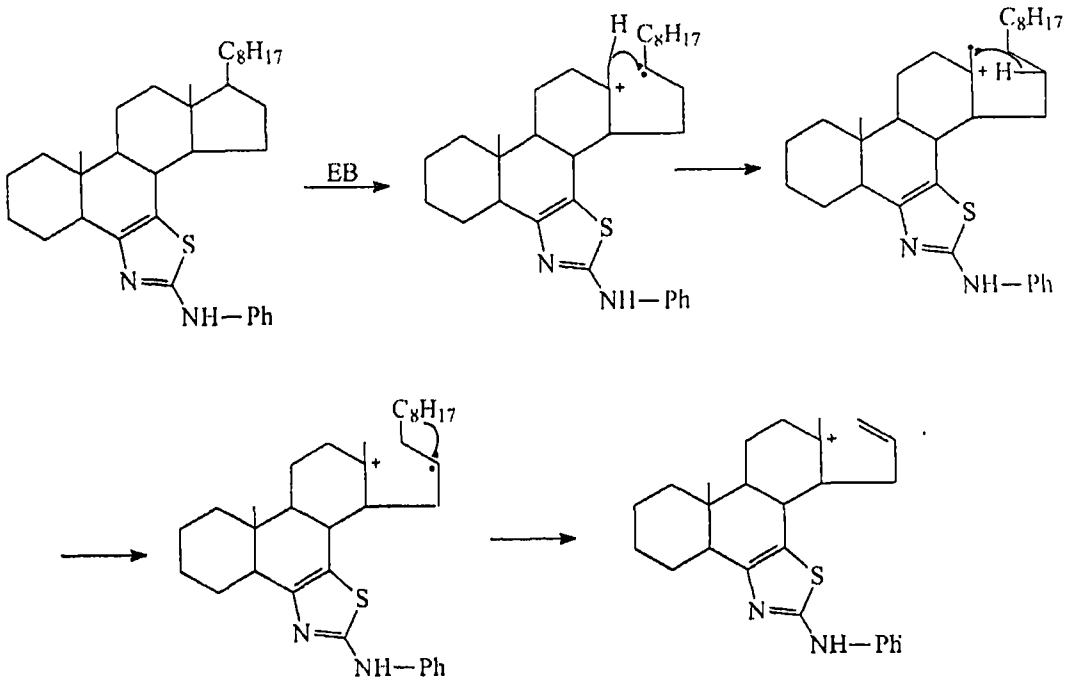
**m/z 426 (M–NHPh)/ 411**

The ion peak 426 corresponds to the loss of –NH–Ph (mass unit 92) form the molecular ion m/z 518.




**m/z 405 (M–$C_8H_{17}$ side chain)**

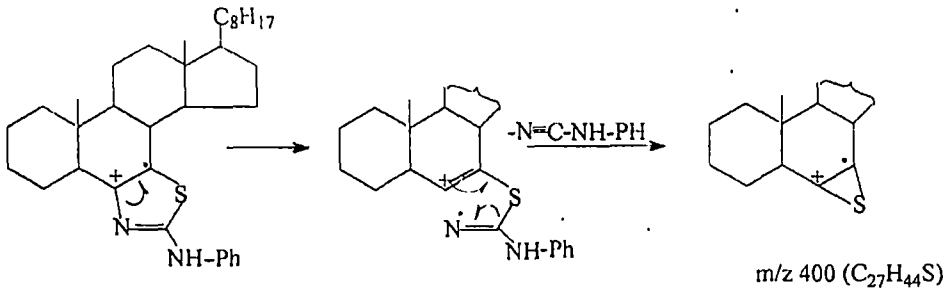
The loss of the side chain ($C_8H_7$) is of regular occurrence in the mass spectra of steroidal compounds belonging to the cholestane series.




m/z 405 ($C_{26}H_{33}N_2S$)

**m/z 400 (M–118)**

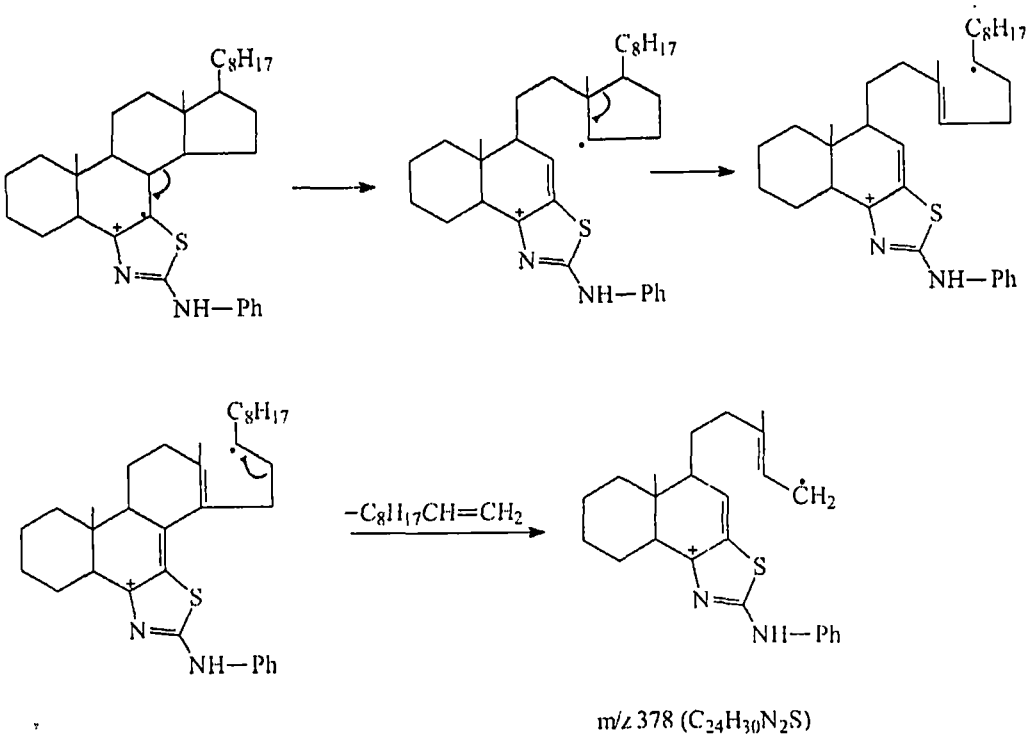
The ion m/z 400 corresponds to the loss PhNHC=N (mass unit 118) from the molecular ion.




m/z 400 ($C_{27}H_{44}S$)

**m/z 378 ($M–C_8H_{17}CH=CH_2$)**

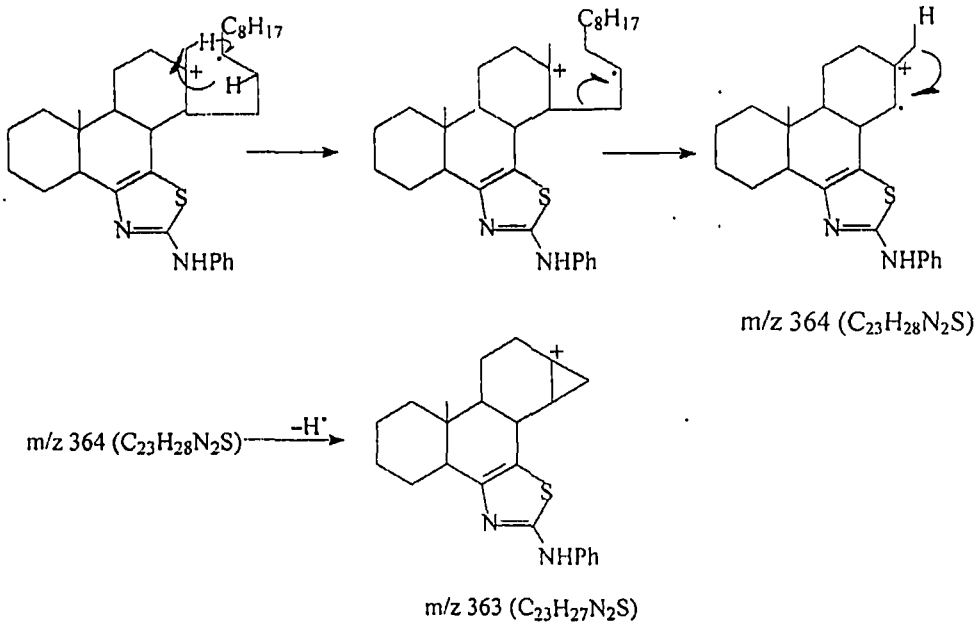
The ion m/z 378 corresponds to the loss of mass unit 140 from the molecular ion. The mass unit is built up of the side chain and a part of ring D, this loss is of common occurrence in the mass spectra of the cholestane derivatives.




m/z 378 ($C_{24}H_{30}N_2S$)

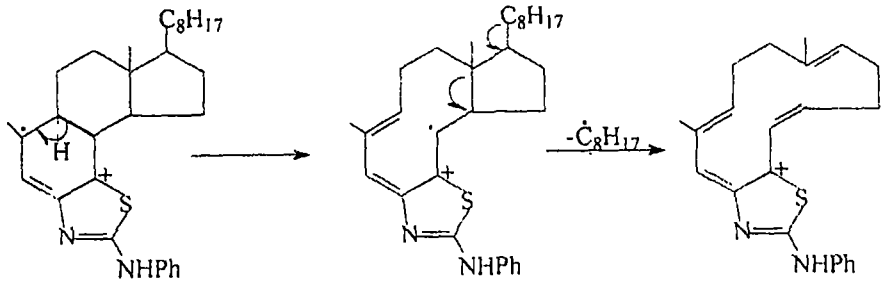
**m/z 364/363**

The ions are derived from combined of the side chain and ring D ($C_{15}$, $C_{16}$ and $C_{17}$) as shown below.




**m/z 349 ($C_{22}H_{25}N_2S$)**

This can be shown to arise by the loss of side chain from the ion m/z 462.

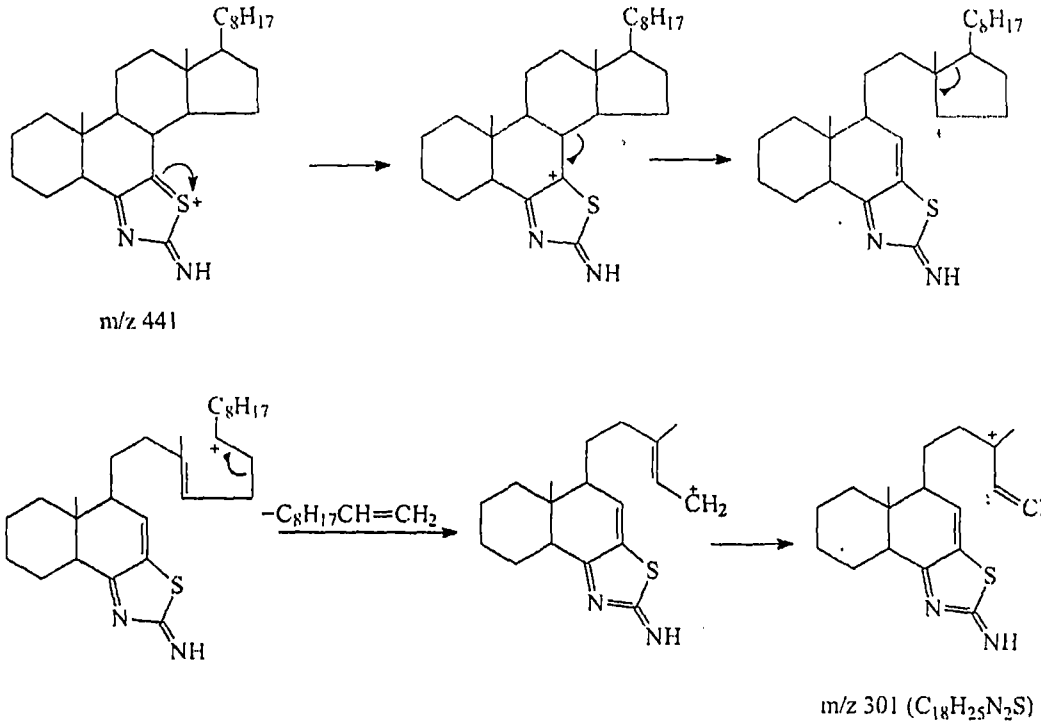


m/z 462 ($C_{30}H_{42}N_2S$)

m/z 349 ($C_{22}H_{25}N_2S$)

**m/z 301 (441–$C_{10}H_{20}$)**

This ion peak at m/z 301 is nearly as strong as the base peak. Most probably the loss involve the expulsion of $C_8H_{17}$–C=$CH_2$ from the 441.

