tained at 185°F. The moisture content of the meats was adjusted in the different runs from 12.3% to 11.7% to 11.0%. The data in Table II show the effect of this moisture difference on the free gossypol and soluble protein contents of the cooked meats.

It is concluded therefore that an extension of the cooking time, in itself, has very little effect upon the reduction of the free gossypol in a finished meal or upon the soluble protein content of a finished meal. Since the data do indicate however that the moisture content of the meats during the cooking stage is critical, this factor is being studied further in order to arrive at the optimum value during the cooking process.

TABLE II

Effect of Moisture During the Cooking of Cottonseed Meats on Free Gossypol Destruction

Moisture contents, %	12.3	11.7	11.0
Free gossypol content of cooked meats, %	0.09	0.12	0.15
Soluble protein value of cooked meats, %	73.5	73.8	80.9
Free gossypol content of finished meal, %	0.04	......	0.06

Acknowledgment

We wish to express our appreciation to J. W. Simmons, Simmons Cotton Oil Company, and P. A. Norris Jr., Kimbell-Norris Oil Mills, for permitting us to obtain and use the data presented in this paper.

REFERENCES

1. Dunning, J. W., Oil Mill Gazetteer, *55*, 20-21 (1950).
2. *Ibid.*, *56*, 64-68 (1951).

[Received on October 16, 1951]

Thermal Properties of Fats and Oils. VIII. Specific Heats, Heats of Fusion, and Entropy of Alpha and Beta Tung Oils[1]

T. L. WARD, W. S. SINGLETON, and R. W. PLANCK, Southern Regional Research Laboratory,[2]
New Orleans, Louisiana

DATA found in the literature for the thermal properties of tung oil include the specific heats of China wood oil over a temperature range of 70° to 155°C. (6) and the specific heats of a tung oil of unknown origin over a temperature range of 0° to 200°C. (3). No other thermal constants could be found. The specific heats of the alpha or liquid tung oil reported in this communication are believed to be the first available for the oil expressed from the nuts of *Aleurites fordii.*

Data are also reported for the specific heats in both solid and liquid states, heats of fusion, entropies at 298.16°K., and heat content and the percentage of liquid glycerides present at any temperature over the complete range of melting for both the alpha (liquid) and beta (solid) forms of tung oil of known origin.

Experimental

Oils. The liquid or alpha tung oil used in this investigation was screw-pressed from the kernels of fruit from the 1949 crop. A portion of this oil was isomerized in the presence of light by the addition of one part of a saturated solution of potassium iodide to 1,000 parts of oil. The mixture was stirred for 15 minutes, filtered, and stored for 5 days, all operations under nitrogen. The isomerized oil was melted before use, put into the calorimeter under nitrogen, and the apparatus sealed.

The alpha tung oil used in the tests contained the equivalent of 82.0% of α-eleostearic acid and 0.0% of β-eleostearic acid when examined spectrophotometrically by the method of O'Connor *et al.* (7). The beta oil contained 10.8% of α-eleostearic acid and 61.4% of β-eleostearic acid. Examination for total eleostearic acid (7) showed the alpha oil contained 80.6% and the beta oil contained 74.6%.

Comparison of the spectrophotometric analyses of the alpha and beta oils before and after calorimetric examination indicated that no change had occurred in the respective contents of α- and β-eleostearic acids. Upon removal from the calorimeter after an interval of about three months, the isomerized sample contained approximately 0.3% by weight of a gel-like material, which was probably oxidized oil.

Apparatus and Method. The calorimetric apparatus and method used in the present investigation have been described in an earlier report (2). Briefly, a weighed sample of oil, weight corrected to vacuum, was sealed in a copper calorimeter, which was enclosed in a semi-adiabatic system, and the calorimeter and sample were brought to the proper temperature level. Liquid nitrogen was used to obtain temperatures below 193°K.(—80°C.), and solid carbon dioxide was used for temperatures from 193° to 273.16°K.(—80° to 0°C.). Melting ice or a constant temperature bath was used for higher temperatures. To obtain the calorimetric data a measured amount of heat was put into the sample by means of an electric current flowing through a resistance, and the resulting changes in temperature were measured potentiometrically. The accuracy of the results obtained is believed to be within 1%.

