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# Chemistry

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Scheme 1: fragmentation scheme with molecular ion $M^+$ ($m/e$ 294) and fragments $A_1$ $m/e$ 224, $A_2$ $m/e$ 209, $_1$ $m/e$ 279, $_2$ $m/e$ 211, $_3$ $m/e$ 171, $_1$ $m/e$ 292, $_1$ $m/e$ 223

Figure 1: Scheme 1: fragmentation scheme with molecular ion $M^+$ ($m/e$ 294) and fragments $A_1$ $m/e$ 224, $A_2$ $m/e$ 209, $_1$ $m/e$ 279, $_2$ $m/e$ 211, $_3$ $m/e$ 171, $_1$ $m/e$ 292, $_1$ $m/e$ 223

Mass spectra of two isomers

Figure 2: Mass spectra of two isomers

## Abstract

## Full Text

# Chemistry

**V. I. Zaretskii, N. S. Vul' fson, V. L. Sadovskaya, S. N. Ananchenko, I. V. Torgov**

## MASS-SPECTROMETRIC STUDY OF D-HOMO-EQUILENIN, D-HOMO-ESTRONE, AND THEIR STEREOISOMERS

*(Presented by Academician M. M. Shemyakin, 15 IV 1964)*

Recently, Djerassi and co-workers ([1]) studied in detail the fragmentation pathways of estrone and its derivatives under the influence of electron impact, and also set forth preliminary considerations on the differences in the mass spectra of equilenin and its 14-$\beta$-isomer. Continuing work in the field of mass-spectrometric investigation of steroids ([2]), we decided to study, using as examples the methyl ether of D-homo-equilenin (I) and its 14-$\beta$-isomer (II), the influence of cis- or trans-fusion of rings C and D on the decomposition pathways of steroid systems of this class under the action of electron impact.

It turned out that, despite the general similarity, the spectra of compounds (I) and (II) differ substantially in the intensities of certain characteristic peaks.

### Scheme 1

Thus, the intensity of the peak with $m/e$ 224 (fragment $A_1$, see Scheme 1) in the spectrum of the methyl ether of D-homo-equilenin (I) is several times lower than in that of its 14-$\beta$-isomer (see Fig. 1 and Table 1). This is probably explained by the greater stability of the trans-decalone system in comparison with the cis form, since fragment $A_1$ is formed directly from the molecular ion as a result of cleavage of the $C_{13}$—$C_{17a}$ and $C_{14}$—$C_{15}$ bonds. The intensity of the peak with $m/e$ 223 (fragment $B_1$) is practically identical in the spect-

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Fig. 2

Figure 3: Fig. 2

**Fig. 1**

···of both isomers. This can readily be explained by the formation of fragment $B_1$ from the molecular ion as a result of the successive cleavage of the same bonds (cleavage of one of the bonds at the junction of rings C and D eliminates the spatial differences between isomers (I) and (II)).

The stereochemical differences in the structures of (I) and (II) are also reflected in the sharp decrease in the intensity of the peak at $m/e$ 211 (fragment $B_2$) on going from the trans-(I) to the cis-structure (II) (see Table 1 and Fig. 1). Fragment $B_2$ may be formed from the ion with $m/e$ 279 ($B_1$; $M-15$), in which the spatial structure of the molecule apparently remains unchanged. Ion $B_1$ then decomposes with detachment of ring D, accompanied by migration of two protons from positions 15, 16, or 17. The increase in the intensity of the peak at $m/e$ 211 in the case of the trans form is explained···

**Fig. 2**

a more favorable spatial arrangement of the migrating protons relative to atoms $C_{13}$ and $C_{14}$. An analogous influence of the spatial arrangement of the migrating proton, depending on trans or cis fusion in a bicyclic system, was noted for isomeric $\alpha$-decalones ([3]).

Fragment $B_2$, further, with loss of ring elements, is converted into fragment $B_3$ ($m/e$ 171), the structure of which is apparently analogous to the ion with $m/e$ 157 formed in the decomposition of 6,7-dehydroestrone ([1]). The fact that the ratios of the peak intensities at $m/e$ 171 and 211 on going from the trans form (I) to the cis form (II) are very close (0.29 and 0.23—Table 1) may serve as confirmation of the proposed mechanism for the formation of these fragments.

The nature of the change in the intensity of the peak with $m/e$ 209 ($A_2$) is opposite to the change in the peak with $m/e$ 211 ($B_2$) (1.9 and 0.23, respectively). This permits

to conclude that the pathways of formation of these fragments are different. Fragment $A_2$ can be formed both from fragment $A_1$ and from fragment $B_1$. However, the relatively close quantitative ratios in the change of the peaks with $m/e$ 209 and 224 (1.9 and 3.46) apparently indicate a greater contribution of pathway A to the formation of fragment $A_2$.