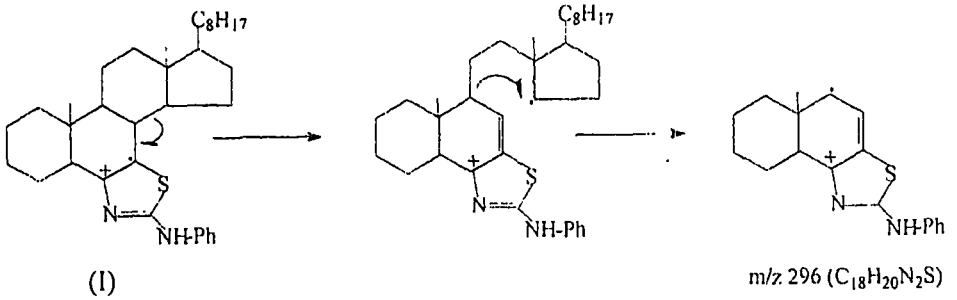


m/z 441

m/z 301 ($C_{18}H_{25}N_2S$)

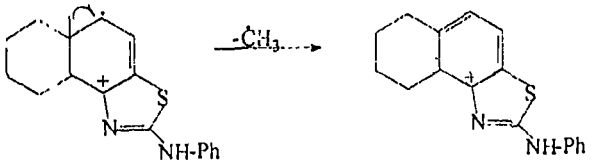
**m/z 296 ($C_{18}H_{20}N_2S$) and m/z 281 ($C_{17}H_{17}N_2S$)**

The m/z 296 ion may arise by the loss of ring C and D along with the side chain from the molecular ions. Further loss of methyl group from the ion m/z 296 gives the ion m/z 281.

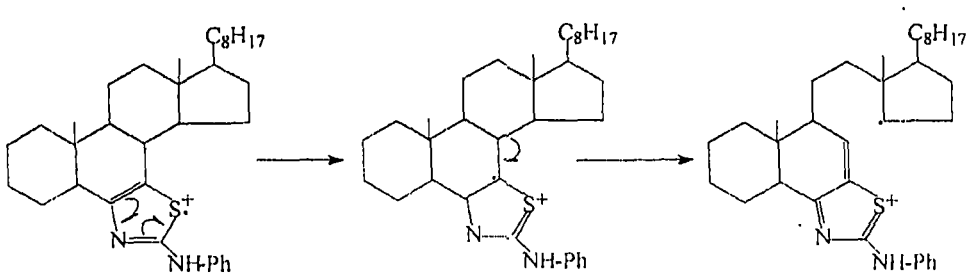


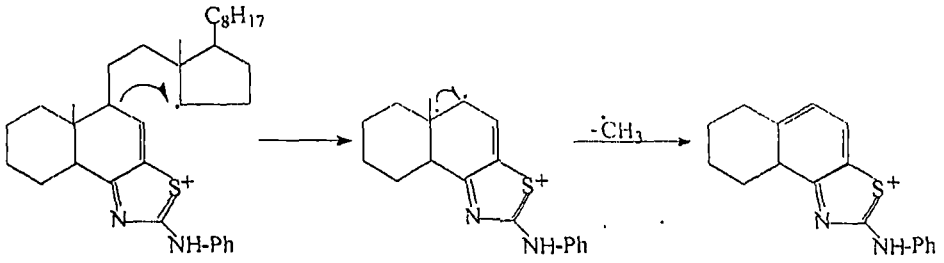

(I)

m/z 296 ($C_{18}H_{20}N_2S$)




m/z 281 ($C_{17}H_{17}N_2S$)



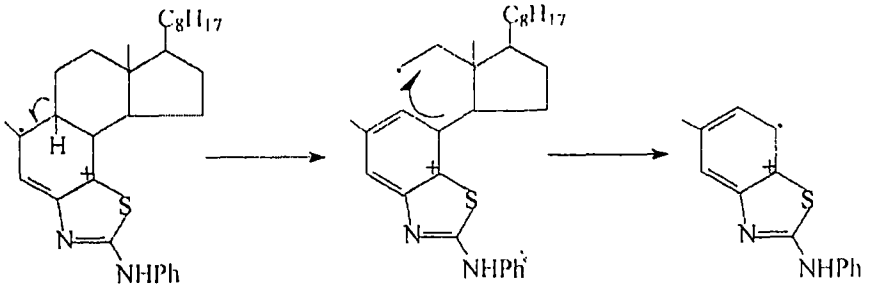




m/z 296 ($C_{18}H_{20}N_2S$)

m/z 281 ($C_{17}H_{17}N_2S$)

**m/z 240 ($C_{14}H_{12}N_2S$)**

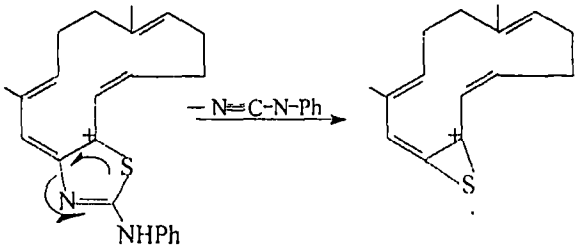
The genesis of the ion m/z 240 can be shown according to the following scheme.



m/z 462 ($C_{30}H_{42}N_2S$) m/z 240 ($C_{14}H_{12}N_2S$)

**m/z 231 ($C_{15}H_{19}S$)**

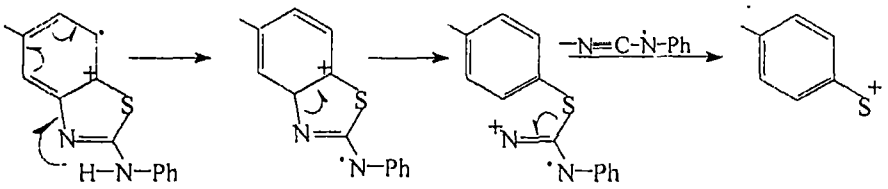
This ion may be shown to arise by the following scheme.



m/z 349 ($C_{22}H_{25}N_2S$) m/z 231 ($C_{15}H_{19}S$)

**m/z 123 ($C_7H_7S$)**

The ion m/z 123 may be shown to arise from the ion 240 as follows.



m/z 240 ($C_{14}H_{12}N_2S$) m/z 123 ($C_7H_7S$)

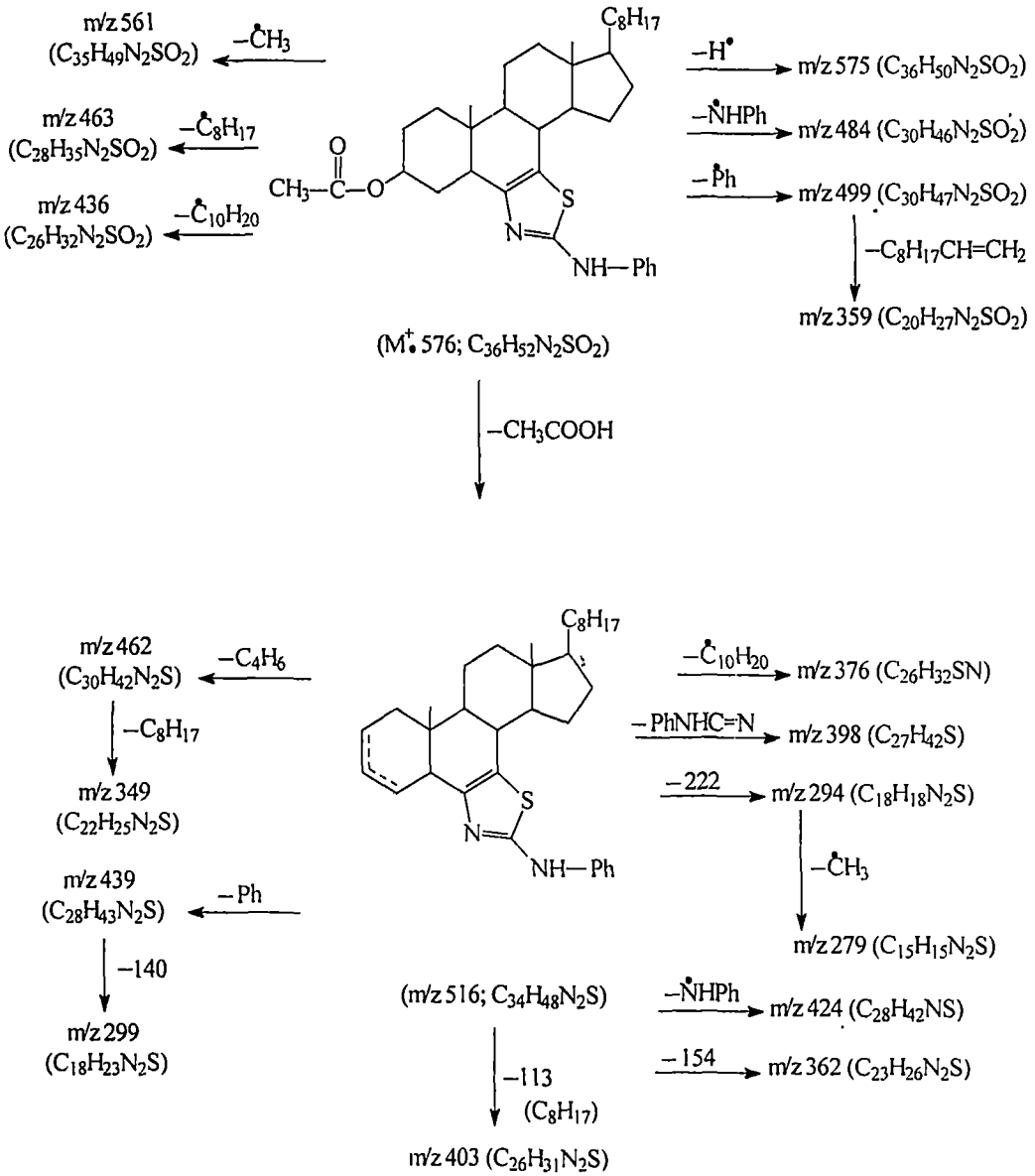
The mass spectra of 3β-acetoxy-2′-N-phenylamino-5α-cholest-6-eno[6,7-d] thiazole (II) (Fig II), 3β-proponoxy-2′-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (III) (Fig.III) were comparable with 2′-N-phenyl amino-5α-cholest-6-eno [6,7-d] thiazole (I) fig ( I)

The mass spectrum of 3β-acetoxy-2′-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (II) Fig.(II), was quite similar to that of the (I ).

