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Rotatory Dispersion of Compounds of the Cedrane Series

Compounds of the cedrane series, the first results of whose study at the Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR were recently reported (1), constitute an interesting subject for the application of the spectropolarimetric method, so successfully used by Djerassi (2) for the investigation of steroid compounds. Until now there have been no data in the literature on spectropolarimetric studies of cedrane compounds, although in several works (3-5) the rotatory dispersion of more complex compounds was studied, compounds which also include the perhydroazulene skeleton.

The cyclic nucleus of cedrane* (I) has several asymmetric centers: four of them (3 asymmetric atoms that are bridgehead atoms of the tricyclic system, and the asymmetric atom bearing the methyl group in the five-membered ring) in all the compounds described below (II–X) have the same configuration; thus, the structural and stereochemical changes affect only the seven-membered ring. These changes consist in the introduction of a hydroxyl group at positions 2 and 3, a carbonyl group at position 2, a double bond at position 2–3, and in the conversion of the methyl group at C_3 into a methylene group (formation of an exocyclic double bond), an oxymethylene group, or an aldehyde group:

[structural formula of cedrane, labeled (I)]

[structural formulas]

II cedrol
$(R_1 = CH_3;\ R_2 = OH;\ R_3 = H)$

III primary cedranol
$(R_1 = CH_2OH;\ R_2 = R_3 = H)$

IV isocedranol
$(R_1 = CH_3;\ R_2 = H;\ R_3 = OH)$

V isocedranone
$(R_1 = CH_3;\ R_2 = H;\ R_3 = O)$

VI α-cedrene
$(R = CH_3)$

Fig. 1. Rotation dispersion of compounds of the cedrane series (in isooctane solutions): II –cedrol; III –primary cedranol; IV –isocedranol; V –isocedranone; VI –α-cedrene; VII –cedrenal; VIII –β-cedrene; IX –isocedrenol; X –isocedrenone

Figure 1: Fig. 1. Rotation dispersion of compounds of the cedrane series (in isooctane solutions): II –cedrol; III –primary cedranol; IV –isocedranol; V –isocedranone; VI –α-cedrene; VII –cedrenal; VIII –β-cedrene; IX –isocedrenol; X –isocedrenone

VII cedrenal
$(R = CHO)$

VIII β-cedrene
$(R = H)$

IX isocedrenol
$(R = OH)$

X isocedrenone
$(R = O)$

* There is no generally accepted numbering for cedrane. We propose carrying it out according to the rules of systematic nomenclature (^{6}). The name of this substance according to systematic nomenclature is: 3,5,5,9-tetramethyltricyclo-(10; 11–4; 10–6)-hendecane.

The rotation-dispersion curves of the listed cedrane derivatives are shown in Fig. 1.

For three compounds, β-cedrene (VIII), isocedrenol (IX), and isocedranol (IV), the rotations are very small. Since the measurements were carried out in dilute solutions (not only because of the small amounts of substance available to us, but also because of the low solubility of these compounds in isooctane), the angles read on the polarimeter in the long-wavelength part of the spectrum amounted to only a few hundredths of a degree; therefore the calculated molecular rotations for these substances (see Table 1) should be regarded only as approximate.

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II –cedrol; **III** –primary cedranol;
IV –isocedranol; **V** –isocedranone;
VI –α-cedrene; **VII** –cedrenal; **VIII** –β-cedrene; **IX** –isocedrenol; **X** –isocedrenone.

Fig. 2. Effect of HCl on the rotation of isocedranone (**V**) and isocedrenone (**X**). Dashed lines –solutions in methanol; solid lines –solutions in methanol + HCl.

Fig. 2. Effect of HCl on the rotation of isocedranone (V) and isocedrenone (X). Dashed lines –solutions in methanol; solid lines –solutions in methanol + HCl

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Cedrol (II) and primary cedranol (III) have somewhat greater rotation, especially in the ultraviolet part of the spectrum. Noteworthy is

attention to the fact that, with the opposite sign, the absolute magnitudes of the rotation for the two alcohols are practically identical. This fact may be compared with Levin' s observation (ˆ7), who established that alcohols of the type $R_1R_2CH{-}(CH_2)$ OH, having the **same** configuration, at $n = 0$ (a case similar to cedrol) and $n = 1$ (a case similar to primary cedranol), have **opposite** signs of rotation. However, the analogy with the aliphatic alcohols studied by Levin is, in our case, nevertheless quite remote, and perhaps the reason for the "antipodal" character of curves *II* and *III* is that the groups decisive for the creation of asymmetry at

