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THE FRAGMENTATION OF TWO 19-HYDROXYMETHYL STEROIDS

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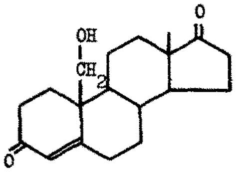
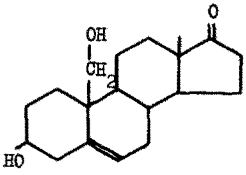
A study of the fragmentation upon electron impact, of 19-hydroxy-3,-17-dioxo-androsta-4-ene (I), and 3,19-dihydroxy-17-oxo-androsta-5-ene (II), revealed an interesting feature.

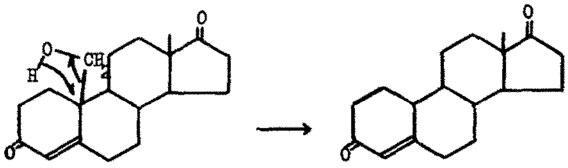


(I)

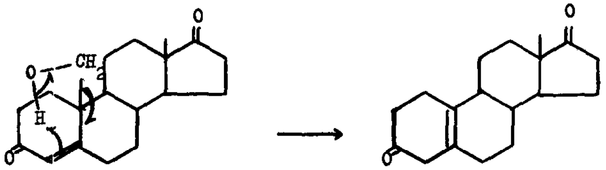


(II)

In the spectrum of the former (Fig. 1), the base peak (m/e 272) corresponds to the elimination of a fragment of 30 mass units, and must arise from the elimination of formaldehyde with transfer of one hydrogen. While this could arise through a four-membered transition state:



it seems more likely that a six-membered transition state involving the double bond operates:



Subsequent fragmentation is of little diagnostic value. It is interesting to note that, contrary to expectation, the loss of the hydroxymethylene group (31 mass units), to give an ion of m/e 271, is not a favoured process, in spite of possible allylic activation and stabilisation of the corresponding positive charge or radical.

In the case of the dihydroxy compound (II) (Fig. 2), there is a pronounced elimination of water, and further expulsion of formaldehyde gives rise to the base-peak in the spectrum (m/e 256). Once again, subsequent fragmentation is of little significance. However, loss of the hydroxymethylene group without hydrogen transfer is more pronounced, as indicated by the peak at m/e 255. This may be due to the primary elimination of water with the introduction of an additional double bond, which might make the expulsion of formaldehyde through a six-membered transition state less favoured.

These observations would support the interpretation of the Swiss authors (1) of the loss of 30 mass units from the ion of m/e 140 in their study of limaspermin.

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REFERENCES

(1) M. Pinar, W. von Philipsborn, W. Vetter and H. Schmid, Helv. Chim. Acta. 54, 2260 (1962).

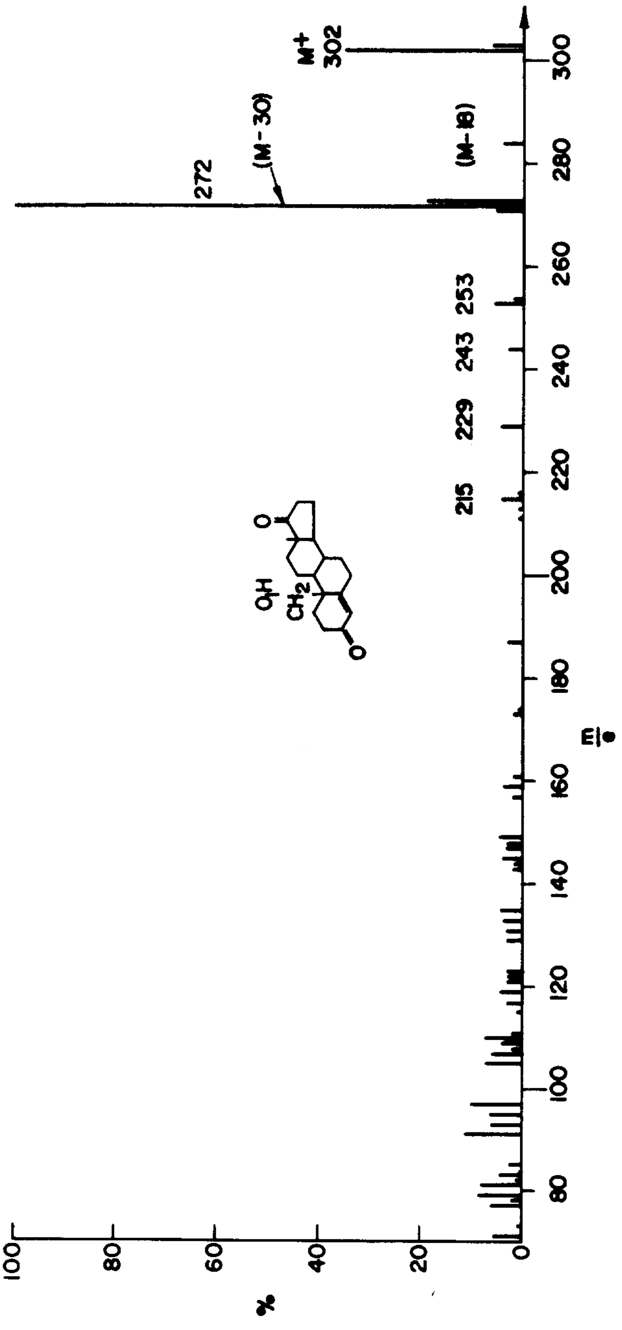
M+
302
272
(M-30)
(M-18)
253
243
229
215
O
OH
CH2
O
%
100
80
60
40
20
0
80
100
120
140
160
180
200
220
240
260
280
300
m/e