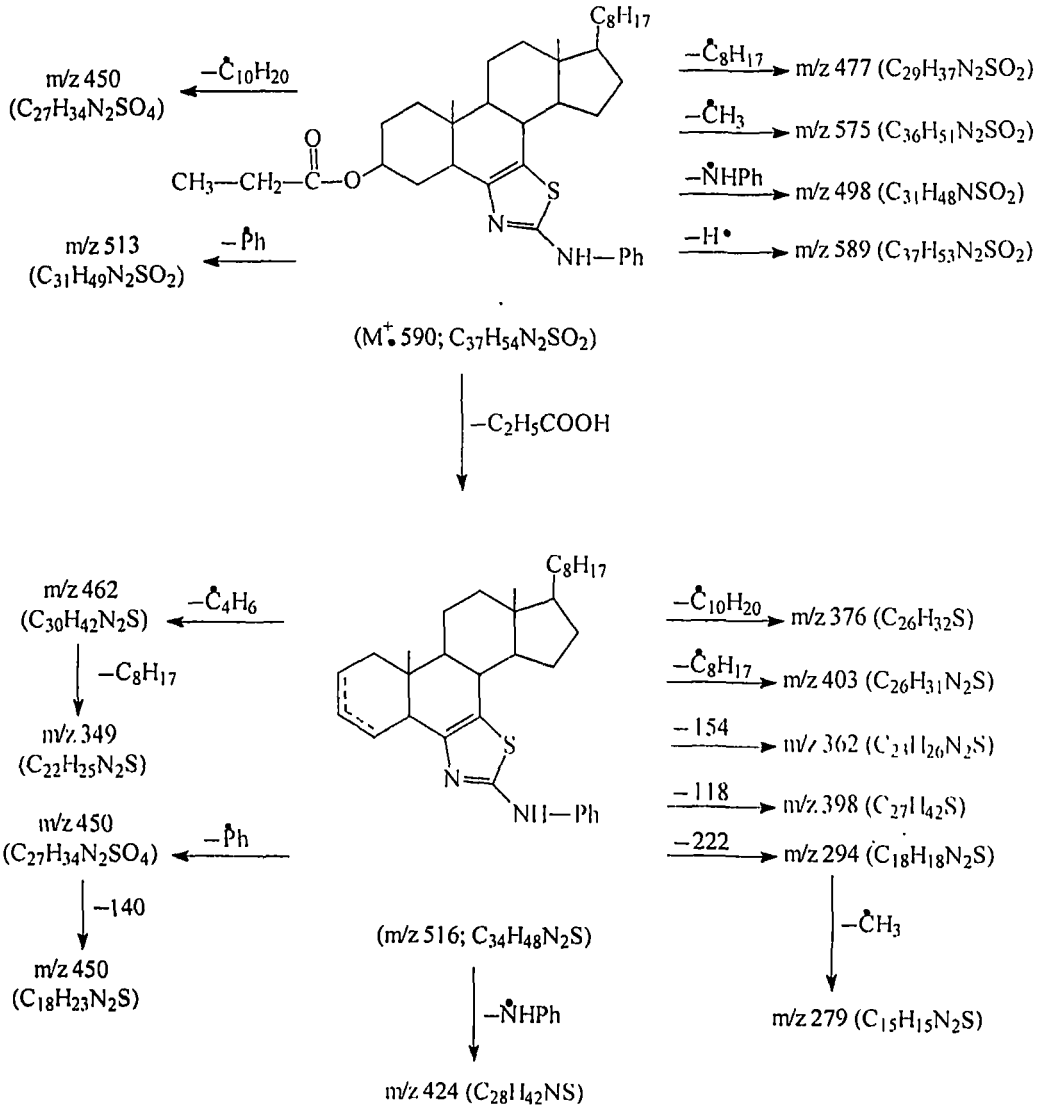
The molecular ion peak of (II) was observed m/z 576 ($C_{36}H_{52}N_2SO_3$). Most of the fragment ions observed in the spectrum of (II) corresponded to the ions obtained and discussed in the spectrum of (I) with a difference of two mass unit, after the elimination of $CH_3COOH$. Some of these ions were m/z 575 (M–H), 561 (M–$CH_3$), 516 (M–$CH_3COOH$), 499 (M–77), 484 (M–NH–Ph), 463 (M–$C_8H_{17}$), 462 (516–54), 439 (516–77), 436 (M–$C_8H_{17}$–CH=$CH_2$), 424 (516–NHPh), 403 (516–$C_8H_{17}$). 398 (516–118), 376 (516–$C_{10}H_{20}$), 362 (516–154), 359 (499–140), 349 (462–113), 299 (439–140), 294 ($C_{18}H_{18}N_2S$), 279 ($C_{17}H_{15}N_2S$), 240 ($C_{14}H_{12}N_2S$), 231 ($C_{15}H_{19}S$), 123 ($C_7H_7S$) and lower mass peaks.

The mass spectrum of 3β- proponoxy -2′-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (III) Fig (III), was comparable with that of (I ). The molecular ion peak was observed at m/z 589 (590–H), 575 (M–$CH_3$), 516 (M–$CH_3COOH$), 513 (M–77), 498 (M–NH–Ph), 477 (M–$C_8H_{17}$), 462 (516–54), 450 (M–140), 439 (516–77), 424 (516–NHPh), 403 (516–$C_8H_{17}$), 398 (516–118), 376 (516–$C_8H_{17}CH=CH_2$), 373 (513–140), 362 (516–$C_8H_{17}$–$CH_2$–CH=$CH_2$), 349 (462–$C_8H_{17}$), 299 (439–140), 294 ($C_8H_{18}N_2S$), 279 ($C_{17}H_{15}N_2S$), 240 ($C_{14}H_{12}N_2S$), 231 ($C_{15}H_{19}S$), 123 ($C_7H_7S$) and lower mass peaks.

## SCHEME – II


m/z 561
(C35H49N2SO2)
–CH3
m/z 463
(C28H35N2SO2)
–C8H17
m/z 436
(C26H32N2SO2)
–C10H20
C8H17
CH3–C–O
O
S
N
NH–Ph
–H•
m/z 575 (C36H50N2SO2)
–NHPh
m/z 484 (C30H46N2SO2)
–Ph
m/z 499 (C30H47N2SO2)
–C8H17CH=CH2
m/z 359 (C20H27N2SO2)
(M+• 576; C36H52N2SO2)
–CH3COOH
m/z 462
(C30H42N2S)
–C4H6
–C8H17
m/z 349
(C22H25N2S)
m/z 439
(C28H43N2S)
–Ph
–140
m/z 299
(C18H23N2S)
C8H17
S
N
NH–Ph
–C10H20
m/z 376 (C26H32SN)
–PhNHC=N
m/z 398 (C27H42S)
–222
m/z 294 (C18H18N2S)
–CH3
m/z 279 (C15H15N2S)
(m/z 516; C34H48N2S)
–NHPh
m/z 424 (C28H42NS)
–154
m/z 362 (C23H26N2S)
–113
(C8H17)
m/z 403 (C26H31N2S)

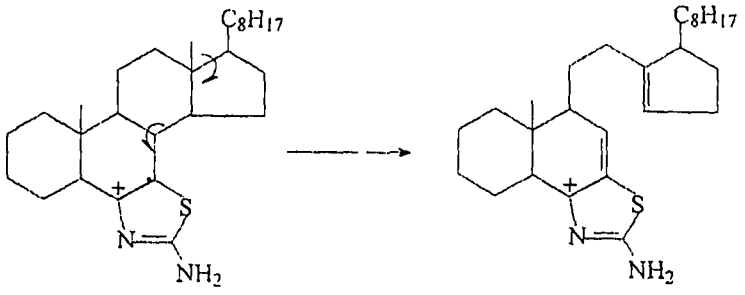
## SCHEME - III


m/z 450
(C27H34N2SO4)
−C10H20
m/z 513
(C31H49N2SO2)
−Ph
−C8H17
m/z 477 (C29H37N2SO2)
−CH3
m/z 575 (C36H51N2SO2)
−NHPh
m/z 498 (C31H48NSO2)
−H•
m/z 589 (C37H53N2SO2)
(M+• 590; C37H54N2SO2)
−C2H5COOH
m/z 462
(C30H42N2S)
−C4H6
−C8H17
m/z 349
(C22H25N2S)
m/z 450
(C27H34N2SO4)
−Ph
−140
m/z 450
(C18H23N2S)
−C10H20
m/z 376 (C26H32S)
−C8H17
m/z 403 (C26H31N2S)
−154
m/z 362 (C21H26N2S)
−118
m/z 398 (C27H42S)
−222
m/z 294 (C18H18N2S)
−CH3
m/z 279 (C15H15N2S)
(m/z 516; C34H48N2S)
−NHPh
m/z 424 (C28H42NS)

The mass spectrum of 2′-amino-5α-cholest-6-eno [6,7-d] thiazole (IV) has been discussed in details and this may be considered as the representative of model for other compounds (V and VI) (fig. IV) gave a molecular ion peak at m/z 442 ($C_{28}H_{46}N_2S$). Other significant ion peaks are at m/z ($M-CH_3$), 400 ($M-CH_2N_2$), 386 ($M-C_4H_8$), 329 ($M-C_8H_{17}$), 302 ($M-C_{10}H_{20}$), 301 (302–H), 273 ($C_{16}H_{21}N_2S$), 246 ($C_{14}H_{18}N_2S$), 231 ($C_{15}H_{19}S$), 221 ($C_{12}H_{17}N_2S$), 216 ($C_{14}H_{16}S$), 164 ($C_8H_8N_2S$), 123 (164–41) and lower mass peak. The fragmentation leading to the formation of interesting and important ions have been suggested in the following scheme.

**m/z 427 ($M-CH_3$)**

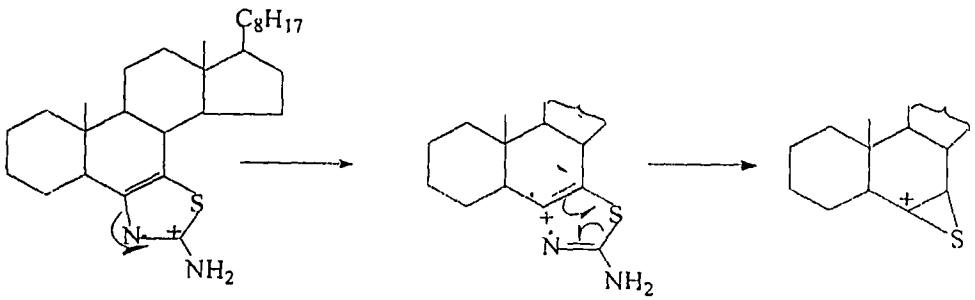
This ion obviously results by the loss of a methyl group from the molecular ion. Loss of methyl group(s) from steroids is of common occurrence,[9] most preferred loss is likely to involve $C_{13}-CH_3$.




M⁺ 442 m/z 427

**m/z 400**

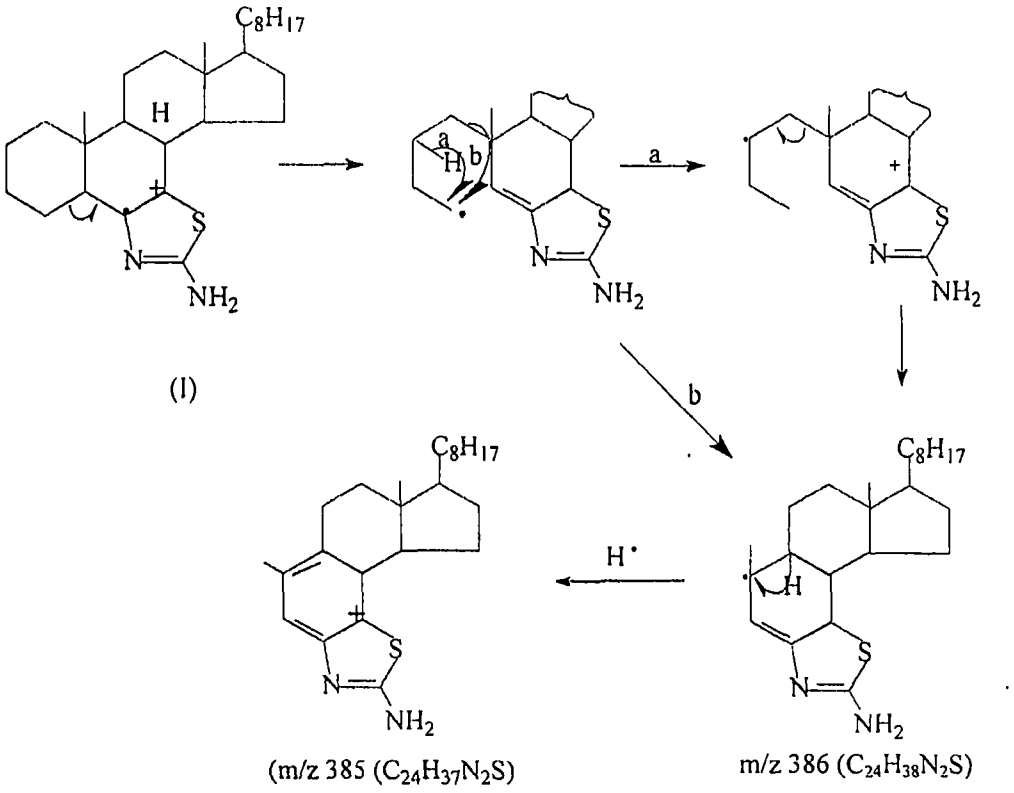
This ion peak at m/z 400 though a weak one but could be of significant in the characterization of the thiazole moiety. The ion corresponds to the loss of $-N\equiv C-NH_2$ from the molecular ion.




m/z 400 ($C_{27}H_{44}S$)

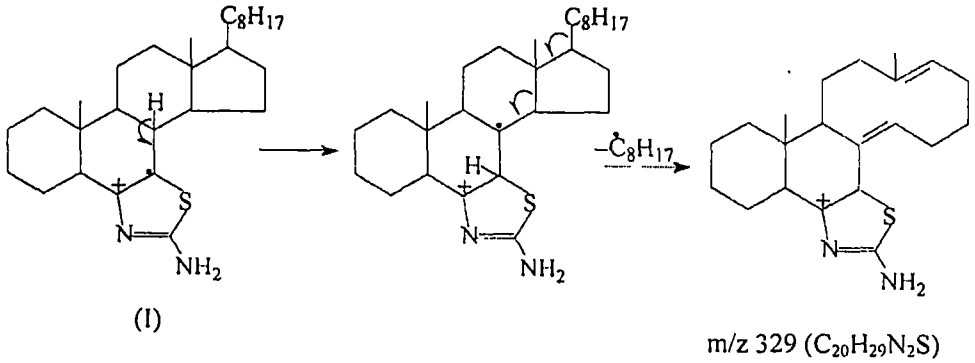
**m/z 386 (M–56)/385**

The ion peak at m/z 386 is nearly as strong as the base peak. The formation of this fragment ion can be explained by loss of ring A as shown below.