Table 1

Molecular rotations of compounds of the cedrane series in isooctane solutions *

Wavelength	Cedrol $c = 1.42$	Primary cedranol $c = 1.02$	Isocedranol $c = 0.15$	Isocedranone $c = 0.62$	α-Cedrene **A $c = 0.98$	α-Cedrene **B $c = 1.0$	Cedrenal $c = 1.1$	β-Cedrene $c = 2.8$	Isocedrenone $c = 0.62$	Isocedrenol $c = 0.36$
589	20.7	−20.5	8	−160	−170	−199	−129	16	4	6
578	24.1	−21.6	8	−165	−175	−203	−132	19	5	6
546	26.5	−22.9	10	−187	−198	−232	−155	21	5	8
435	47.8	−46.4	17	−332	−354	−415	−348	30	10	46
405	58.2	−56.8	18	−412	−435	−513	−498	29	12	79
365	77.8	−78	23	−601	−592	−698	−943	26	19	208
334	103	−106	35	−982	−795	−925	−111	21	33	745
313	153	−125	40	−990	−1030	−1165	−75	21	43	−150
303	153	−131		−473	−1180	−1355		49	56	−667
297	153	−134	53	−212	−1250	−1450		46		−695
289	219	−140	63	0	−1320	−1550			74	−704
280				232	−1440	−1630				

* Additional points for isocedranone: −1040 (328), −1110 (322), 90 (285); for cedrenal: −764 (385), −982 (278), −1050 (277), −1080 (375), −1060 (374), −900 (372), −905 (368), −962 (362), −1130 (359), −1200 (357), −1040 (354), −885 (351), −710 (349), −677 (344), −588 (339), −135 (328), −80 (322), −385

(307); for isocedrenone: +124 (385 mμ), +155 (378 mμ), +306 (454 mμ), 389 (349 mμ), +493 (344 mμ), +613 (339 mμ), +721 (339 mμ), +510 (326 mμ).

** Preparation A was obtained by dehydration of cedrol; preparation B, by dehydration of pseudocedrol.

C_3 groups—OH in cedrol and CH_2OH in primary cedranol—occupy antipodal positions.

All the compounds mentioned so far have smooth* curves of rotatory dispersion, as is to be expected for hydrocarbons and alcohols that have no optically active absorption bands in the spectral region accessible to spectropolarimetric measurements. α-Cedrene (VI) also has a smooth curve; however, the magnitudes of rotation for this substance are incomparably greater than for the preceding ones. We had at our disposal two preparations of α-cedrene. The first of them was obtained directly by dehydration of cedrol with formic acid (⌒1). The second preparation was obtained from α-cedrene of the above-mentioned origin by converting it, under the action of perbenzoic acid, into the oxide, which was reduced by the action of lithium aluminum hydride to pseudocedrol; from the latter, upon dehydration, α-cedrene was again obtained. It turned out that the rotation of α-cedrene obtained by the second route is greater than the rotation of α-cedrene formed directly upon dehydration of cedrol. Since, for all wavelengths, the rotation of the first preparation amounts to 85–86% of the rotation of the second, there is no doubt as to their chemical and steric identity; but the first of them apparently contains an admixture of racemate; any optically active impurity, for example β-cedrene, having a small positive rotation, would disrupt the strict proportionality of the rotatory-dispersion curves of the two preparations.

* To describe rotatory-dispersion curves we use the terms introduced by Djerassi (⌒2, ⌒8), translating *plain curves* as "smooth curves," *peak* as "peak," and *trough* as "trough."

The dispersion curves acquire a different character from that of the hydrocarbons and alcohols considered above when a carbonyl chromophore is present in the compound under study. In this case an anomaly appears (a peak or a trough) associated with the carbonyl absorption band. On the dispersion curve of isocedranone (V) there is a trough at 320 mμ; on the dispersion curve of isocederenone (X) there is a peak at 334 mμ; and cedrenal (VII) gives a dispersion curve with a complex Cotton effect, characterized by the presence of two troughs at 375 and 357 mμ. The presence of anomalies in the carbonyl derivatives of cedrene is in complete agreement with all the work of Djerassi, who observed analogous anomalies in steroid ketones (2).

The author mentioned also showed that anomalies caused by the presence of a carbonyl group disappear upon formation of hemiacetals, which readily occurs when traces of hydrochloric acid are added to methanolic solutions of ketones (9). Having measured the rotatory dispersion of cedrane ketones in methyl alcohol before and after acidification with a drop of conc. HCl, we found phenomena different from those observed by Djerassi. In both ketones, after acidification, not only was disappearance of the ketone anomaly not observed, but, on the contrary, the magnitude of the rotation at the maximum increased (see Fig. 2). The reason for this behavior of isocedranone and isocederenone is not yet clear.

The synthetic part of the work was carried out at the Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR.

Measurements of rotatory dispersion were carried out in the Department of Organic Chemistry of Moscow State University named after M. V. Lomonosov, using a photoelectric spectropolarimeter ([10]) in tubes from 0.5 to 4 dm in length. Owing to the slight absorption of the compounds studied in the ultraviolet, no difficulties arise in the measurements. The results of the measurements are summarized in Table 1.

At present we are continuing the study of the rotatory dispersion of compounds of the cedrane series.

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