Polarographic Behaviour of Some Steroidal Olefins

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Halve-wave-potentials of five steroidal olefins were measured by anodic polarography. They show oxidation-potentials in the range of 0.7–0.9 V. Differences in potentials are correlated to shape of the molecules.

During experiments dealing with the activation of some steroidal olefins such as 7-dehydrocholesterol and ergosterol to highly reactive alkylating species under mild "physiologically-similar" conditions, we became interested in the oxidation potentials of those sterols. Such oxidation potentials can be measured by means of polarography.

Experimental

The sterols 7-dehydrocholesterol (**1a**), ergosterol (**1b**), cholesterol (**2**) and lumisterol (**3**), and vitamin D_3 (**4**) were purified by cristallisation from methanol. Tetrabutyleammoniumperchlorate and dichloromethane (Merck: "uvasole") were used without further purification. Polarograms were obtained by the "Polarecord" model E 261 from Metrohm AG Herisau, Switzerland. A sworking electrode a rotating platinum electrode, as reference a Ag/Ag^+-electrode was used.

1.5 mg of the sterol was dissolved in 25 ml of a 0.1 M solution of tetrabutyleammoniumperchlorate in dichloromethane. This solution, which was kept under nitrogen, was electrolysed by increasing the voltage automatically from 0.5 to 1.5 V (0.25 to 1.25 V).

Three polarograms were obtained for each sterol. The halve-wave potentials were determined by graphical extrapolation.

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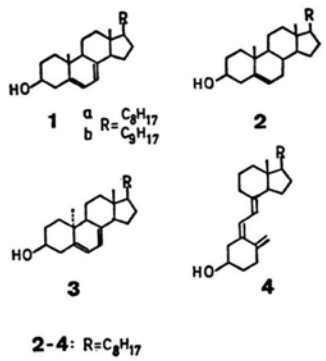
Results and Discussion

The results of the measurements are shown in the following chart:

Sterol	$E_{1/2}$ (V)
1a	0.71
1b	0.76 [1]
2	0.92
3	0.84
4	0.84



It is known from the literature that the height of the oxidation potentials of organic molecules can be correlated to their molecular shape [2].

Usually alkenes have oxidation-potentials of about 2 V, alkadienes, depending on substitution, between 1.3 V to 1.8 V [2, 3].

Thus it seems obvious that the ridgitity of the steroid system is directly responsible for the further lowering of the potentials of the -ene, -diene moiety in the molecules.

The potentials of 7-dehydrocholesterol (**1a**) and ergosterol (**1b**) are similar. One more double-bond in the side-chain of **1b** seems to have no influence on the potential.

As expected, the potential of cholesterol **2** with only one double-bond in ring B is somewhat higher than those of **1a, b**. The potentials of **3** and **4**, however, are in comparison to those of **1a, b** exceptional.

In lumisterol **3** CH_3-18 is located in β-, and CH_3-19 in α-position.

(In **1a, b** both are on the β-side of the molecule.)

Thus **3** is sterically more hindered than **1a, b**, relative to electrode-surface (*i.e.* hindered diffusion as a result of shape).

Similar steric interaction may play a role in the case of vitamin D_3 (**4**).

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[2] L. Eberson and K. Nyberg, Tetrahedron **32,** 2185 (1976).

[3] H. Baltes, E. Steckhan, and H. J. Schäfer, Chem. Ber. **111,** 1294 (1978).