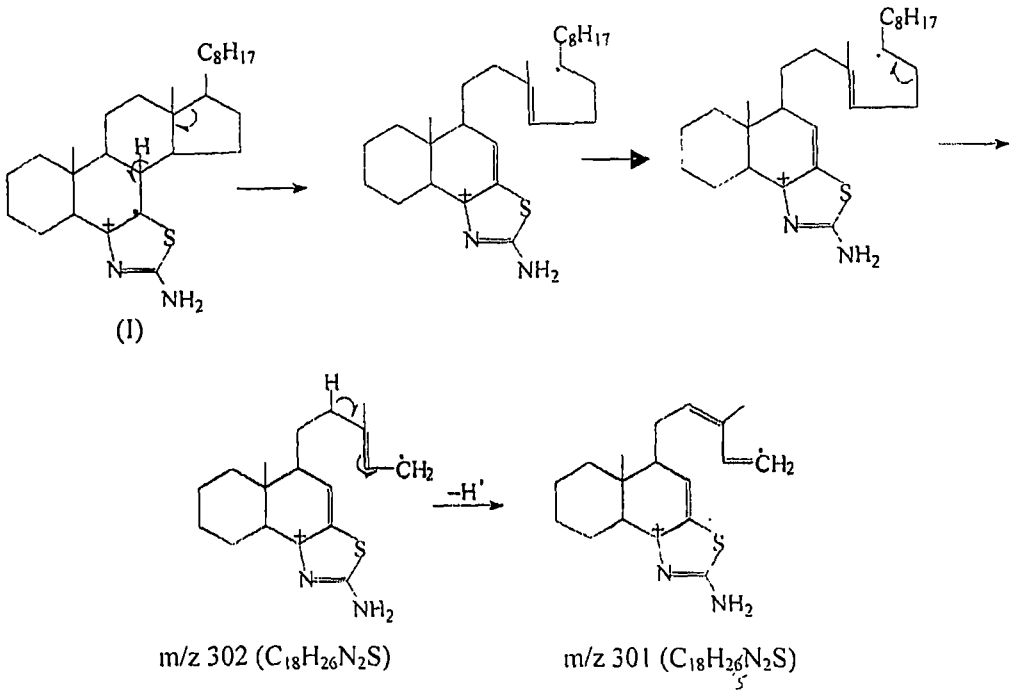

**m/z 329 (M–113; side chain)**

The ion peak at 329 corresponds to the loss of $C_8H_{17}$ (mass unit 113) from the molecular ion. The loss of side chain is of regular occurrence in the mass spectra of steroidal compound. It can also be shown according to the following.



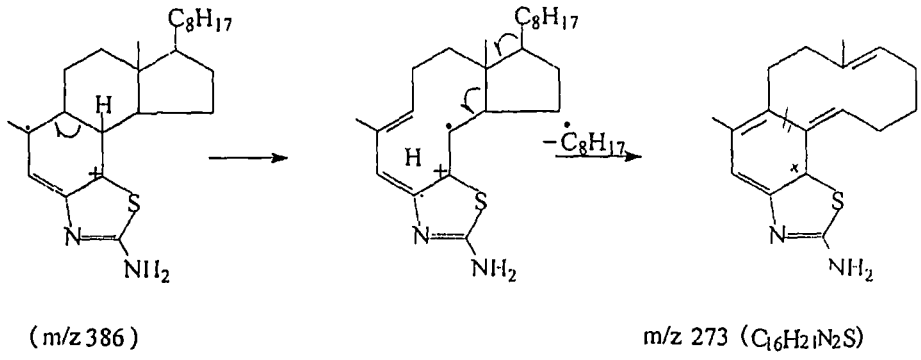
**m/z 302 and 301**

The ion m/z 302 corresponds to the loss of mass unit 140 from molecular ion. The mass unit 140 built up of the side chain and a part of ring D ($C_{16}$ and $C_{17}$)




**273 (386–$C_8H_{17}$)**

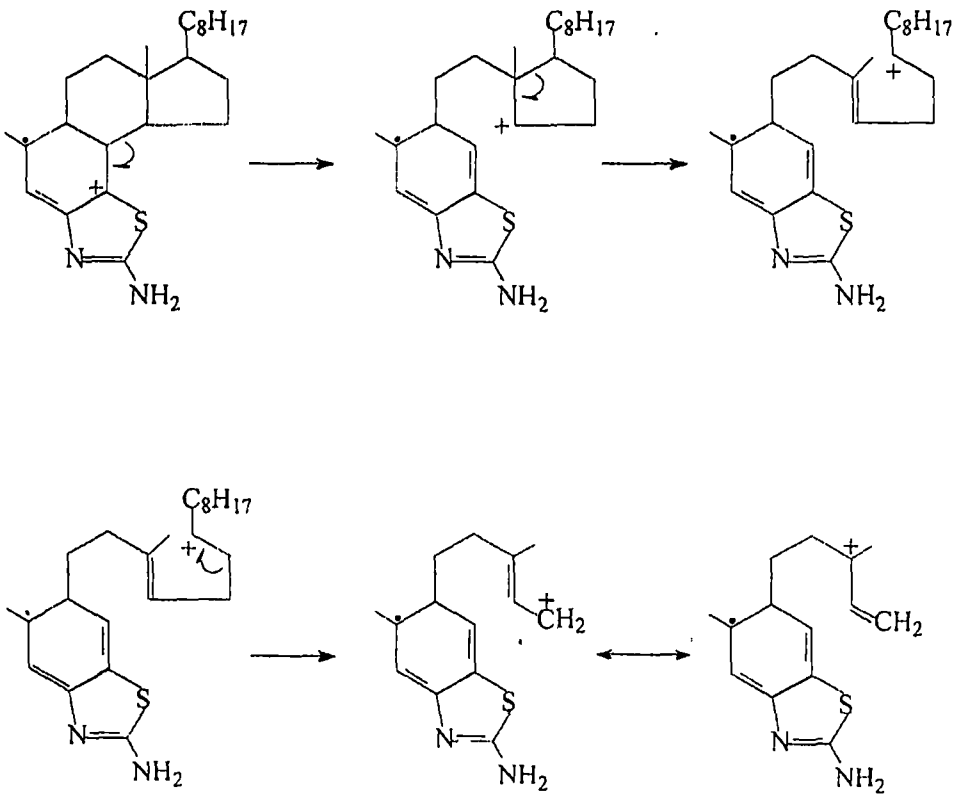
The ion peak at 273 corresponds to the loss of the $C_8H_{17}$ side chain (mass unit 113) from the ion m/z 386.




**246 (386–$C_{10}H_{20}$)**

The loss of side chain and part of ring D gave an important ion peak at m/z 246. These losses important ion peak at m/z 246. These loses may occur from the

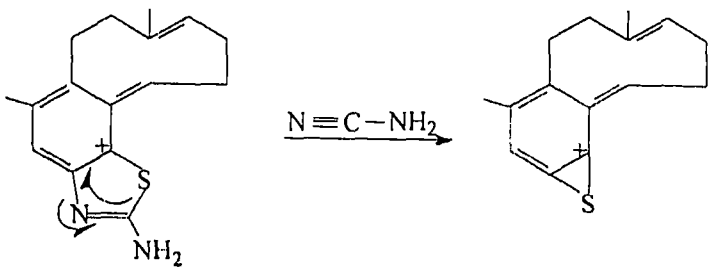
molecular ion itself or from some daughter ions. The formation of these ions, corresponding to the combined loses of the side chain and part of ring D has been shown to occur in the manner shown below:



m/z 246 ($C_{14}H_{18}N_2S$)

**m/z 231 ($C_{15}H_{19}S$)**

This ion can be shown to a rise from the ion m/z 273 by the loss of $\overset{\Downarrow}{N}\equiv C-NH_2$

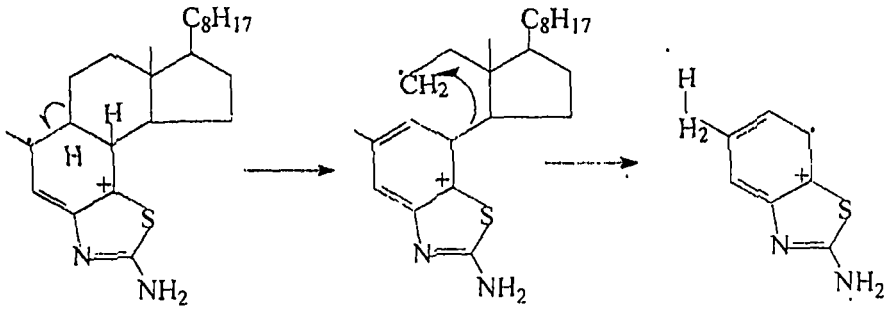


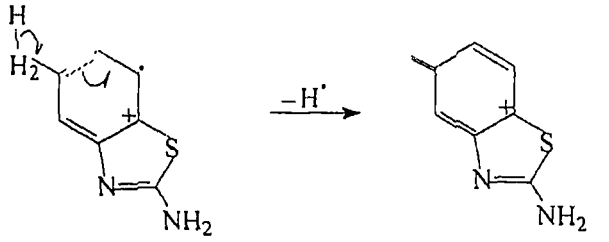
m/z 273

m/z 231 ($C_{15}H_{19}S$)

**m/z 164 ($C_8H_8N_2S$), 163 ($C_8H_7N_2S$)**

These can be shown to be formed from the base peak 386.