It should be noted that in the spectrum of the methyl ether of D-homo-equilenin (I) the intensity of the peak $M-2$ ($m/e$ 292, fragment $G_1$, see Fig. 1 and Scheme 1) is considerably greater than in that of its cis-isomer (II). This is explained by the possibility of 1,2-trans-diaxial elimination of hydrogen atoms from positions 14 and 15 in the case of the trans-isomer (I). The structure of the fragments

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shown in Scheme 1 is confirmed by literature analogies[1].

Table 1

Characteristic peaks in the spectra of the methyl ether of D-homo-equilenin (I) and its 14-$\beta$-isomer (II)

| $m/e$ | Peak intensity (in % of $M^+$) I | Peak intensity (in % of $M^+$) II | Intensity ratio II:I |
|---|---|---|---|
| 292 | 30.8 | 7.9 | 0.25 |
| 279 | 40 | 29.2 | 0.73 |
| 224 | 13 | 45 | 3.46 |
| 223 | 22.7 | 28.4 | 1.25 |
| 211 | 40.5 | 9.5 | 0.23 |
| 209 | 12.7 | 24.2 | 1.9 |
| 171 | 14.5 | 4.2 | 0.29 |

Table 2

Characteristic peaks in the spectra of D-homo-estrone (III), its 8-$\alpha$-isomer (IV), and their methyl ethers (IIIa and IVa)

| $m/e$ | Peak intensity (in % of $M^+$) III | Peak intensity (in % of $M^+$) IIIa | Peak intensity (in % of $M^+$) IV | Peak intensity (in % of $M^+$) IVa | Intensity ratio IV:III | Intensity ratio IVa:IIIa |
|---|---|---|---|---|---|---|
| 213 | 38.2 | – | 57 | – | 1.53 | – |
| 227 | – | 19.7 | – | 27 | – | 1.37 |
| 199 | 9.1 | – | 21.9 | – | 2.4 | – |
| 213 | – | 7.6 | – | 13.1 | – | 1.72 |
| 185 | 28 | – | 28 | – | 1.0 | – |
| 199 | – | 44 | – | 49.5 | – | 1.13 |
| 159 | 25.7 | – | 22 | – | 0.86 | – |
| 173 | – | 19.5 | – | 16.3 | – | 0.84 |
| 146 | 21.2 | – | 52.5 | – | 2.47 | – |
| 160 | – | 17.5 | – | 46.2 | – | 2.64 |

In addition to the isomeric methyl ethers (I) and (II), we studied the mass spectra of D-homo-estrone (III), its 8-$\alpha$-isomer (IV), and the corresponding methyl ethers (IIIa, IVa). The fragmentation pathways of the compounds studied are in agreement with Djerassi' s scheme proposed by him for estrone. The presence of a six-membered ring D in the compounds we studied explains the appearance in their spectra of peaks with $m/e$ 199 and 213 ($D_1$ and $D_2$), analogous to the peaks with $m/e$ 185 and 199 in the spectra of estrone and its methyl ether[1].

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$D_1$, R = H ($m/e$ 199) $D_2$, R = $CH_3$ ($m/e$ 213)

$E_1$, R = H ($m/e$ 146) $E_2$, R = $CH_3$ ($m/e$ 160)

The difference in the nature of the fusion of rings B and C is reflected in the sharp increase in the intensity of the peaks with $m/e$ 146 and 160 (fragments $E_1$ and $E_2$), as well as of the peaks of fragments $A_1$ and $A_2$, on going from the trans- (III, IIIa) to the cis-structure (IV, IVa) (see Fig. 2 and Table 2). This can be explained by the greater stability of the trans-isomer in comparison with the cis-isomer. An analogous regularity is observed in the spectra of estrone and its 8$\alpha$-isomer.

The mass spectra were obtained on an MX-1303 instrument with an inlet system made of stainless steel, at a temperature of 200° and an ionization energy of 70 eV.

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## References Cited

1. C. Djerassi, J. M. Wilson et al., *J. Am. Chem. Soc.*, **84**, 4544 (1962).

2. S. N. Ananchenko et al., *Tetrahedron*, **20** (1964). H. C. , . . et al., *Izv. AN SSSR, Ser. Khim.*, 1964, 184.

3. E. Lund, H. Budzikiewicz et al., *J. Am. Chem. Soc.*, **85**, 941 (1963).

*Note: Figure translations are in progress. See original paper for figures.*

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