decylbenzenesulfonate was isolated as a yellow hygroscopic solid. The yield was 41%.

Anal. Calcd. for $C_{48}H_{32}O_6S_2Ba$: Ba, 14.36. Found: Ba, 14.38.

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Polyenes. V. The Structure of Cyclocitrylidenecyanoacetic Acid and the Purity of β-Cyclocitral[1]

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The absorption spectrum of cyclocitrylidenecyanoacetic acid[2] obtained by the condensation of β-cyclocitral and cyanoacetic acid in aqueous sodium hydroxide, exhibits two maxima: one at 307 mμ (ε 4350) and the other at 223 mμ (ε 5500). Comparison with the spectra of other alkylidenecyanoacetic acids[2] indicated that the cyclocitrylidenecyanoacetic acid was perhaps a mixture of α- and β-isomers. However, ozonization of the compound in question failed to yield any isogeronic acid as would have been expected if an appreciable amount of α-form had been present. Only geronic acid could be isolated from the ozonization, indicating that the low maximum at 223 mμ is probably not due to the presence of the α-form.

β-Cyclocitral has been prepared several times in this Laboratory by the method of Tiemann.[2,3] The final steps in this process involve recrystallization of the semicarbazone of the crude cyclocitral until pure β-cyclocitral semicarbazone has been obtained. The β-cyclocitral is then recovered from its semicarbazone by steam distillation in the presence of phthalic anhydride. The β-cyclocitral obtained in this way[2] had the following physical properties: $n^{17}\mathrm{D}$ 1.4965, $n^{25}\mathrm{D}$ (calcd.) 1.4933; $\lambda_{\max.}$ 249 mμ (ε 7700) in 95% ethanol. Koster[4] reports the refractive indices of pure α- and β-cyclocitral to be 1.4691 and 1.4953 respectively at 25°. On the basis of these values the β-cyclocitral obtained previously in this Laboratory by the above described method is approximately 93% β-form.

In view of the fact that regeneration of β-ionone from its semicarbazone by steam distillation in the presence of phthalic anhydride causes partial rearrangement to the α-form[5] it was considered possible that such a partial rearrangement could occur in the cyclocitral series also. In order to test this hypothesis, pure β-cyclocitral semicarbazone was hydrolyzed by shaking with cold dilute sulfuric acid, a procedure which has been shown to produce the purest β-ionone from its semicarbazone.[5,6] The β-cyclocitral obtained in this way had the following physical properties: $n^{21.4}\mathrm{D}$ 1.4971, $n^{25}\mathrm{D}$ (calcd.) 1.4957; $\lambda_{\max.}$ 249 mμ (ε 11600). It is apparent that the hydrolysis with cold sulfuric acid yields a product with a higher β-content than did the steam distillation method. It is highly probable that the product obtained in the cold is 100% β-cyclocitral. The extinction coefficients at 249 mμ indicate that the β-content of the cyclocitral prepared by the steam distillation method may be as low as 66%.

The hydrolysis of the β-cyclocitral semicarbazone proceeds at a much slower rate than β-ionone semicarbazone. Six normal sulfuric acid was required to accomplish the hydrolysis at an appreciable rate whereas the ionone derivative hydrolyses rapidly when shaken with two normal acid.

Ozonization of the pure β-cyclocitral yielded pure geronic acid with no trace of isogeronic acid detectable.

Experimental

Preparation of Cyclocitrylidenecyanoacetic Acid.—Condensation of 1.0 g. of the pure β-cyclocitral ($n^{21.4}\mathrm{D}$ 1.4971) with cyanoacetic acid in aqueous sodium hydroxide yielded crystalline cyclocitrylidenecyanoacetic acid whose physical properties were identical with those previously described from this Laboratory.[2]

Ozonization of Cyclocitrylidenecyanoacetic Acid.—One gram of cyclocitrylidenecyanoacetic acid was ozonized in 10 ml. of glacial acetic acid. Excess ozone appeared in the issuing stream of oxygen even at the very beginning of the ozonolysis. The ozonide was decomposed in the presence of hydrogen peroxide and treated by the procedure previously described.[7] The crude semicarbazone obtained proved to be the geronic acid derivative. Repeated fractional extractions with hot ethyl acetate[8] failed to reveal the presence of any isogeronic acid semicarbazone.

Hydrolysis of β-Cyclocitral Semicarbazone with Cold Sulfuric Acid.—β-Cyclocitral semicarbazone, 19.8 g., m. p. 165–166° (uncor.), was shaken under nitrogen with 100 ml. of petroleum ether and 100 ml. of 6 *N* sulfuric acid for nine hours. The ether layer was separated and the aqueous layer extracted several times with petroleum ether. The combined petroleum ether solutions were dried over anhydrous potassium carbonate. Distillation of the residue left after removal of the solvent yielded 11.2 g. (78% yield) of β-cyclocitral, b. p. 92–96° (12 mm.) (see text for other physical properties).

Ozonization of β-Cyclocitral.—Pure β-cyclocitral (11.2 g.) was ozonized in 40 ml. of acetic acid and the ozonide decomposed by pouring into 50 ml. of water containing hydrogen peroxide. After standing overnight, 50 ml. more water was added and the solution was slowly distilled until 50 ml. of distillate had collected. Three grams of unreacted β-cyclocitral was recovered as an oil in the distillate. More water was added to the still-pot residue and the solution was extracted with ether in a liquid–liquid extractor for forty-eight hours. After removal of the ether, distillation and redistillation of the residue yielded 4.6 g. (51% yield) of pure geronic acid, b. p. 133–135° (3 mm.), $n^{25}\mathrm{D}$ 1.4525, neut. equiv. 173 (calcd. 172). The melting point (162–163°) of the crude semicarbazone prepared from this geronic acid indicated the absence of any impurity of isogeronic acid. This geronic acid was used in experiments reported elsewhere.[7]

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[2] Andrews, Cristol, Lindenbaum and Young, THIS JOURNAL, **67**, 715 (1945).

[3] Tiemann, *Ber.*, **33**, 3719 (1900).

[4] Koster, *ibid.*, **77**, 553 (1944).

[5] Young, Cristol, Andrews and Lindenbaum, THIS JOURNAL, **66**, 855 (1944).

[6] Heilbron, Johnson, Jones and Spinks, *J. Chem. Soc.*, 727 (1942).

[7] Young and Linden, THIS JOURNAL, **69**, 2042 (1947).

[8] Karrer, Morf and Walker, *Helv. Chim. Acta*, **16**, 975 (1933); Karrer, Helfenstein, Wehrli and Wettstein, *ibid.*, **13**, 1094 (1930).