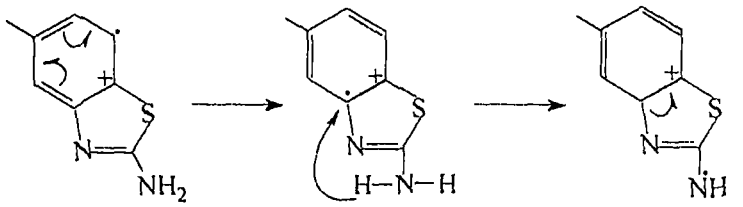




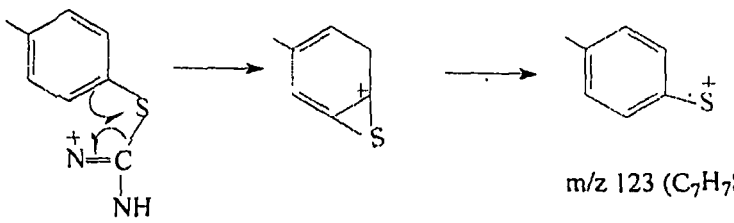
m/z 164 ($C_8H_8N_2S$) m/z 163 ($C_8H_7N_2S$)

**m/z 123 ($C_7H_7S$)**

This important ion may be shown to arise from the ion m/z 164 by the loss of $N{\equiv}C{-}NH_2$



m/z 164

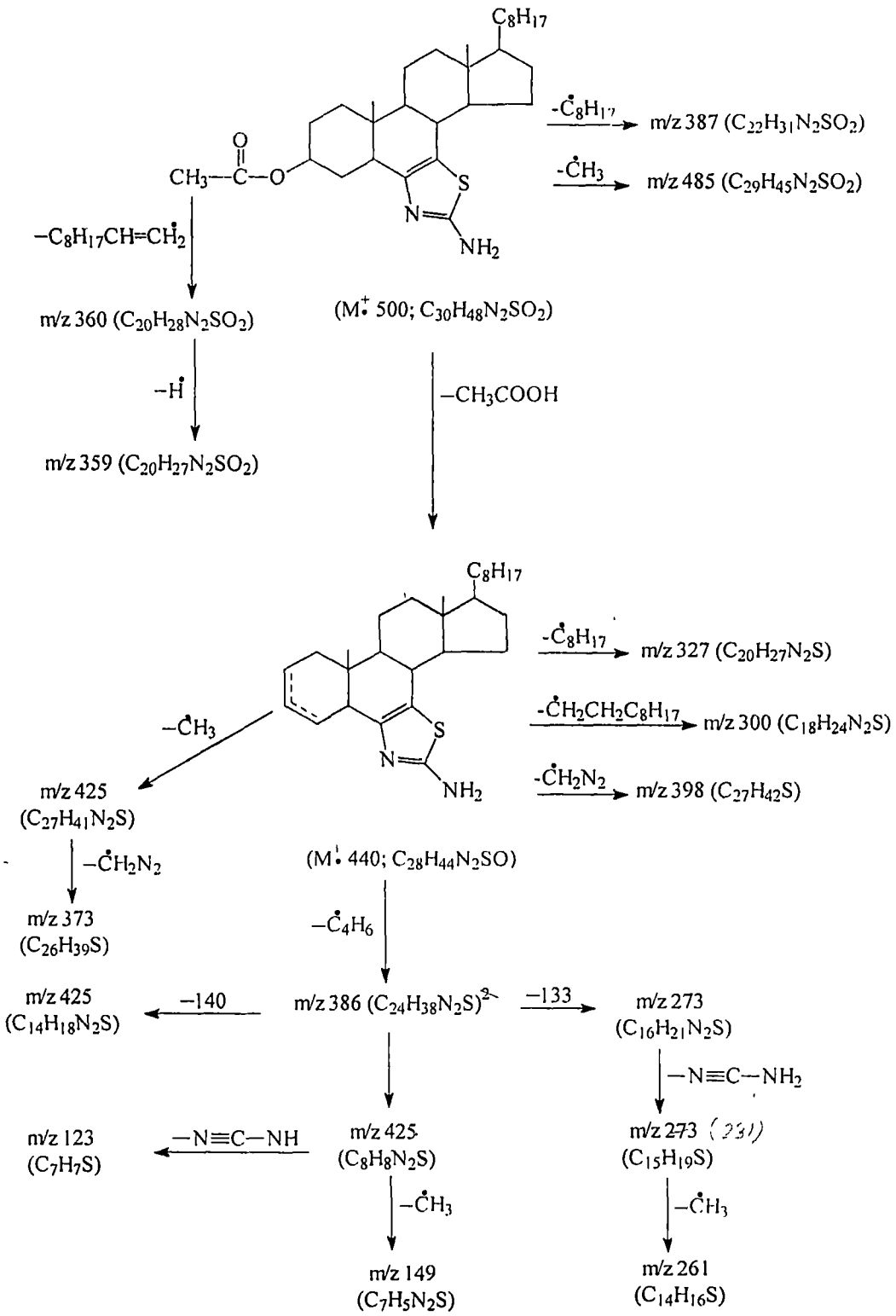


m/z 123 ($C_7H_7S$)

The mass spectra of 3β-acetoxy-2′-amino-5α-cholest-6-eno [6,7-d] thazole (V), 3β-proponoxy-2′-amino-5α-cholest-6-eno [6,7-d] thazole (VI) were comparable with that of 2′-amino-5α-cholest-6-eno [6,7-d] thazole (IV).

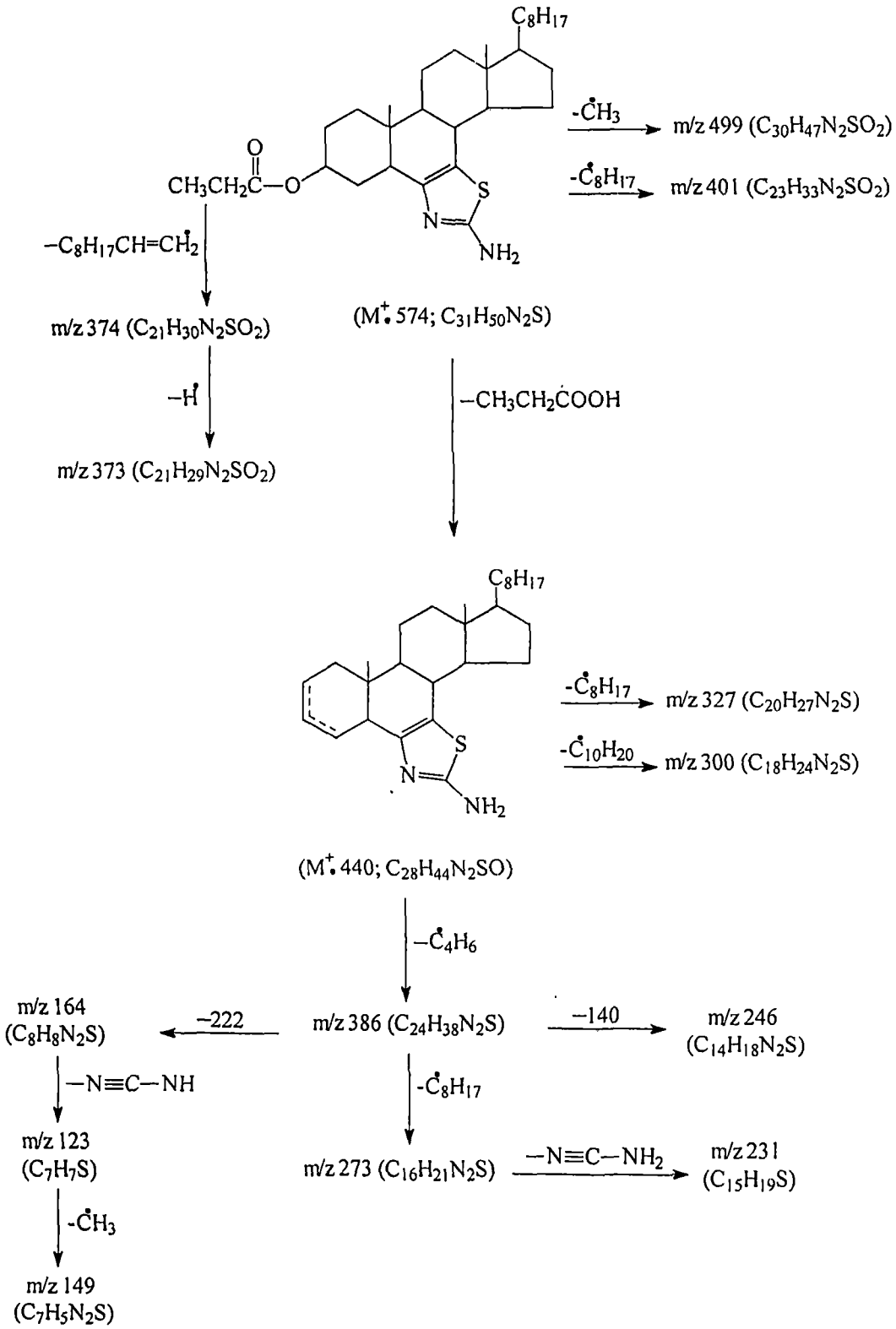
The mass spectrum of (IV) (fig.IV) gave molecular ion peak at m/z 500. Most of the fragment ions were formed after the loss of $CH_3COOH$ as 1,2-elemination process. The ions m/z 440, 425, 398, 386, 385, 327, 300, 291, 273, 246, 231, 164, 163, 149 and 123 obtained from (IV) are comparable with those obtained from (V) with 2 mss unit difference. Acetate containing ions m/z 485, 387, 360 and 359 were also recorded in the spectrum of ( V), which can also be accounted by fragmentations shown in case of (IV), formation of various fragment ions from (II) in shown in scheme (IV).

## SCHEME – IV


C8H17
-C8H17
m/z 387 (C22H31N2SO2)
-CH3
m/z 485 (C29H45N2SO2)
CH3—C—O
O
S
N
NH2
-C8H17CH=CH2
m/z 360 (C20H28N2SO2)
(M+ 500; C30H48N2SO2)
-H
m/z 359 (C20H27N2SO2)
-CH3COOH
C8H17
-C8H17
m/z 327 (C20H27N2S)
-CH2CH2C8H17
m/z 300 (C18H24N2S)
-CH3
-CH2N2
m/z 398 (C27H42S)
m/z 425
(C27H41N2S)
-CH2N2
(M+ 440; C28H44N2SO)
m/z 373
(C26H39S)
-C4H6
m/z 425
(C14H18N2S)
-140
m/z 386 (C24H38N2S)2+
-133
m/z 273
(C16H21N2S)
-N≡C—NH2
m/z 123
(C7H7S)
-N≡C—NH
m/z 425
(C8H8N2S)
m/z 273 (231)
(C15H19S)
-CH3
-CH3
m/z 149
(C7H5N2S)
m/z 261
(C14H16S)

The mass spectrum of 3β-proponoxy-2′-amino-5α-cholest-6-eno [6,7-d] thiazole (VI) (Fig.VI) was quite similar to that of (IV). The highest mass peak was observed at m/z 514. This is also the base peak of the molecule (VI). The other fragment ions were obtained at m/z 499, 473, 440, 401, 398, 386, 385, 374, 373, 327, 300, 291, 273, 246, 231, 164, 163, 149, 123 and lower mass peaks. It evident from ions that most of them arise after the loss of a molecule of propionic acid from the molecular ion and a difference of two mass unit is therefore observed in the fragment ions obtained from (VI) and those from the 3β-substituted thiazole (VI) Scheme (V) shows various fragment ion from (IV-VI). A comparison of the spectra of these three thiazoles (IV-VI) (Fig. IV-VI) clearly showed remarkable similarity between them which can be made use of in the interpretation of the of other such compounds.

