[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

A Spectroscopic Study of Eleostearic Acids from Chinese Wood Oil

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In a publication by one of the authors[1] a method is described for the isolation of eleostearic acids in Chinese wood oil. The present study deals with the characterization of such acids by means of absorption spectra.

The only paper dealing with the absorption spectra of eleostearic acids is by Manecke and Volbert.[2] They did not state how their acids were prepared and the spectroscopic technique was such that only broad general absorption bands were found.

A Hilger rotating sector photometer H16 in conjunction with a Hilger E316 spectrograph was used for determining the absorption characteristics of solutions of the various eleostearic acids. The light source was a tungsten spark, 20,000 volts, condensed. The absorption cells were 1 cm. long, with quartz end plates, plane to within 0.2 μ and parallel to within five minutes.

A solution of the α-eleostearic acid, 1:160,000, in 90% alcohol, showed well-defined absorption bands, as did also the β-eleostearic acid.

In order to check the purity of the acids they were recrystallized several times from 90% alcohol and the absorption characteristics determined for each crystallization. No significant change was noted after the first crystallization. The purity was further checked by several crystallizations from ethyl acetate and comparing the absorption with that obtained from the ethyl alcohol crystallizations. In each case a solution of 1:160,000 in 90% ethyl alcohol was used, and again no significant change was noted.

Table I and Fig. 1 show the results thus obtained.

TABLE I

α-Eleostearic acid

[a]Log$_{10}$ T	λ			
0.6	2564			2849
.625	2566			2848
.65	2568			2847
.675	2574			2846
.7	2576			2844
.725	2578			2842
.75	2584	2776		2837
.775	2608	2763	2792	2830
.8	2626	2755	2796	2825
.825	2661	2752	2817	
.85	2666	2738		
.875	2671	2737		
.9	2676	2727		
.95	2684	2722		
1.00	2686	2713		
1.05	2704			

β-Eleostearic acid

Log$_{10}$ T	λ			
0.6	2536			2827
.625	2538			2822
.65	2544			2822
.675	2548			2822
.7	2552			2819
.725	2553			2818
.75	2554			2817
.775	2557	2738		2817
.8	2558	2728	2757	2817
.825	2566	2726	2765	2816
.85	2568	2721	2767	2812
.875	2575	2717	2777	2809
.9	2638	2715	2785	2807
.95	2641	2706	2797	
1.00	2647	2703		
1.05	2652	2701		
1.10	2657	2696		
1.15	2667	2691		

[a] See Bureau of Standards Scientific Paper No. 440. 1922. b is taken to be 1 cm. c as 1:160,000 is taken as unity.

There are numerous references in the literature concerning the effect of visible and ultraviolet light on α-eleostearic acid. Inasmuch as a light source was used in characterizing the eleostearic acids, it was essential to determine the effect, if any, of such a light source on the solutions of the α-eleostearic acid in the concentrations used. To accomplish this, two series of spectrograms were made on the same solution, the first to establish the absorption and the second to find if any change had occurred due to the light source. No change was discernible.

It is a matter of great interest to determine whether or not the eleostearic acid obtained from Chinese wood oil treated with sulfur (the so-called beta) is identical with the acid obtained by irradiating an alcoholic solution of α-eleostearic acid with a mercury vapor lamp. An absorption cell containing a 1:160,000 solution of α-eleostearic acid in 90% ethyl alcohol and a second

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[1] Thomas and Thomson, THIS JOURNAL, **56**, 898 (1934).

[2] Manecke and Volbert, *Farben.-Ztg.*, **32**, 2829 (1927).

cell, containing 90% ethyl alcohol, were irradiated at a distance of 25 cm. from the burner for various periods of time. Spectrograms were made after each period of irradiation and the results are presented in Fig. 2.