FIGURE I

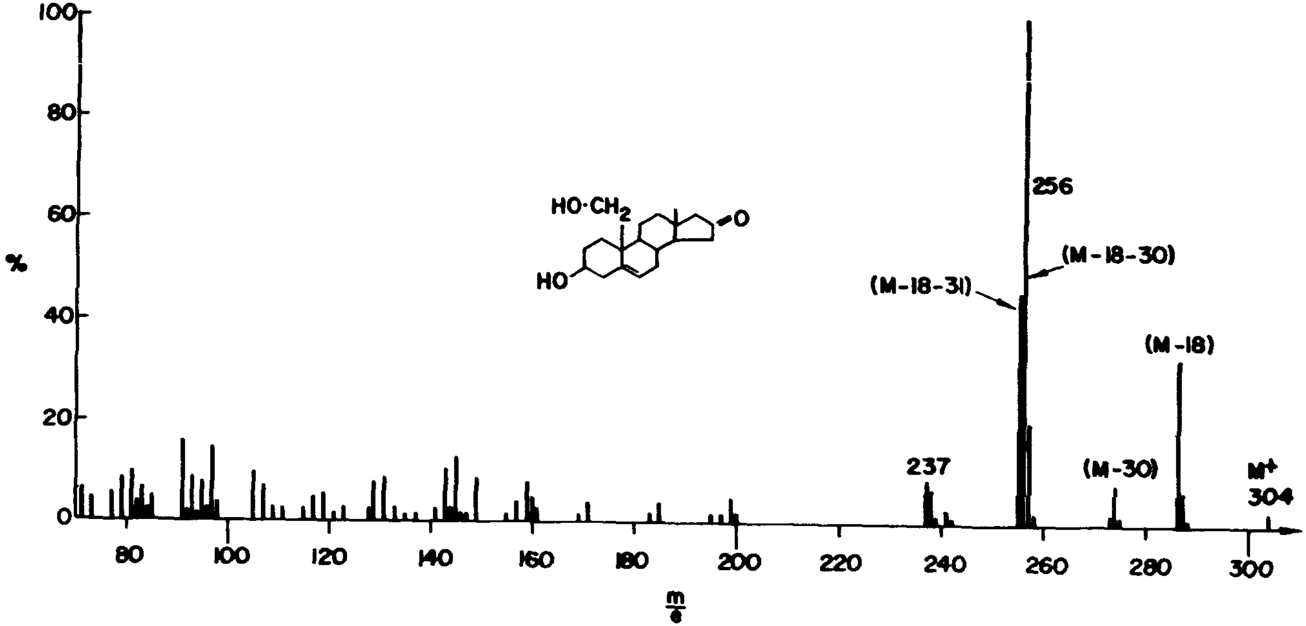
100
80
60
40
20
0
%
HO·CH2
HO
O
256
(M-18-30)
(M-18-31)
(M-18)
237
(M-30)
M+
304
80
100
120
140
160
180
200
220
240
260
280
300
m/e

FIGURE 2