The thermochemical calorie, which is equal to 4.1840 absolute joules, was used in all calculations.

Prior to the thermal investigation it was found that beta tung oil melted at three different temperatures; each melting point is dependent upon the rate of cooling of the liquid oil. Slow cooling of the melt in capillary tubes produced a solid with a melting point of 52.8°C. Such cooling was attended by considerable

---

[1] A report of a study made under the Research and Marketing Act of 1946.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

supercooling; the melt remained in the liquid state until approximately 10° below the melting point. Moderate and very rapid cooling in capillary tubes produced solids which melted at 44° and 28°C., respectively, when plunged into a constant temperature bath maintained at these temperatures (4). Furthermore the rapidly cooled form of the beta oil, when melted in a constant temperature bath at 28°C., immediately resolidified and subsequently melted at 44° C. These different melting points of beta tung oil, obtained after solidification at different rates of cooling, indicate the possibility of polymorphic modifications of a major constituent of isomerized tung oil. The corresponding oils tentatively have been designated as Forms I, II, and III, in descending order of their melting points. Attempts to induce variable melting points of alpha tung oil were unsuccessful.

The alpha and beta tung oils were slowly solidified in the calorimeter over a period of several days whenever the stable forms of the respective oils were desired. To induce the lowest melting form of beta tung oil in the calorimeter, the melted sample was quickly chilled by immersing the calorimeter and contents in liquid nitrogen.

Results and Discussion

Specific Heat. The specific heats of the slowly cooled alpha and beta tung oils were determined and the values used to develop equations for calculating the specific heats of these materials in both the solid and liquid states. These equations relate specific heat, C_p, in calories per gram degree, to any temperature, t, in °C.:

Alpha tung oil
Solid state (—184° to —43°C.) $C_p = 0.404 + 0.001\,t$
Liquid state (9° to 80°C.) $C_p = 0.463 + 0.0011\,t$

Beta tung oil
Solid state (—178° to 27°C.) $C_p = 0.390 + 0.0013\,t$
Liquid state (67° to 87° C.) $C_p = 0.489 + 0.00016\,t$

The observed specific heats, together with the deviations of the calculated from the observed values, are given in Table I.

TABLE I

Specific Heats of Alpha and Beta Tung Oils

Alpha			Beta		
Temperature	C_p observed	Deviation of calculated from observed	Temperature	C_p observed	Deviation of calculated from observed
°K.	*cals./g.*	*cals./g.*	*°K.*	*cals./g.*	*cals./g.*
	Solid	Solid		Solid	Solid
93.16	0.222	+0.002	100.00	0.165	0.000
123.16	0.252	+0.002	125.00	0.198	—0.001
148.16	0.279	0.000	150.00	0.230	0.000
173.16	0.304	0.000	175.00	0.261	+0.001
198.16	0.329	0.000	200.00	0.293	+0.002
223.16	0.354	0.000	225.00	0.325	+0.002
	Liquid	Liquid		Liquid	Liquid
283.16	0.474	0.000	325.00	0.495	+0.002
298.16	0.491	0.000	350.00	0.501	0.000
323.16	0.519	—0.001			
348.16	0.547	—0.001			

The specific heat-fusion data for both alpha and beta tung oils indicate that melting occurred over two principal temperature ranges. One component of the alpha form of the oil began melting at approximately 230°K.(—43°C.), and at 263°K.(—10°C.) the rate of solid- to liquid-phase transformation increased. Most of the oil seemed to be melted at 276°K.(+3°C.) although some crystals persisted possibly as high as 310° K.(37°C.). The isomerized (beta) oil began melting at 255°K.(—18°C.), and at 300°K.(27°C.) the solid- to liquid-phase rate increased. Approximately the same amount of heat was required and was supplied at a constant rate in each of the stages of melting of the alpha oil whereas the beta oil required most of the heat energy in the final stage of melting.

