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Dilatometric Investigations of Fats. VII. Melting Dilation and Polymorphism of an Alpha and Beta Tung Oil^{1,2}

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DESPITE the large volume of consumption and the multiplicity of application of tung oil there is little reliable information available with respect to its thermal properties. The specific heats of tung oils of unknown history have been reported by two groups of investigators (3, 4), and Ward, *et al.* (7), recently reported data for the heat capacity of domestic tung oil (*Aleurites fordii*). No data have heretofore been reported for the change in volume which accompanies heating of tung oil or with respect to the polymorphism exhibited by this oil.

Data are reported here for the changes in volume occurring during heating and cooling of a specific tung oil, the expansibilities of the alpha and beta forms of the oil in the solid and liquid states, the melting dilation and absolute specific volume of each oil at various temperatures over their ranges of melting, and the interplanar spacings, calculated from x-ray diffraction patterns, for the three crystalline forms of beta tung oil.

Experimental

Oils. The tung oil used in the present investigation was a fresh commercial product, expressed from the nuts of *Aleurites fordii*. A portion of alpha (liquid) tung oil was isomerized to the beta (solid) isomer by adding 0.5% powdered potassium iodide, stirring for 4 hours, and filtering. The oil treated in this manner isomerized and solidified overnight. Spectrophotometric analysis of the original and isomerized oil by the method of O'Connor, *et al.* (5), showed that the alpha oil contained glycerides equivalent to 82.0% alpha, no beta, and 80.6% total eleostearic acid. The beta (isomerized) oil contained glycerides equivalent to 14.9% alpha, 58.0% beta, and 74.0% total eleostearic acid.

Polymorphism. Three polymorphic forms of beta tung oil (7) were observed.

Form I, which had the highest melting point (52.8°C.), was obtained in the present investigation when the beta oil was either melted and allowed to cool for several hours, or when it was solidified and tempered.

Form III was obtained by rapidly cooling the melted beta oil by immersing it in a mixture of acetone and dry ice.

TABLE I
Interplanar Spacings of Isomerized (Beta) Tung Oil

Form I		Form II		Form III	
"d" Spacing	Intensity ^a	"d" Spacing	Intensity ^a	"d" Spacing	Intensity ^a
4.54	F (broad)	4.55	M	4.49	F
4.14	VS	4.19	VS	4.02	VS (broad)
3.81	S	3.92	VS	2.28	F
3.58	M	2.30	F		
3.44	M				
3.23	M				
2.87	M				
2.53	M				
2.27	F				

^a VS = very strong; S = strong; M = medium; F = faint.

Form II was obtained when Form III was melted at 28°C. and allowed to resolidify at the same temperature. The resolidified material (Form II) was observed to melt when placed in a bath held at 44.4°C. or to be transformed without melting to the highest melting modification (Form I) if tempered at about 42-43°C. for a short time.

The transformation of beta tung oil from the lowest melting (Form III) to the highest melting Form I proceeded in the direction of thermodynamic stability and was not reversible in the solid state.

Polymorphism in alpha tung oil was not detected although considerable supercooling was evident to below -38°C., which is the practical limit of the dilatometric method employed.

X-ray diffraction patterns corresponding to Forms I, II, and III were obtained by photographing beta tung oils contained in capillary tubes. The freshly prepared Form III was aligned on the camera mount contained in a large cooler maintained at 0°C., and the mounted sample placed in an insulated box cooled to 0°C. with dry ice. This precaution was necessary to avoid exceeding the transition temperature of Form III during the time it was exposed to the radiation. Forms I and II were photographed satisfactorily at room temperature.

The diffraction photographs were obtained with a General Electric Diffraction X-ray Unit, Model XRD, using CuK_α radiation with a nickel filter (0.0007-inch thick) and a plate distance of approximately 6 centimeters. The "d" spacings of Forms I, II, and III were calculated from the photographs. The spacings and their intensities are recorded in Table I.

