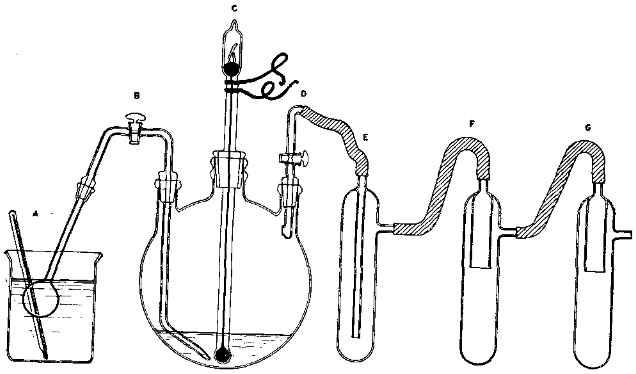

FIG. 1. Laboratory deodorizer.

The temperature of the oil or fat in the flask is controlled by means of the "metastatic type" mercury thermoregulator (C). This differs from the usual mercury thermoregulator by having a ground glass joint and a *spherical* mercury reservoir. The spherical reservoir permits complete immersion of the bulb even with small amounts of material although this type of bulb, having a minimum surface area, is a little less sensitive than a cylindrical bulb. The regulator was made according to specification by the Philadelphia Thermometer Company, and has a 24/40 joint and a bulb about 2 cm. in diameter which will pass through the female portion of a 24/40 joint. A reducing bushing, 29/42 to 24/40, is used in the center neck of the flask, and it is convenient to remove and insert the thermoregulator *plus* the bushing since this minimizes strain on the stem of the regulator. The thermoregulator is connected to the lower heating element of the hemispherical Glas-Col mantle through a relay, and the amount of current passing into the element is further governed by a Variac.

The flask outlet tube (D) carries a 1 mm. stopcock to permit isolation of the flask under vacuum and leads into a series of traps (E, F, G) joined to each other by pressure tubing. Trap (E), which catches readily condensable material, is immersed in ice and salt and has a narrow center tube reaching almost to the bottom of the trap. Traps (F) and (G) are held in dry ice and liquid air, respectively, and have short, wide center tubes that will not freeze up readily. They prevent water vapor from passing into the vacuum pump that joins to trap (G) to evacuate the entire system.

The vacuum in the flask can be broken, after cooling the contents, without aerating the fat by rotating the flask on its side until the inlet tube (B) is above the surface of the fat and then admitting air or inert gas through the inlet tube after removal of the water bulb (A) and the traps. This procedure has been found preferable to breaking the vacuum at (D) since small amounts of condensate in the outlet tube might be carried back into the flask.

The details of construction and operation may readily be varied to suit individual requirements. For example, the inlet tube (B) can be provided with a side arm to permit addition of materials during deodorization.

With this deodorization apparatus, using one hour's treatment at 240°C., bland oils and shortenings of low free fatty acid content (less than 0.05%, as oleic acid) have been consistently obtained.

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Thermal Properties of Fats and Oils. VII. Hydrogenated and Unhydrogenated Peanut Oils[1]

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AVAILABLE data on the heat capacity of vegetable oils (1, 2, 3, 4,) do not include any information on peanut oils. It is believed that the present communication is the first report of the calorimetric examination of both hydrogenated and unhydrogenated peanut oils over their complete range of melting. The temperature ranges investigated were, for the hydrogenated oil, 84° to 350°K.(−189.16° to +76.84°C.), and for the unhydrogenated oil, 110° to 330°K.(−163.16° to +56.84°C.). The specific heats of the oils in both the liquid and solid states were determined, and heats of fusion or latent heats of the oils calculated from the specific heat data. In addition, the relative amounts of solid and liquid glycerides in both hydrogenated and unhydrogenated peanut oils at various temperatures over their entire melting ranges have been estimated from the calorimetric data.

The apparatus used and the general procedure followed in making the calorimetric measurements and calculating the specific heats and heats of fusion have been described in a previous publication (5). The method of Bailey, *et al.*, (6) was used in calculating the amounts of solid glycerides melting over specific temperature intervals.

Materials

The peanut oil used in these experiments was refined, bleached, deodorized, and a portion of it hydrogenated under selective conditions for linoleic and oleic acid. The characteristics of the two oils determined by the Official Methods of Analysis of the American Oil Chemists' Society (7), are given in Table 1. Spectrophotometric examination of the hydrogenated oil indicated the presence of 0.4% of linoleic acid.

