glyceride in tung oil, further work being carried on for developing the latter analysis into a reliable method.

4. The chemical kinetics for the absorption of halogen from Wijs solution by α-eleostearic acid has been studied and two specific reaction rates have been determined.

5. Böeseken's assumption of a bimolecular reaction for the second stage halogen absorption by α-eleostearic acid from Wijs solution has been found incorrect. A combination of two simultaneous bimolecular reactions has been suggested

$$CH_3(CH_2)_3CHClCHClCH{=}CHCHClCHCl(CH_2)_7COOH$$

$$\xrightarrow{+ICl} CH_3(CH_2)_3CHClCHClCHICHClCHClCHCl(CH_2)_7COOH$$

$$\xrightarrow{+I_2} CH_3(CH_2)_3CHClCHClCHICHICHClCHCl(CH_2)_7COOH$$

6. The variation of the iodine value of tung oil with temperature, excess of reagent and time of contact with reagent has been explained.

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[A CONTRIBUTION FROM THE YALE IN CHINA SCHOOL OF SCIENCE, HUA CHUNG COLLEGE]

Physicochemical Studies of Alpha and Beta Eleostearic Acids. I. Molar Refractivity and Parachor

BY S. W. WAN AND M. C. CHEN

Alpha and beta eleostearic acids were names suggested by Maquenne[1] for the isomeric eleomargaric and eleostearic acids so named and first isolated from the oil of *Eleococca Vernicia* by Cloez.[2] Tung oil is mainly a triglyceride of the alpha acid, and because of its special properties which make tung oil a highly important and useful material, a large amount of data has been accumulated. However, there were differences in opinion concerning its constitution[3] until Böeseken and co-workers[4] suggested the formula, $CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7COOH$ which has correlated many important phenomena not satisfactorily explained before. Although experimental findings from different sources have not entirely converged toward a common conclusion, most investigations seem to confirm this constitution.

One of the arguments put forth by Böeseken and co-workers[4] for suggesting the above formula was based upon the molar refractivity of the eleostearic acids. Melting points of 47 and 67° were given, respectively, for the specimens of alpha and beta isomers prepared for their experiments. Since then the method of preparation has been much improved. The authors have followed the method of Thomas and Thomson[5] with increased repetition of recrystallization, and have obtained from a large batch of original crystals a small crop of highly purified product with melting points higher than the previously reported values. A series of physicochemical determinations is being made with the highly purified alpha and beta eleostearic acids thus obtained.

Experiments and Data.—Alpha and beta eleostearic acids were prepared from their corresponding glycerides in tung oil, the beta-glyceride being formed when tung oil was allowed to stand in contact with a trace of sulfur. Density, surface tension and index of refraction of the alpha and beta acids were determined, respectively, at 50 ± 0.01° and 75 ± 0.01°. The surface tension of each was measured by the capillary rise method and the index of refraction by the use of an Abbe refractometer. The following data were obtained.

TABLE I

Acid	α-Eleostearic	β-Eleostearic
Melting point, °C.	49.0–49.2	71.5–72.0
Density	0.9028 at 50°	0.8909 at 75°
Surface tension	33.42 at 50°	31.04 at 75°
Refractive index	1.5112 at 50°	1.5022 at 75°

Results and Discussion

From the above data the parachor, P, and molar refractivity, R, of the eleostearic acids were calculated and are given in Tables II and III. P' and R' in the tables are, respectively, the theoreti-

(1) Maquenne, *Compt. rend.*, **135**, 696 (1902).

(2) Cloez, *ibid.*, **81**, 469 (1875); **82**, 501 (1876); **83**, 943 (1877).

(3) Kametaka, *J. Chem. Soc.*, **83T**, 104 (1903); Mania, *Chem. Inst., Univ. Kiel. Ber.*, **42**, 674 (1909); Vercruysse, *Bull. soc. chim. Belg.*, **32**, 151 (1923); Nicolet, THIS JOURNAL, **43**, 938 (1921); Ishio, *J. Pharm. Soc., Japan*, **529**, 228 (1926); Eibner, Merz and Munzert, *Chem. Umschau*, **31**, 69 (1924).

(4) Böeseken and Ravenswaay, *Rec. trav. chim.*, **44**, 241 (1925); *Verslag. Akad. Wetenschappen, Amsterdam*, **34**, 204 (1925); Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927); Böeseken, Hoogl, Broek and Smit, *ibid.*, **46**, 619 (1927).

(5) Thomas and Thomson, THIS JOURNAL, **56**, 898 (1934).

cal parachor, and the theoretical molar refractivity less exaltation due to conjugation of double bonds between carbon atoms. In calculating the theoretical values, Böeseken's formula for eleostearic acid and the data compiled by Sugden[6] and Smyth,[7] respectively, for parachor and molar refractivity were adopted. In Table III are also given for comparison the data of Böeseken and Ravenswaay, those of Ishio, and those of Toyama and Tsuchiyu for punicic and trichosanic acids, considered as stereoisomers of eleostearic acid.

TABLE II

Acid	P	P'	Diff.
α-Eleostearic	741.0	709.0	32.0
β-Eleostearic	736.9	709.0	27.0

TABLE III

R for α-eleostearic acid	92.36
R for β-eleostearic acid	92.20
R' for above acids	85.47
Böeseken's R for α-acid	93.05
Ishio's value for α-acid	98.62
R for punicic acid	92.4
R for trichosanic acid	92.4

An explanation is desirable for the difference between P and P' since it cannot be accounted for by the conjugation of double bonds which, although having a large influence upon many other physical constants, shows no measurable effect on parachor. Interpretation of these results has to be postponed until further investigation in this Laboratory throws more light on the nature and amount of exaltation in molar refractivity due to conjugated double bonds in general. Nevertheless, the technique of the present procedure has been tested with a sample of purified oleic acid giving the results in Table IV.

TABLE IV

	Molar refractivity of oleic acid	Parachor of oleic acid
Observed value	86.6	731.4
Calculated value	86.4	731.0

Maleic anhydride was suggested by Kaufmann and Baltes[8] for detection and determination of conjugated double bonds in fats and oils. However, it does not seem satisfactory in distinguishing between the presence of two and of three conjugated double bonds. Incidentally, it may be pointed out that the reaction products between maleic anhydride and the alpha and beta eleostearic acids reported by Kaufmann and Baltes were, respectively, the reverse of those reported by Morrel and Samuels[9] and Morrel.[10] As a rule, it is very difficult to obtain clear-cut results from eleostearic acid by chemical methods alone.

Summary

Highly purified specimens of alpha and beta eleostearic acids having melting points higher than previously reported values were prepared, and their molar refractivity and parachor were determined accurately. The molar refractivity of the alpha acid was compared with data from other sources. For the molar refractivity and parachor of the beta acid and the parachor of the alpha acid, no previous data were available. Other physicochemical measurements are being made with both eleostearic acids.

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(6) Sugden, "The Parachor and Valency," Routledge, London, 1930.

(7) Smyth, "Dielectric Constant and Molecular Structure," Reinhold Publishing Corp., New York, N. Y., 1931.

(8) Kaufmann and Baltes, *Fette Seifen*, **43**, 93 (1936).

(9) Morrel and Samuels, *J. Chem. Soc.*, 2251 (1932).

(10) Morrel, *Chemistry & Industry*, **56**, 795 (1937).