UDC 578.088:547.924

OPTICAL ROTATORY DISPERSION OF STEROIDS WITH VARIOUS CHROMOPHORES

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 36–39, 1969

Steroids with carbonyl chromophores are very convenient objects for the structural applications of the phenomenon of optical rotatory dispersion (ORD). However, other steroid compounds not containing a ketonic chromophore are also optically active in the visible region [1, 2]. It was therefore of interest to carry out a comparative investigation of the optical rotatory dispersion of steroids with various chromophoric groups.

We have measured the ORD of steroids containing the following chromophores: ketone (C=O), diene ($>C=C-C=C<$), and an ordinary C=C bond. The measurements were carried out on an ORD-UV-5 spectropolarimeter of the Japanese firm Jasco in the 200–600 mμ region. As solvents we used methanol and dioxane. All the measurements were carried out at 20° C in a quartz cell 1 cm long. The results of the measurements are given in Figs. 1 and 2.

Steroids with a carbonyl chromophore are the best-studied group of compounds of the steroid series. From Fig. 1, a, it can be seen that a 4α-methyl group affects both the position and the amplitude of the Cotton effect in the 300-mμ region if methanol is used as the solvent.

For the 4α-methyl derivative in dioxane, only some decrease in the peak value of the positive Cotton effect is found. Moreover, when the solvent is changed, 4 α-methylcholest-7-en-3-one gives a smaller bathochromic shift than cholest-7-en-3-one.

In Fig. 1, b, the ORD curves show that the Cotton effect has maxima of both signs and is found at longer wavelengths in the case of the 7-oxosteroids than in the case of the 3-oxosteroids. Different substituents at C_3 have an appreciable influence only on the magnitude of the optical rotation. The form of the ORD curve remains practically unchanged. The bathochromic shift on passing from methanol to dioxane for 7-oxocholesterol is 6 mμ.

The ORD curves of steroids containing the diene $>C=C-C=C<$ chromophore are given in Fig. 1, c, d, (the ultraviolet absorption band of this chromophore is located in the 260–280 mμ region and the anomalous ORD in the 200–300 mμ region).

The Cotton effect is ambiguous with respect to zero rotation, the negative amplitude showing a characteristic doublet splitting with maxima at 296 and 282 mμ. The bathochromic shift is slight, but the amplitude of the Cotton effect in dioxane is higher than in methanol.

The ORD curves of ergosterol and 7-dehydrocholesterol are almost identical, i. e., they reflect the identical environment of the chromophore in the two molecules.

As can be seen from Fig. 2, the optical rotation rises sharply in the shorter-wave region of the spectrum. It is not excluded that the ORD is anomalous—below 240 mμ—, but it is impossible to observe the Cotton effect since the absorption band of a single C=C bond is below 220 mμ and the measurement of the optical rotation is interfered with by the strong absorption both of the substance itself and of the solvent.

As is known, saturated steroids not containing C=O and $>C=C-C=C<$ groups have approximately constant optical rotations over the whole spectral range. Moreover, ORD anomalies are absent in the case of steroids with a disturbed cyclopentanoperhydrophenanthrene skeleton (Vitamins D_2 and D_3), regardless of the presence of chromophoric groups. Thus, ORD curves similar to those given in Fig. 2 may be a criterion of the presence of a single double bond in steroid compounds preserving the polycyclic nucleus of the molecule.

So far as concerns the structure of the chromophore itself, on the basis of the ORD measurements of steroids with various chromophores given, it may be concluded that the magnitude of the optical rotation in the ultraviolet is the greater, the greater the area of delocalization of the π-electrons, i. e., the rotation near the absorption bands is to some extent proportional to the geometrical dimensions of the chromophore.

Conclusions

1. On the basis of a comparative study of the ORD of steroids containing as chromophores the groups C=O, $>C=C-C=C<$ and C=C, it has been established that in all the compounds the ORD is anomalous in the UV region of the spectrum.

2. In steroid compounds the magnitude of the optical rotation increases with an increase in the geometrical dimensions of the chromophoric group.

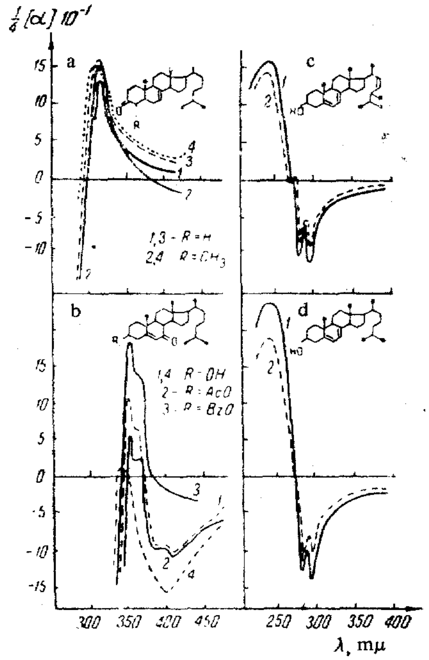

Fig. 1. Optical rotatory dispersion of steroids with various chromophores: a) 3-oxosteroids at a concentration of 2 mg/ml. 1, 3) Cholest-7-en-3-one (in dioxane and methanol); b) 7-oxosteroids at a concentration of 2 mg/ml. 1, 4) 7-oxocholesterol (in dioxane and methanol); 2) 7-oxocholesterol acetate (in dioxane); 3) 7-oxocholesterol benzoate (in dioxane). c) Ergosterol at a concentration of 0.04 mg/ml. 1) Solution in dioxane; 2) solution in methanol. d) 7-Dehydrocholesterol at a concentration of 0.04 mg/ml. 1) Solution in dioxane; 2) solution in methanol.

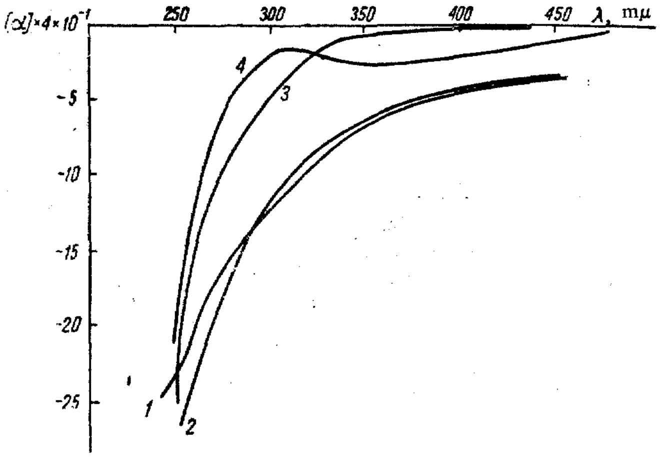

Fig. 2. Optical rotatory dispersion of steroids containing a single C=C bond at a concentration of 1 mg/ml (solutions in dioxane). 1) Cholesterol; 2) cholesterol acetate; 3) metastenol; 4) lathosterol.

3. The ORD curves of steroid compounds with various π-electronic chromophores are highly specific and can be used to study their structure and for identification purposes.

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22 November 1967

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