Specific Heats

The specific heats of the hydrogenated and unhydrogenated peanut oils in the solid and liquid states are given in Table II. Solution of simultaneous equa-

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[1] Presented at the 41st annual meeting of the American Oil Chemists' Society, Atlanta, Georgia, May 1-3, 1950.

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

TABLE I

Characteristics of Hydrogenated and Unhydrogenated Peanut Oil

Characteristic	Peanut oil	
	Unhydrogenated	Hydrogenated
Iodine value	94.0	62.5
Thiocyanogen value	72.6	61.8
Saponification value	191.4	......
Free fatty acids, as oleic, percentage	0.04	0.08
Composition of fatty acids, percentage[a]		
Saturated	17.2	27.76
Oleic	56.6	71.8
Linoleic	26.2	0.44

[a] Compositions of the oils were calculated on the basis of thiocyanogen values of pure oleic acid as 89.3 and for linoleic acid as 96.7.

tions using the data from Table II yielded the following equations for expressing specific heat (*Cp*, calories per gram[3] per degree) in terms of the temperature (*t* degrees C.):

Unhydrogenated peanut oil:

For the solid state (—163.16° to —33.16°C.):
$Cp = 0.5042 + 0.00195t$
For the liquid state (+26.84° to +56.84°C.):
$Cp = 0.4914 + 0.0004t$

Hydrogenated peanut oil:

For the solid state (—189.16° to —43.16°C.):
$Cp = 0.4418 + 0.00159t$
For the liquid state (+46.84° to +76.84°C.):
$Cp = 0.4715 + 0.00117t$

Deviations of the observed specific heats from the values calculated by means of these equations are included in Table II.

TABLE II

Specific Heats of Hydrogenated and Unhydrogenated Peanut Oils

Hydrogenated			Unhydrogenated		
Temp., °K.	Cp, cals./g.	Deviation of obs. from calc. values	Temp., °K.	Cp, cals./g.	Deviation of obs. from calc. values
		Solid			
100	0.1665	0	125	0.2150	+0.0005
140	0.2303	—0.0002	150	0.2645	—0.0003
170	0.2777	+0.0001	175	0.3125	+0.0005
200	0.3255	0	200	0.3615	+0.0002
230	0.3732	0	225	0.4105	0
		Liquid			
320	0.5262	+0.0001	300	0.5020	+0.0001
330	0.5380	0	325	0.5125	—0.0004
340	0.5500	—0.0003	......	....	....
350	0.5612	+0.0002	......	....	....

A comparison of the specific heats of hydrogenated and unhydrogenated peanut and cottonseed oils (4) indicates that peanut oil has a higher specific heat than the corresponding cottonseed oil, in both solid and liquid states, when compared at the same temperatures. For both peanut and cottonseed oils the specific heats of the unhydrogenated oils were found to be less than that of the hydrogenated oils in the liquid state whereas in the solid state the reverse is true.

Heats of Fusion

The heat of fusion of the unhydrogenated peanut oil was found by calculation to be 21.7 calories per gram. Melting was first detected at 233.1°K.(—40.0° C.), and was complete at 291.3°K.(+18.2°C.). The point of half-fusion of the oil was taken as 266.1°K. (—7.0°C.).

The heat of fusion of the hydrogenated peanut oil was found by calculation to be 24.7 calories per gram. Melting was first detected at 246.24°K.(—26.86°C.) and persisted up to 311.99°K.(38.89°C.). The point of half-fusion was taken as 286.71°K.(13.61°C.).

Since the solidification of each oil was carried out very slowly, over a period of several days, it was assumed that both the hydrogenated and unhydrogenated peanut oils were in a relatively stable crystalline form at the beginning of fusion determinations.

While the value of 21.7 cals./g. for the heat of fusion of the unhydrogenated peanut oil was only slightly higher than the corresponding value of 20.6 cals./g. previously reported (4) for unhydrogenated cottonseed oil, the heat of fusion of hydrogenated peanut oil, 24.7 cals./g., was less than the reported value of 27.4 cals./g. for hydrogenated cottonseed oil. However the iodine values of the hydrogenated cottonseed and peanut oils were 59.5 and 62.5, respectively, and the heat of fusion of the hydrogenated cottonseed oil consequently would be expected to be slightly higher than that of the hydrogenated peanut oil although other factors may be involved.