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Expansibility. Samples of alpha and beta tung oils were sealed in dilatometers of the gravimetric type (1, 2), using mercury as the confining liquid. The dilatometers containing the beta oil were cooled rapidly in the manner previously found to yield the low-melting Form III. The low-melting form was maintained in some of the dilatometers, and the remaining samples transformed to Form II at 28°C. Form I was obtained by tempering samples of Form II at 42-43°C. The melting points of other samples treated in the same manner were determined to verify the identity of each form.

All samples were slowly cooled to about -45°C., and the determination of their expansibilities were begun at approximately -38°C., and continued to 30°C. for alpha tung oil, and to 60°C. for the beta oil. The expansibilities of the alpha oil and Forms I, II, and III of the beta oil in the solid state, and the alpha oil and Form I of the beta oil in the liquid state were determined. The melting dilations of the alpha oil and of Form I of the beta oil were calculated at the points of half-fusion, 0.1° and 44.6°C., respectively. This method is used for materials in which the melting range is distributed over a considerable temperature interval (2). The melting dilations of Forms II and III of beta tung oil were calculated at their respective transition temperatures, namely, 44.4° and 28.0°C.

Results

Alpha Tung Oil. The initial expansion of the alpha tung oil (0.00059 ml./g./°C.) appeared high, in comparison with the average expansion in the solid state observed with other vegetable oils (2), such as cottonseed (0.00030 ml./g./°C.). The high initial expansion of the alpha oil indicated that melting had begun at a temperature below -38°C., which is the lower limit of the dilatometric method when mercury is used as the confining liquid. In a previously reported calorimetric examination of tung oil, Ward, *et al.* (7) observed that alpha tung oil began to melt at approximately -43°C. The value, 0.00030 ml./g./°C., was therefore used for the expansion of alpha tung oil in the solid state, which gave a calculated melting dilation of 0.058 ml./g. for this form of the oil. Melting of alpha tung oil was complete at 12.8°C. The expansibility of the liquid state was found to be 0.000815 ml./g./°C.

The absolute density of alpha tung oil, determined by the pycnometer method, was 0.9309 g./ml. at 30°C., which value is in the approximate range of linseed-type oils, but is higher than cottonseed and peanut oils, as might be expected because of the greater unsaturation and presence of conjugation in tung oil as compared with the latter oils.

The absolute specific volume of alpha tung oil at each of several temperatures over the range of -38° to 30°C. was calculated from the data for density and expansibility and the resultant values are shown in Table II.

Beta Tung Oil. The expansibilities of the solid states of Forms I, II, and III of beta tung oil were 0.00039, 0.00046, and 0.00047 ml./g./°C., respectively. The first evidence of melting in the most stable form occurred at about -10°C. Forms II and III began to transform at approximately 18° and -10°C., respectively, temperatures which are considerably below the actual transition temperatures of these two materials. Expansion of the liquid state of beta tung oil was 0.00087 ml./g./°C. The calculated melting dilations

TABLE II
Specific Volumes of Alpha and Beta Tung Oil at Various Temperatures

Temp.	Alpha tung oil	Beta tung oil		
		Form I	Form II	Form III
°C.	ml./g.	ml./g.	ml./g.	ml./g.
-38.35	0.9772	0.9708	0.9780	0.9809
-33.20	0.9805	0.9730	0.9804	0.9833
-25.95	0.9869	0.9758	0.9839	0.9865
-22.43	0.9928	0.9772	0.9858	0.9863
-15.18	0.9998	0.9800	0.9894	0.9891
-12.50	1.0019	0.9812	0.9907	0.9896 ^a
- 9.10	1.0022	0.9830	0.9936	0.9904
- 5.50	1.0027	0.9853	0.9976	0.9894
- 0.66	1.0090	0.9887	1.0028	0.9922
+ 1.70	1.0185	0.9905	1.0052	0.9906
4.45	1.0310	0.9920	1.0083	0.9926
7.32	1.0404	0.9941	1.0112	0.9947
10.15	1.0507	0.9961	1.0149	0.9968
12.70	1.0585	0.9985	1.0183	0.9991
15.48	1.0625	1.0020	1.0221	1.0022
17.57	1.0641	1.0047	1.0246 ^a	1.0045
19.86	1.0657	1.0075	1.0266	1.0078
23.50	1.0688	1.0123	1.0225	1.0129
26.90	1.0715	1.0167	1.0250	1.0176
30.00	1.0742	1.0235	1.0292	1.0225
36.90		1.0330	1.0385	1.0335
40.10		1.0366	1.0445	1.0384
44.70		1.0455	1.0557	1.0476
48.90		1.0543	1.0685	1.0593
51.35		1.0659	1.0835	1.0716
55.00		1.0922	1.0922	1.0922
59.95		1.0966	1.0965	1.0966