## SCHEME –V


C8H17
-CH3
m/z 499 (C30H47N2SO2)
-C8H17
m/z 401 (C23H33N2SO2)
CH3CH2C—O
O
S
N
NH2
–C8H17CH=CH2
m/z 374 (C21H30N2SO2)
(M+• 574; C31H50N2S)
–H•
m/z 373 (C21H29N2SO2)
–CH3CH2COOH
C8H17
-C8H17
m/z 327 (C20H27N2S)
-C10H20
m/z 300 (C18H24N2S)
(M+• 440; C28H44N2SO)
–C4H6
m/z 164
(C8H8N2S)
–222
m/z 386 (C24H38N2S)
–140
m/z 246
(C14H18N2S)
—N≡C—NH
-C8H17
m/z 123
(C7H7S)
m/z 273 (C16H21N2S)
—N≡C—NH2
m/z 231
(C15H19S)
-CH3
m/z 149
(C7H5N2S)

# *Figures*

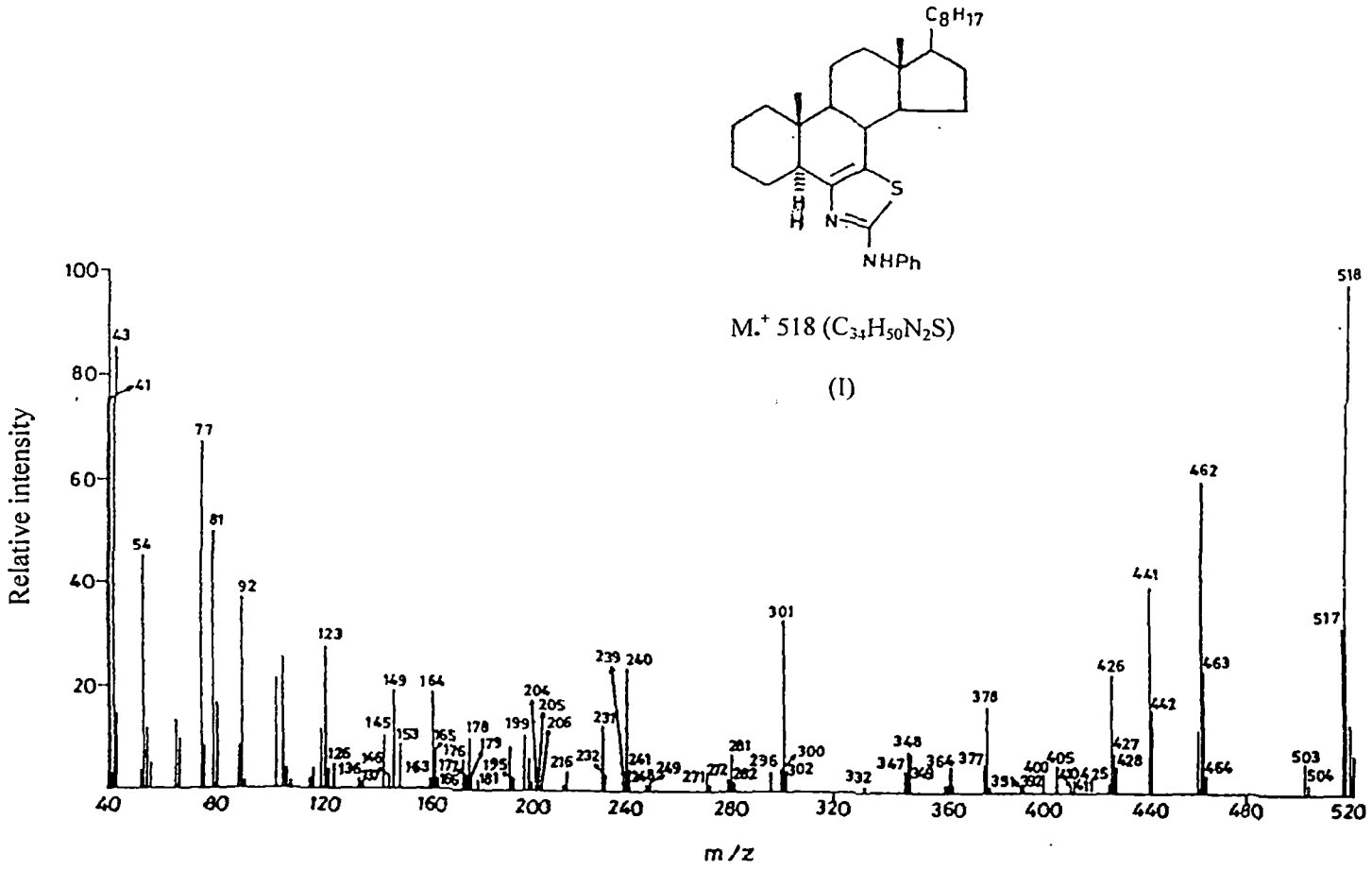



Fig. I

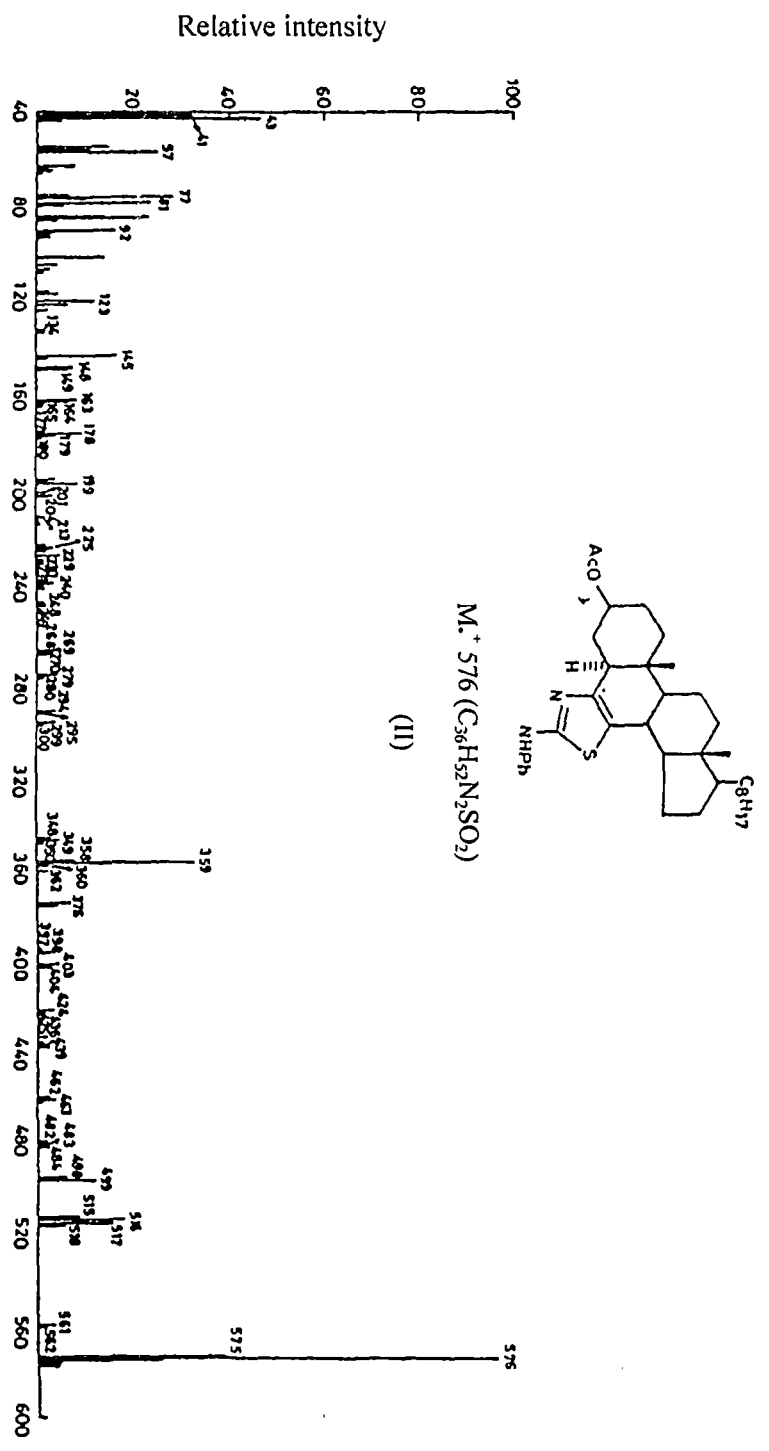



Fig. II

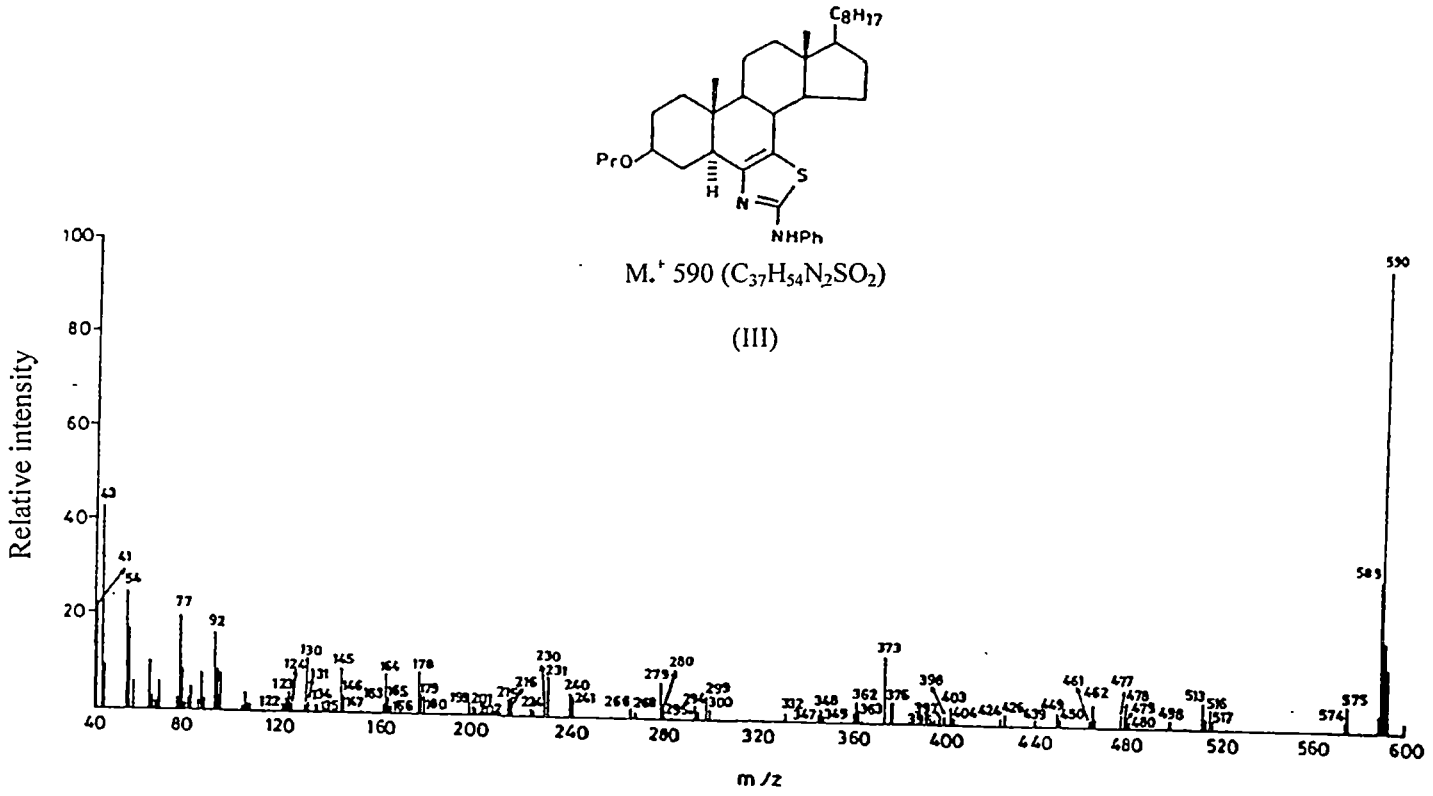
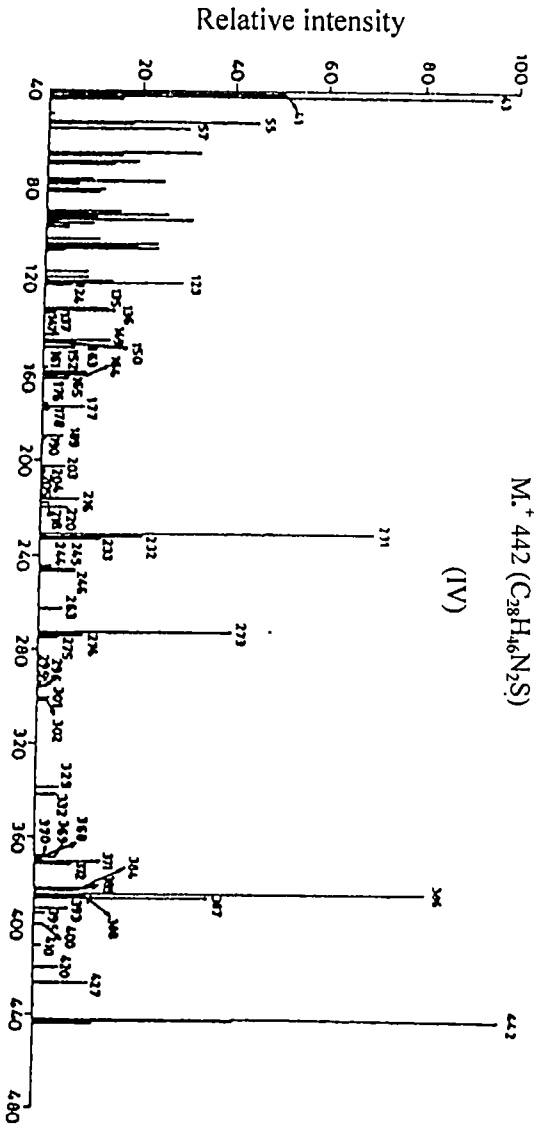
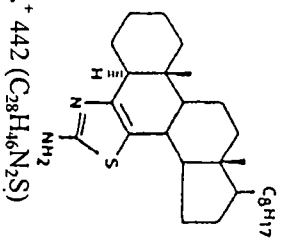