Heat Contents and Liquid-Solid Composition

Experimental values for the heat contents of the hydrogenated and unhydrogenated peanut oils as functions of temperature are shown graphically in Figure 1. Each point on the curves represents the heat content at a state of equilibrium between the liquid and solid phases present at that temperature. Since the heat content at any temperature represents the combined heat of fusion and specific heat, the amount of liquid glycerides present at any temperature could be calculated by the method of Bailey and Oliver (6). The latter workers assumed uniform melting over small intervals of temperature, and also that there were no substantial differences in the heats of fusion

TABLE III

Proportions of Solid and Liquid Glycerides at Different Temperatures in Hydrogenated Peanut Oil

Temp., °K.	Heat content, accumulated, cal./g.	Distribution of heat content in the interval		Liquid phase accumulated and adjusted to 100% total
		To sensible heat, cal./g.	To latent heat, cal./g.	
210.10	....	....	....	0
221.52	4.006	4.006	0	0
222.20	4.226	.245	0	0
225.57	5.325	1.225	0	0
232.10	7.522	2.425	0	0
238.89	9.939	2.594	0	0
242.40	11.258	1.370	0	0
246.28	12.796	1.537	.001	.004
252.76	15.433	2.620	.017	.073
256.92	17.191	1.717	.041	.238
262.57	19.828	2.376	.261	1.29
265.55	21.586	1.274	.484	3.24
267.21	22.905	0.719	.600	5.66
270.61	25.981	1.479	1.597	12.10
272.88	28.618	0.998	1.639	18.71
276.51	31.695	1.613	1.464	24.61
279.45	34.771	1.322	1.754	31.68
281.19	36.529	0.789	0.969	35.59
283.64	39.166	1.119	1.518	41.71
286.12	42.023	1.142	1.715	48.62
289.29	45.319	1.474	1.822	55.97
290.27	46.418	0.459	0.640	58.55
291.79	47.956	0.715	0.823	61.87
294.88	50.593	1.465	1.172	66.60
296.19	51.472	0.626	.253	67.62
298.69	54.109	1.202	1.436	73.41
300.94	56.746	1.090	1.547	79.65
303.61	60.262	1.303	2.213	88.57
304.51	61.361	0.442	0.657	91.22
306.11	62.899	0.789	0.749	94.24
307.07	63.778	0.475	0.404	95.87
311.99	67.294	2.491	1.025	100.00

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[3] The factor 1/4.1833 was used to convert international joules to calories.

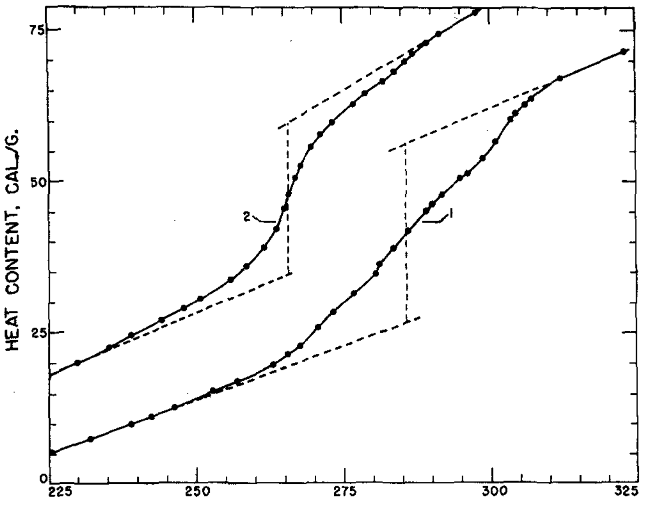

FIG. 1. Heat contents of hydrogenated and unhydrogenated peanut oils: (1) hydrogenated; (2) unhydrogenated.

of glycerides melting in the oils at different temperatures. These same assumptions were considered to be valid in the case of peanut oil.

The calculated compositions of the hydrogenated and unhydrogenated peanut oils at different temperatures, in terms of the amounts of solid and liquid glycerides present in the sample, are shown in Tables III and IV. A comparison of the accumulated heat contents of unhydrogenated cottonseed oil, previously reported (6), with the values calculated for unhydrogenated peanut oil indicates that in the temperature range in which the liquid phases of both oils are predominant, the accumulated heat content of the peanut oil was greater than that of the cottonseed oil at identical temperatures. This would indicate a higher content of liquid phase in peanut oil than in cottonseed oil at the same temperatures, or conversely, a greater content of solid glycerides present in cottonseed oil.