^a Transformation to highest-melting form began.

of Forms I, II, and III were 0.078, 0.067, and 0.061 ml./g., respectively.

The absolute density of beta tung oil by the pycnometer method was 0.9156 g./ml. at 55°C. From the data for density and expansibility the specific volumes of the samples over the temperature range of -38°C. to 60°C. were calculated with the results shown in Table II.

Reference to Figure 1, in which the specific volumes of the three forms of the beta oil are plotted as functions of temperature, shows that Forms II and III transformed in the dilatometer during the determination of their expansibilities, as is evident by the contraction which occurred in both products. Melting of original Form I, as well as of the transformed samples, was complete at 52.8°C.

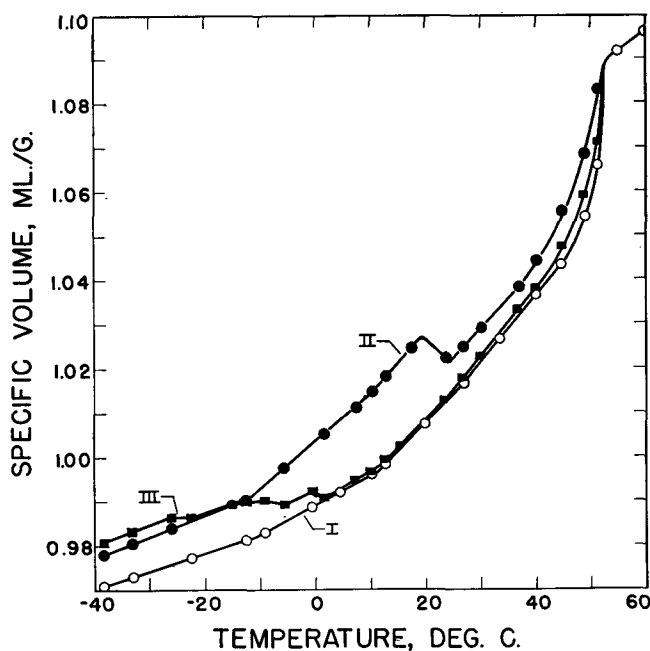


FIG. 1. Specific volume as a function of temperature of Forms I, II, and III of beta tung oil.

Solids-Liquid Ratio. The contents of solid and liquid phases of the alpha tung oil and Form I of beta tung oil were calculated (6) over the ranges of temperature employed. From the results, which are shown graphically in Figure 2, it is evident that the amount

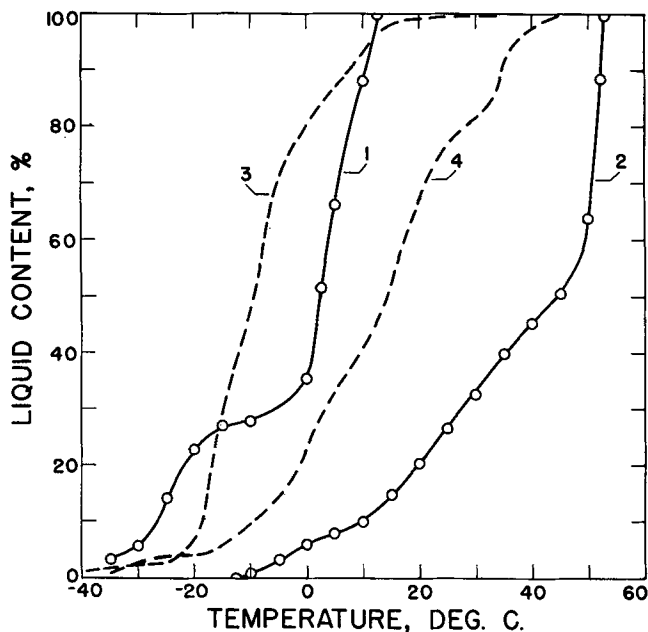


FIG. 2. Percentage of glycerides in the liquid state over the melting range: (1) alpha tung oil; (2) beta tung oil; (3) cottonseed oil; (4) hydrogenated cottonseed oil (I.V. 59.5).