C8H17
PrO
H
N
S
NHPh
M.+ 590 (C37H54N2SO2)
(III)
Relative intensity
m/z

**Fig. III**




$M.^+$ 442 ($C_{28}H_{46}N_2S$)

(IV)

Fig. IV

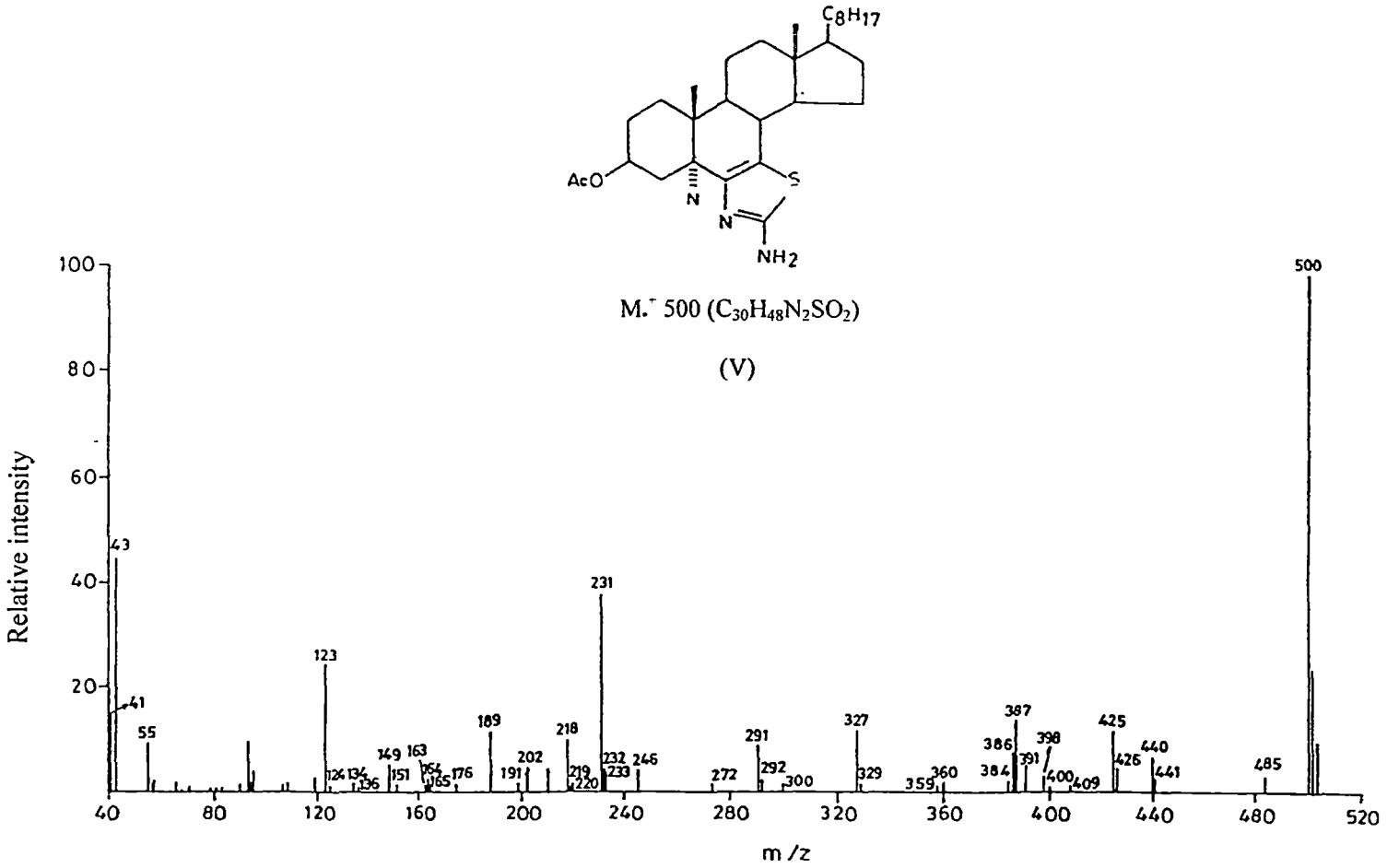

C8H17
AcO
S
N
N
NH2
M.+ 500 (C30H48N2SO2)
(V)
Relative intensity
m /z
100
80
60
40
20
40
80
120
160
200
240
280
320
360
400
440
480
520
500
43
41
55
123
231
189
218
202
191
149
163
151
176
291
327
387
386
398
384
391
425
426
440
441
485
272
292
300
329
359
360
400
409
246
232
233
219
220

Fig. V

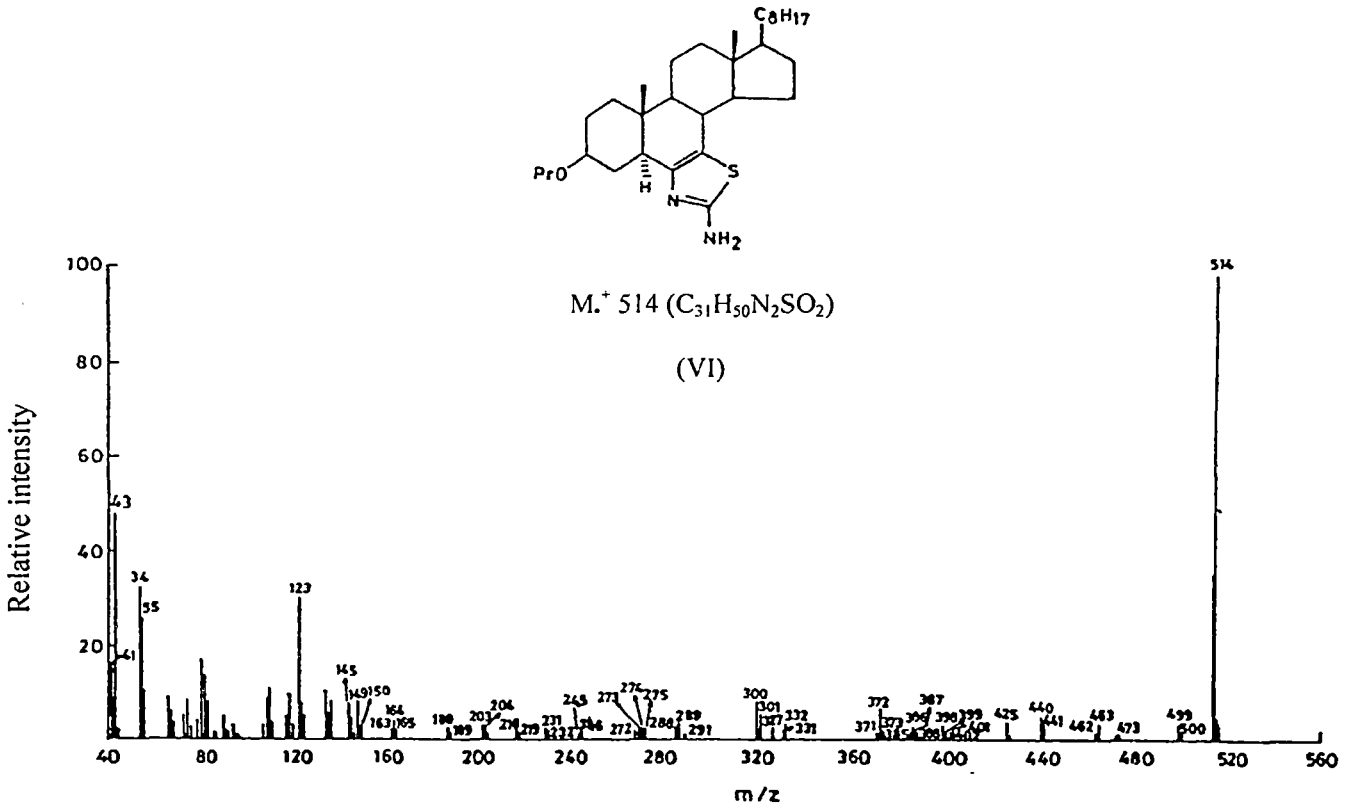

C8H17
PrO
H
S
N
NH2
M.+ 514 (C31H50N2SO2)
(VI)
Relative intensity
m/z
100
80
60
40
20
40
80
120
160
200
240
280
320
360
400
440
480
520
560
514
123
145
43
34
55
41

**Fig. VI**

# *Experimental*

The mass spectrum were measured on JMS-300/AIE MS-9, mass spectrometer at 70 ev using direct insertion sample inlet system at a source temperature of about 200°C. The accurate mass measurements were related to fragment ions of heptacosafluorotributylamine at a resolving power of 15,000.

The values of m/z of fragment ion from various compounds are tabulated below. The values in parenthesis are relative abundance (%) of the peak with respect to base peak taken as 100%, and the compositions of fragment ions as determined by accurate mass measurement.

**2'-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (I)**

$M^+$ 518 (100.00; $C_{34}H_{50}N_2SO_2$), 517 (33.00; $C_{34}H_{49}N_2S$),504 (1.90), 503 (4.00; $C_{33}H_{47}N_2S$), 464 (3.50), 463 (24.3), 462 (61.00; $C_{30}H_{42}N_2S$), 461 (12.50; $C_{30}H_{41}N_2S$), 442 (13.50), 441 (40.00; $C_{28}H_{45}N_2S$), 428 (5.46), 427 (5.20), 426 (23.50; $C_{28}H_{44}NS$) 425 (2.00), 411 (3.00; $C_{27}H_{41}NS$), 410 (2.80), 405 (5.20; $C_{26}H_{33}N_2S$), 400 (3.50; $C_{27}H_{44}S$), 392 (1.53), 391 (1.60), 378 (13.50; $C_{24}H_{30}N_2S$), 377 (5.00), 365 (2.00), 364 (6.70; $C_{23}H_{28}N_2S$), 363 (5.08; $C_{23}H_{27}N_2S$), 362 (2.50), 349 (10.00; $C_{22}H_{25}N_2S$), 248 (5.60), 347 (6.20), 332 (1.50), 302 (4.03), 301 (34.00; $C_{18}H_{25}N_2S$), 300 (2.07), 296 (4.20; $C_{18}H_{20}N_2S$), 282 (2.00), 281 (9.09; $C_{17}H_{17}N_2S$), 280 (2.70), 272 (2.00), 271 (3.50), 249 (1.60), 248 (2.30), 241 (5.00), 240 (24.00; $C_{14}H_{12}N_2S$), 239 (1.80), 232 (3.50), 231 (13.40; $C_{15}H_{19}S$), 216 (2.50), 215 (1.00), 205 (1.50), 204 (2.40), 202 (1.50), 201 (6.03), 199 (13.00), 195 (3.80), 194 (9.06), 181 (2.50), 179 (3.7), 177 (2.50), 176 (7.00), 175 (11.5), 166 (2.40), 165 (8.00), 164 (20.00), 163 (2.91), 153 (10.25), 150 (4.37), 149 (22.30), 147 (1.50), 146 (6.00), 145 (11.28), 137 (1.50), 136 (1.60), 126 (5.05), 124 (13.10), 123 (28.21; $C_7H_7S$), 122 (12.00), 119 (11.00), 118 (3.17), 107 (26.00), 105 (23.42), 94 (1.50), 93 (2.18), 92 (32.50), 91 (8.00), 83 (11.07), 81 (50.00), 78 (10.00), 77 (68.00), 69 (11.00), 67 (18.00), 57 (6.00), 56 (18.00), 55 (40.00), 54 (46.00), 53 (5.00), 44 (1.45), 43 (86.00), 41 (46.58).