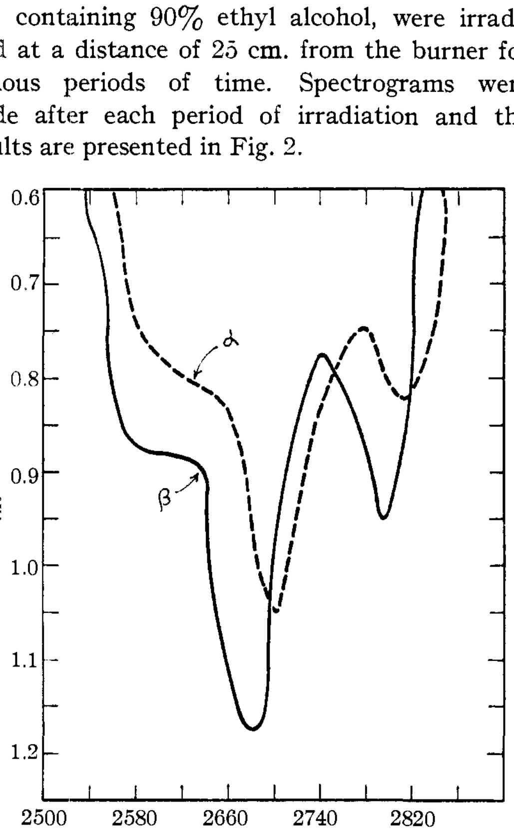

Fig. 1.—Absorption spectra of α-eleostearic and of β-eleostearic acids.

An examination of Fig. 2 makes it clear that irradiation causes profound changes to take place in the structure of the α-eleostearic acid. During the first two minutes there is a tendency to pass over into the "beta" form but continued irradiation apparently leads to the production of a whole series of compounds.

As cells only 1 cm. long were available for irradiation purposes it was impossible to obtain enough material at this concentration to explore this more fully. A 15% solution of α-eleostearic acid in 90% ethyl alcohol was therefore irradiated in an open 200-cc. beaker for two hours at a distance of 30 cm. from the burner. The 200-cc. beaker was placed at the bottom of a tall 4-liter beaker into which a stream of carbon dioxide was passed during irradiation. The eleostearic acid was then recrystallized three times and the absorption spectrum determined of a 1:160,000 solution in ethyl alcohol.

Within the experimental error of the method and dealing only with that portion of the spectrum lying between 2500 and 2850 Å. spectroscopically the eleostearic acid from the solid glyceride, and the eleostearic acid formed by irradiating a solution of the α-eleostearic acid under the conditions specified, appear to be identical.

The Estimation of α-Eleostearic Acid and β-Eleostearic Acid in the Presence of One Another.—An examination of Fig. 1 indicates the possibility of determining the percentages of α- and β-eleostearic acids in the presence of each other.

To test out the feasibility of this, solutions in 90% ethyl alcohol were made containing various proportions of α- and β-eleostearic acids (concentration 1:160,000) and absorption spectrograms made of such solutions. The tungsten line 2658 Å. was used for making the transmittancy measurements.

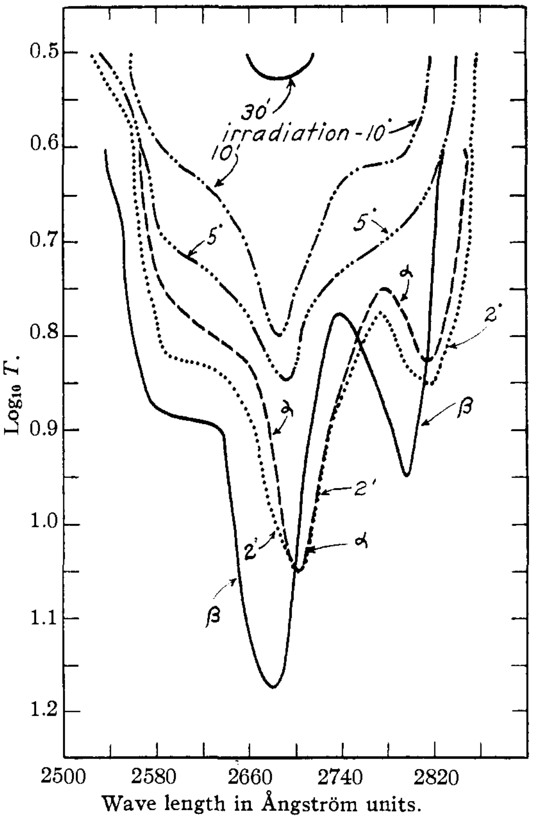

Fig. 2.—Influence of light from a Hanovia mercury vapor lamp on 1:160,000 solution of α-eleostearic acid in 90% ethyl alcohol. The numbers refer to irradiation times in minutes.