of glycerides in the liquid state increased substantially during the final 10 degrees of the melting range. For comparison, the solid-liquid composition of cottonseed oil (6) is shown in the same figure. A similarly rapid increase in the content of liquid during the latter part of the melting range was also observed by Ward, *et al.* (7), during a calorimetric examination of tung oil.

Volume Change on Isomerization. The volume change accompanying the isomerization of alpha to beta tung oil at a constant temperature of 30°C. was determined dilatometrically, both in the dark and under ordinary laboratory illumination. Alpha tung oil was stirred with 0.5% powdered potassium iodide for one hour, filtered, and immediately placed in a series of dilatometers, some of which were coated with black paint to exclude light. The oil confined in the dilatometers at the beginning (zero volume change) of the experiment had a glyceride composition equivalent to 74.2% alpha, 3.4% beta, and 78.3% eleostearic acid. The volumes of the various samples, calculated at intervals until approximate equilibrium was reached (3,189 hours), are shown graphically in Figure 3. The tung oil in the clear glass dilatometers isomerized rapidly with a decrease in volume of 4% whereas the samples in the blackened dilatometers isomerized more slowly and reached approximate equilibrium with a decrease in volume of only about 2.4%. The glyceride composition of the oil in the clear dilatometers after isomerization was equivalent to 15.5% alpha, 58.1% beta, and 76.4% total eleostearic acid. The calculated

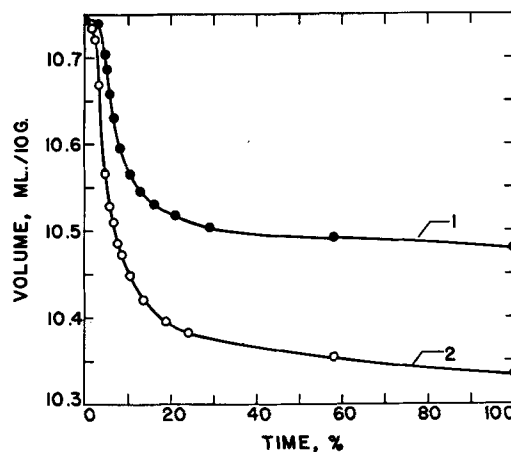


FIG. 3. Change in volume during isomerization of alpha to beta tung oil: (1) dark; (2) light.

increase in density of tung oil in isomerizing from the alpha (0.9309) to the beta (0.9730) form was 0.0421 g./ml., at 30°C.

Summary

Three polymorphic forms of beta tung oil have been recognized and differentiated on the bases of their melting points and x-ray diffraction spacings. These modifications, which melt at 52.8°, 44.4°, and 28.0°C., have been designated as Forms I, II, and III, respectively. Polymorphism was not observed in alpha tung oil.

The expansibilities of alpha tung oil and the three original polymorphic modifications of beta tung oil have been determined in both the solid and liquid states, and the melting dilation of each substance was calculated. The absolute densities of the alpha and beta oils were determined, and the absolute specific volumes over the ranges of melting of all these substances were calculated and reduced to graphic form.

Forms II and III of the beta oil irreversibly transformed to Form I with contraction in volume during dilatometric examination.

The contents of solid and liquid phases of alpha and beta tung oils were calculated over the ranges of melting of these oils. The amount of glycerides in the liquid state was found to increase substantially during the final 10 degrees of the melting range.

The isomerization of alpha to beta tung oil under ordinary laboratory illumination was found to be accompanied by a decrease in volume of about 4% and an increase in density. Isomerization in the absence of light reached approximate equilibrium with a decrease in volume of only about 60% of that occurring in the presence of light.

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