The determined specific heat of the alpha tung oil is within approximately 4% of that reported by Long *et al.* (6), but is considerably higher than that reported by Clark and co-workers (3). Since both groups used imported oils, it is quite possible that the samples differed and also were unlike the present oil, which was of domestic origin.

Rapid cooling of the isomerized tung oil contained in the calorimeter apparently induced the formation of a low-melting polymorphic modification similar to that obtained by cooling in a capillary tube since the specific heat of the oil cooled in this manner was approximately 0.042 cals./g./°C. higher than that of the tempered sample, both in the solid state. The slopes of the curves representing specific heat as a function of temperature for the tempered and rapidly cooled samples, both completely solid, were the same.

Rapid cooling of the alpha form of tung oil did not result in any discernible polymorphic modification, nor was the specific heat of a sample cooled in this manner different from that of the tempered alpha form of the oil.

Heat of Fusion. The heats of fusion of the tempered alpha and beta tung oils were calculated from data obtained in duplicate experiments to be 21.02 and 16.12 cals./g., respectively. The points of half-fusion were taken to be 273.2°K.(0.1°C.) for the alpha form of the oil and 323.3°K.(50.2°C.) for the beta form of the oil.

The heat of fusion of the alpha tung oil falls between the values previously reported for peanut and cottonseed oils (8, 10) and is considerably higher than that of the isomerized (beta) oil. Of the few cis and trans isomers for which heats of fusion have been reported, the trans isomer has the greater value; however no data have been reported for compounds containing a conjugated polyethenoid structure similar to that occurring in tung oil. It is generally agreed that the trans configuration of eleostearic acid predominates in beta tung oil, and it would therefore

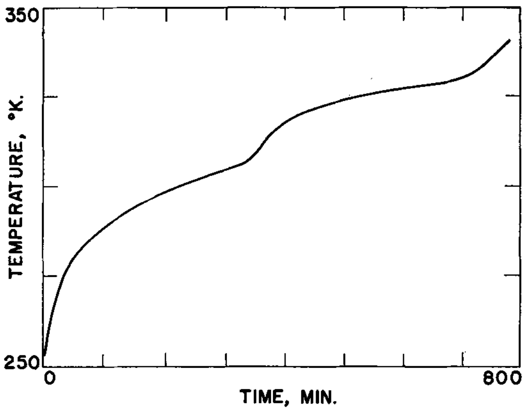

FIG. 1. Time-temperature fusion curve of beta tung oil showing transformation of rapidly cooled sample.

be expected to have a higher heat of fusion than the alpha form of the oil.

The heat of fusion of rapidly cooled beta tung oil could not be accurately calculated because of its slow transformation into a higher melting form during heating over a temperature range below the melting point (capillary method) of the low melting form. This transformation is clearly evident in Figure 1, which represents the time-temperature relationship at constant heat input during fusion of the rapidly cooled beta tung oil.

The intermediate form of beta tung oil is not represented in the calorimetric curve because of the continuous nature of the heating.

Heat Content and Percentage of Liquid Glycerides. Data for the heat content and the estimated percentage of liquid glycerides present in the oils at various temperatures, calculated by the method of Bailey and Oliver (1), are presented in Table II.

TABLE II

Proportions of Liquid Glycerides at Different Temperatures in Alpha and Beta Tung Oils

Alpha oil			Beta oil		
Temperature	Heat content, accumulated	Liquid phase, accumulated and adjusted to 100% total	Temperature	Heat content, accumulated	Liquid phase, accumulated and adjusted to 100% total
°K.	*cals./g.*	%	*°K.*	*cals./g.*	%
248.310	10.08	....	304.536	1.04	0.42
251.129	11.20	0.29	310.891	4.78	3.26
256.171	13.44	1.53	315.877	8.32	7.36
261.892	16.80	6.22	317.544	9.98	10.29
266.576	20.72	14.54	318.915	11.65	13.72
271.203	26.32	29.13	320.324	13.73	18.45
274.343	31.92	46.44	323.287	19.97	34.59
276.921	39.20	71.68	325.787	28.29	58.37
278.001	43.12	85.64	327.324	34.36	79.51
278.827	44.80	90.88	328.312	38.48	88.33
279.540	45.64	92.85	330.079	40.35	91.68
280.932	47.32	96.87	331.999	41.60	92.70
282.198	48.72	100.00	334.087	43.06	94.11
			338.290	46.38	98.17
			339.260	47.42	100.00