The results are recorded in Table II and Fig. 3.

Discussion

During the course of the experimental work a number of interesting points arose in connection

TABLE II

LOG$_{10}$ T FOR VARIOUS MIXTURES OF THE α- AND β-ELEOSTEARIC ACIDS AT λ2658Å.

Mixture, %			
Alpha +	Beta	Calcd.	Found
...	100	...	1.175
10	90	1.15	1.15
20	80	1.12	1.125
50	50	1.037	1.025
80	20	0.955	0.95
90	10	.927	.925
100	...	...	.90

with the stability of alcoholic solutions of the α-eleostearic acid. It was found that if solutions of the acid, containing a few per cent. of the acid, were allowed to stand with a small amount of air in volumetric flasks at about $-3°$, acetaldehyde was noted. In one such case the alcohol was distilled off and acetaldehyde identified in the distillate. Allowing alcoholic solutions to stand in the absorption cells, in a fairly well lighted room, permitted changes to take place that could be easily demonstrated by a change in the absorption spectrum of the solution. As a result of these experiences it was customary to determine the absorption spectrum as soon as the solution was made up.

Absorption in the region from about 2580 to about 2650 Å. in the case of α-eleostearic acid and from about 2570 to about 2630 Å., in the case of β-eleostearic acid, is somewhat uncertain. There may be one or more maxima here but it was impossible to settle this question visually.

It will be noted that there is not perfect agreement between the figures in Table I and those in Table II for the absorption at 2658 Å. This is partly due to the difficulty experienced in completely freeing the crystals from mother liquor. The crystals cannot be dried at elevated temperatures nor can they be kept very long at room temperature in contact with air. Some difficulty may therefore be anticipated in the exact duplication of concentrations.

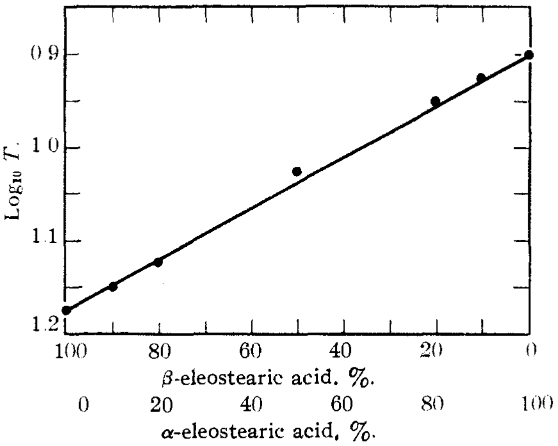

Fig. 3.—Log$_{10}$ T for various mixtures of the α- and β-eleostearic acids at 2658 Å.

Acknowledgment.—The assistance of Dr. and Mrs. Reginald Auchincloss and of the Royal Baking Powder Company to one of us (A. D.) is gratefully acknowledged.

Summary

The absorption characteristics of α- and β-eleostearic acids are very similar, yet sufficiently different to enable them to be identified easily by this means.

Although it is well recognized that light may cause profound changes in the acids, yet the light sources used in characterizing the acids had, under the conditions specified, no apparent action. A much stronger source, however, did cause very decided changes in the structure of the α-eleostearic acid.

The alpha acid, 15% solution in 90% ethyl alcohol, irradiated for two hours under certain standard conditions, was converted into an acid that had the same absorption spectrum, in the region 2500 to 2850 Å. as the acid obtained from the solid glyceride.

It is possible to determine spectroscopically the percentage composition of a mixture of α- and β-eleostearic acids.

NEW YORK, N. Y.

RECEIVED NOVEMBER 3, 1933