**3β-Acetoxy-2' -N-phenylamino-5α-cholest-6-eno [6,7 -d] thiazole (II)**

M+ 576 (100.00; $C_{36}H_{52}N_2SO_2$), 575 (36.50; $C_{36}H_{51}N_2SO_2$), 562 (2.50), 561 (4.46; $C_{35}H_{46}N_2SO_2$), 518 (11.20), 517 (16.08), 516 (20.13; $C_{34}H_{48}N_2S$), 515 (12.50), 499 (13.60; $C_{30}H_{47}N_2SO_2$), 498 (11.50), 484 (3.52; $C_{30}H_{46}NSO_2$), 483 (2.70), 482 (2.18), 464 (2.20), 463 (5.30; $C_{28}H_{35}N_2SO_2$), 462 (3.50; $C_{30}H_{42}N_2S$), 440 (1.50), 439 (3.15; $C_{28}H_{43}N_2S$), 438 (2.30), 436 (3.80; $C_{26}H_{32}N_2SO_2$), 425 (2.00), 424 (3.50), 404 (3.40), 403 (11.30; $C_{26}H_{31}N_2S$), 398 (3.00; $C_{27}H_{42}S$), 397 (2.40), 396 (2.50), 376 (12.50; $C_{20}H_{27}N_2SO_2$), 358 (10.00),350 (2.00), 349 (5.00; $C_{22}H_{25}N_2S$), 348 (3.50), 300 (10.00), 299 (5.00; $C_{18}H_{23}N_2S$), 295 (1.50), 294 (4.00; $C_{18}H_{18}N_2S$), 280 (2.80), 279 (6.00; $C_{17}H_{15}N_2S$), 270 (2.00), 269 (2.00), 268 (2.50), 249 (1.50), 248 (1.50), 242 (2.10), 240 (4.50; $C_{14}H_{12}N_2S$), 231 (2.50; $C_{15}H_{19}S$), 230 (2.43), 229 (6.30), 228 (3.30), 225 (3.50), 216 (1.00), 213 (2.64), 204 (3.50), 203 (2.50), 201 (2.57), 199 (9.56), 198 (1.50), 197 (4.05), 180 (2.08), 179 (5.00), 178 (10.50), 177 (2.90), 165 (1.50), 164 (5.30), 163 (10.28), 149 (7.14), 148 (7.50), 146 (1.50), 145 (17.50), 126 (3.00), 124 (5.00), 123 (13.40; $C_7H_7S$), 122 (6.50), 119 (4.20), 118 (3.53), 107 (3.00), 105 (5.70), 103 (15.40), 95 (2.80), 94 (3.90), 92 (14.20), 88 (2.48), 87 (25.20), 8 (5.00), 81 (24.00), 78 (8.30), 77 (31.00), 76 (7.00), 66 (2.35), 65 (1.50), 64 (8.40), 57 (25.35), 56 (12.20), 55 (16.00), 44 (5.50), 43 (47.88),41 (30.90).

**3β-Propionoxy-2'-N-phenylamino-5α-cholest-6-eno [6,7-d] thiazole (III)**

$M^+$ 590 (100.00; $C_{37}H_{54}N_2SO_2$), 589 (34.00; $C_{37}H_{53}N_2SO_2$), 575 (6.70; $C_{36}H_{51}N_2SO_2$), 574 (3.40), 517 (1.52), 516 (4.50; $C_{34}H_{48}N_2S$), 514 (2.32), 513 (6.56; $C_{31}H_{49}SO_2$), 498 (2.62), 479 (2.08), 478 (2.52), 477 (3.50; $C_{29}H_{37}N_2SO_2$), 462 (5.15; $C_{30}H_{42}N_2$), 461 (2.9), 450 (2.49; $C_{27}H_{34}N_2SO_2$), 449 (3.48), 439 (2.40), 426 (3.50), 424 (1.39; $C_{28}H_{42}NS$), 404 (3.17), 403 (5.37; $C_{26}H_{31}N_2S$), 398 (3.10), 397 (1.50), 396 (1.50), 376 (3.36; $C_{26}H_{32}S$), 373 (18.20; $C_{21}H_{29}N_2SO_2$), 364 (2.41), 363 (3.30), 362 (4.88; $C_{23}H_{26}N_2S$), 361 (1.98), 349 (4.30; $C_{22}H_{25}N_2S$), 348 (2.40), 347 (2.50), 332 (2.00), 300 (2.00), 299 (6.00; $C_{18}H_{23}N_2S$), 295 (2.70), 294 (3.00; $C_{18}H_{18}N_2S$), 280 (3.42), 279 (12.79; $C_{17}H_{15}N_2S$), 268 (1.81), 266 (2.30), 241 (4.00), 240 (6.70; $C_{14}H_{12}N_2S$), 231 (10.35; $C_{15}H_{19}S$), 230 (3.52), 225 (1.28), 224 (1.70), 216 (1.50), 215 (1.70), 202 (1.70), 201 (2.36), 199 (3.50), 180 (3.20), 179 (5.92), 178 (9.25), 166 (2.85), 165 (2.80), 164 (8.00), 163 (2.54), 147 (1.50), 146 (5.60),

145 (10.78), 135 (1.20), 134 (1.35), 131 (2.50), 130 (2.30), 126 (1.50), 124 (1.00), 123 (5.0; $C_7H_7S$), 122 (4.28), 121 (1.50), 107 (2.30), 105 2.50), 103 (4.50), 94 (7.50), 93 (7.93), 92 (18.00), 88 (3.75), 87 (7.50), 82 (6.50), 79 (10.30), 78 (9.50), 77 (22.50), 76 (2.50), 68 (4.00), 67 (2.50), 64 (11.00), 57 (2.00), 56 (7.50), 55 (18.40), 54 (27.50), 44 (9.70), 43 (45.80),41 (23.50).

**2′-amino-5α-cholest-6-eno [6,7-d] thiazole (IV)**

MS, $M^{\cdot+}$ 442 (100.00; $C_{28}H_{46}N_2S$), 427 (12.50; $C_{27}H_{43}N_2S$), 420 (5.00) 410 (2.50), 400 (2.5; $C_{27}H_{44}S$), 395 (3.75), 388(5.00), 387 (36.25), 386(85.50; $C_{24}H_{38}N_2S$), 385 (8.75; $C_{24}H_{37}N_2S$), 384 (100.00; $C_{28}H_{46}N_2S$), 372 (7.5), 371(18.75), 370 (2.5), 369(5.00), 368(3.75), 332 (5.00), 329 (5.00; $C_{20}H_{29}N_2S$), 302 (2.94; $C_{18}H_{26}N_2S$), 301 (3.75; $C_{18}H_{25}N_2S$), 269 (3.00), 295 (2.5), 275 (4.20), 274 (11.25), 273 (43.75; $C_{16}H_{21}N_2S$), 263 (5.00), 246 (7.50; $C_{14}H_{18}N_2S$), 245 (7.50), 244 (4.50), 233 (14.00), 232 (23.14), 231 (72.50; $C_{15}H_{19}S$), 220 (6.25), 218 (2.50), 216 (8.75; $C_{14}H_{16}S$), 205 (3.75), 204 (2.50), 203 (5.00), 190 (2.50), 189 (5.00), 178 (2.50), 177 (11.25), 176 (2.5), 165 (7.5), 164 (12.50; $C_8H_8N_2S$), 163 (10.00; $C_8H_7N_2S$), 161 (2.50), 152 (7.50), 150 (6.25), 149 (16.25; $C_7H_5N_2S$), 147 (5.00), 137 (7.5), 136 (17.50), 135 (15.00), 124 (6.25), 123 (32.50; $C_7H_7S$), 122 (16.25), 121 (10.00), 119 (6.25), 110 (5.00), 108 (27.50), 107 (27.5), 105 (12.50), 91 (16.25), 83 (10.00), 82 (11.25), 80 (7.5), 79 (27.5), 77 (10.00), 71 (15.00), 70 (7.50), 69 (25.00), 68 (15.00), 67 (30.00), 57 (30.00), 56 (15.00), 55 (45.00), 53 (10.00), 44 (12.50), 43 (95.00), 41 (50.00).

**3β-Acetoxy-2′-amino-5α-cholest-6-eno [6,7-d] thiazole (V)**

MS, $M^{\cdot+}$ 500 (100.00; $C_{30}H_{48}N_2SO_2$), m/z 485 (3.75; $C_{29}H_{45}N_2SO_2$), 441 (2.50), 440 (6.25; $C_{28}H_{44}N_2S$), 426 (2.50), 425 (12.50; $C_{27}H_{41}N_2S$), 409 (2.50), 400 (2.50), 398 (3.75; $C_{27}H_{42}S$), 391 (5.00), 387(15.00; $C_{22}H_{31}N_2SO_4$), 386 (8.20; $C_{24}H_{38}N_2S$), 384 (3.00), 360(2.50), 327 (12.00; $C_{20}H_{27}N_2S$), 300 (2.80; $C_{18}H_{24}N_2S$), 292 (2.50), 291 (10.00), 273 (2.80; $C_{16}H_{21}N_2S$), 246 (4.10; $C_{14}H_{18}N_2S$), 231 (39.00; $C_{15}H_{19}S$), 220 (2.50), 219 (2.50), 218 (12.50), 202 (5.00), 191 (2.50), 189 (12.50), 176 (2.50), 165 (2.50), 164 (3.00; $C_8H_{18}N_2S$), 163 (2.50; $C_8H_{17}N_2S$), 151 (2.50), 149 (5.00; $C_7H_5N_2S$), 136 (2.50), 134 (2.50), 124 (1.80), 123 (26.00; $C_7H_7S$), 119 (2.90), 109

(2.50), 107 (2.50), 95 (3.75), 94 (2.50), 93 (10.00), 90 (2.50), 83 (1.25), 81 (3.75), 79 (1.25), 71 (2.50), 68 (2.50), 66 (3.75), 57 (6.25), 56 (2.50), 55 (10.00), 43 (40.00), 42 (2.50), 41 (13.75).

**3β- proponoxy -2'-amino-5α-cholest-6-eno [6,7-d] thaizole (VI)**

$M^+$. 514 (100.00; $C_{31}H_{50}N_2SO_2$), 499 (4.00; $C_{30}H_{47}SO_2$), 474 (1.50), 473 (2.01), 463 (3.00), 462 (2.04), 441 (2.50), 440 (6.25; $C_{28}H_{44}N_2S$), 425 (4.00), 402 (1.08), 401 (2.50; $C_{23}H_{33}N_2SO_2$), 400 (1.50), 399 (2.06), 398 (4.00; $C_{27}H_{42}S$), 388 (2.50), 387 (1.50), 386 (4.00; $C_{24}H_{38}N_2S$), 385 (2.00), 374 (2.02; $C_{21}H_{30}N_2SO_2$), 373 (7.00; $C_{21}H_{29}N_2SO_2$), 372 (1.00), 332 (3.00), 331 (1.50), 301 (5.00), 300 (10.00; $C_{18}H_{24}N_2S$), 291 (1.80), 289 (4.00), 275 (2.50), 274 (2.00), 273 (5.50; $C_{16}H_{21}N_2S$), 272 (2.01), 246 (3.50), 245 (1.00), 232 (3.23), 231 (3.00; $C_{15}H_{19}S$), 219 (1.50), 218 (1.80), 204 (2.00), 203 (4.50), 189 (2.00), 188 (2.40), 165 (1.00), 164 (5.00; $C_8H_{18}N_2S$), 163 (2.50; $C_8H_{17}N_2S$), 150 (3.00), 149 (8.00; $C_7H_5S$), 146 (3.50), 145 (7.50), 137 (8.00), 136 (5.00), 135 (10.50), 125 (6.30), 124 (7.00), 123 (30.50; $C_7H_7S$), 121 (2.50), 119 (10.00), 118 (5.00), 110 (11.00), 109 (6.00),96 (1.00),95 (3.50), 92 (2.07), 91 (2.40), 90 (5.00), 86 (1.00), 83 (7.50), 82 (15.00), 81 (2.80), 80 (17.40), 76 (6.50), 73 (6.06), 68 (4.30), 67 (6.20), 66 (10.00), 56 (10.09), 55 (23.20), 54 (34.00), 44 (2.70), 43 (48.30), 41 (18.00).