At temperatures below the melting point the heat energy supplied to the alpha form of the oil was comparable to that supplied to peanut oil hydrogenated to an iodine value of about 60 (10) although the liquid content of the former greatly exceeded that of the latter. The isomerized (beta) oil was completely melted at approximately the same temperature as a sample of cottonseed oil hydrogenated to an iodine value of 60 (1). Melting in tung oil occurs over a much shorter temperature interval than it does in either cottonseed or peanut oils, which is attributable to the high percentage (80%) of homotriglyceride (eleostearin) in tung oils. For the same reason the rate of solid- to liquid-phase transformation of both the alpha and beta forms of tung oil increased sharply in approximately the final 10° of the melting interval compared to cottonseed and peanut oils.

Entropy. The molal entropies of the two tung oils were calculated from the specific heat data, using the extrapolation method of Kelly, Parks, and Huffman (5, 9) and revised data for standard substances. Expressed as molal entropy units, the values at 298.16° K. were calculated to be 252.15 and 231.04 for the alpha and beta tung oils, respectively.

Summary

Beta tung oil belongs to that group of substances which are capable of existing in more than one crystalline form, each of which has a distinct melting point. Three different melting points of the beta tung oil were observed, each dependent upon the rate of cooling. Forms I, II, and III have been used to distinguish beta tung oil melting at 52.8°, 44°, and 28° C., respectively.

Equations were developed to express in cals./g./°C. the specific heats of the stable forms of tung oil.

Alpha tung oil
Solid state (—184° to —43°C.) $C_p = 0.404 + 0.001\,t$
Liquid state (9° to 80°C.) $C_p = 0.463 + 0.0011\,t$

Beta tung oil
Solid state (—178° to 27°C.) $C_p = 0.390 + 0.0013\,t$
Liquid state (67° to 87° C.) $C_p = 0.489 + 0.00016\,t$

The specific heat of beta tung oil was found to be higher when the sample was rapidly cooled than when it was slowly cooled or tempered.

The heat of fusion of the beta form of tung oil was calculated to be 16.12 cals./g., and for the alpha form to be 21.02 cals./g. Entropies at 298.16°K. were 231.04 and 252.15 entropy units for the two forms of these oils, respectively.

The liquid glycerides present at any temperature in the melting range were estimated from the data for the heat contents of the oils. The rate of liquid-phase formation at constant heat input of both alpha and beta tung oils, unlike that of cottonseed and peanut oils, increased sharply during the final 10° of the interval owing to the greater homogeneity of the glycerides of the former.

REFERENCES

1. Bailey, A. E., and Oliver, G. D., Oil and Soap, *21*, 300-302 (1944).
2. Bailey, A. E., Todd, S. S., Singleton, W. S., and Oliver, G. D., Oil and Soap, *21*, 293-297 (1944).
3. Clark, Paul E., Waldeland, C. R., and Cross, Robert P., Ind. Eng. Chem., *38*, 350-353 (1946).
4. Ferguson, R. H., and Lutton, E. S., Chem. Revs., *28*, 357-364 (1941).
5. Kelly, K. K., Parks, G. S., and Huffman, H. M., J. Phys. Chem., *33*, 1802-1805 (1929).
6. Long, G. S., Reynolds, J. B., and Napravnik, Joseph, Ind. Eng. Chem., *26*, 864-868 (1934).
7. O'Connor, R. T., Heinzelman, D. C., McKinney, R. S., and Pack, F. C., J. Am. Oil Chem. Soc., *24*, 212-216 (1947).
8. Oliver, G. D., Singleton, W. S., Todd, S. S., and Bailey, A. E., Oil and Soap, *21*, 297-300 (1944).
9. Parks, G. S., and Huffman, H. M., private communication.
10. Ward, T. L., and Singleton, W. S., J. Am. Oil Chem. Soc., *27*, 423-426 (1950).

[Received on October 18, 1951]