TABLE IV

Proportions of Solid and Liquid Glycerides at Different Temperatures in Unhydrogenated Peanut Oil

Temp., °K.	Heat content, accumulated, cal./g.	Distribution of heat content in the interval		Liquid phase, accumulated and adjusted to 100% total
		To sensible heat, cal./g.	To latent heat, cal./g.	
175.10	....	......	......	......
190.10	4.92	4.92	0	0
210.10	12.16	7.24	0	0
220.10	16.07	3.91	0	0
230.10	20.18	4.11	0	0
235.18	22.33	2.15	0	0
235.30	22.582	0.05	0.20	0.81
239.07	24.598	1.64	0.38	2.34
244.11	27.118	2.23	0.29	3.51
247.94	29.134	1.73	0.29	4.68
250.66	30.646	1.25	0.26	5.73
255.79	33.922	2.38	0.90	9.36
258.64	36.190	1.35	0.92	13.07
261.65	39.214	1.44	1.58	19.44
263.64	42.238	0.96	2.06	27.75
265.02	45.766	0.67	2.86	39.28
265.75	48.034	0.36	1.91	47.00
266.86	50.806	0.55	2.22	55.96
267.85	52.822	0.49	1.53	62.12
269.64	55.846	0.89	2.13	70.72
271.08	57.862	0.72	1.30	75.96
273.05	59.878	0.99	1.03	80.12
276.86	62.902	1.94	1.08	84.48
278.88	64.414	1.04	0.47	86.38
281.84	66.682	1.53	0.74	89.37
283.67	68.194	0.96	0.55	91.59
285.63	69.958	1.03	0.73	94.54
286.98	71.218	0.72	0.54	96.72
289.28	72.982	1.25	0.51	98.78
291.42	74.494	1.20	0.31	100.00
300.10	79.544	5.05	0.00	100.00

The composition of liquid-solid glycerides in hydrogenated and unhydrogenated peanut oils, and the micropenetration values of the hydrogenated sample determined by the method of Feuge and Bailey (8), are plotted as a function of temperature in Figure 2. From this figure, the graphical determination of the correlation between the contents of solid glycerides and micropenetration values of the hydrogenated peanut oil were determined, with the results shown in Table V.

TABLE V

Relationship Between the Content of Solid Glycerides and Micropenetration Values for Progressively Hydrogenated Peanut Oil

Solid glycerides, percentage	Micropenetrations, mm./10
45.9	20
38.9	30
35.5	40
34.1	50
33.3	60
32.8	70
32.3	80
31.1	100
26.9	125
22.8	150
18.0	200
11.5	250
8.2	300

Effect of Hydrogenation

The effects of hydrogenation on the content of solid glycerides at ordinary temperatures were calculated for progressively hydrogenated peanut oil on the basis of the present data and previously published micropenetration values (8). The results are shown in Figure 3. It will be seen that a reduction of the iodine value of peanut oil by 1 unit produces an increase in the content of solid glycerides of approximately 1 to 2%. This increase is approximately twice as large as that occurring in cottonseed oil hydrogenated in the same manner, probably due to original compositions.

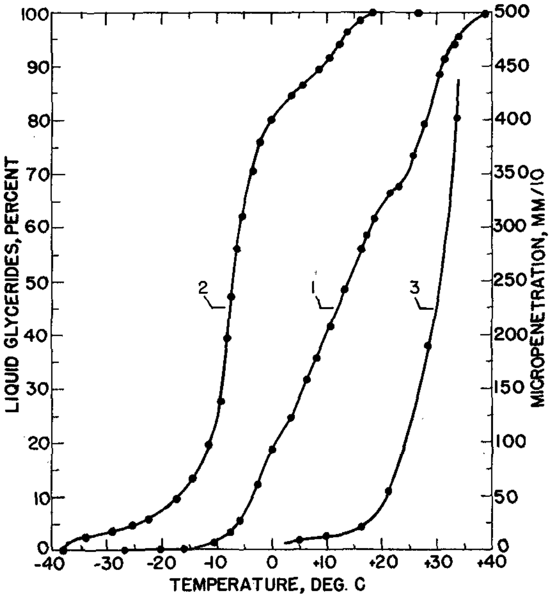

FIG. 2. Content of liquid glycerides of hydrogenated and unhydrogenated peanut oils, and micropenetration values of the hydrogenated oil as a function of temperature: (1) hydrogenated; (2) unhydrogenated; (3) micropenetration values.

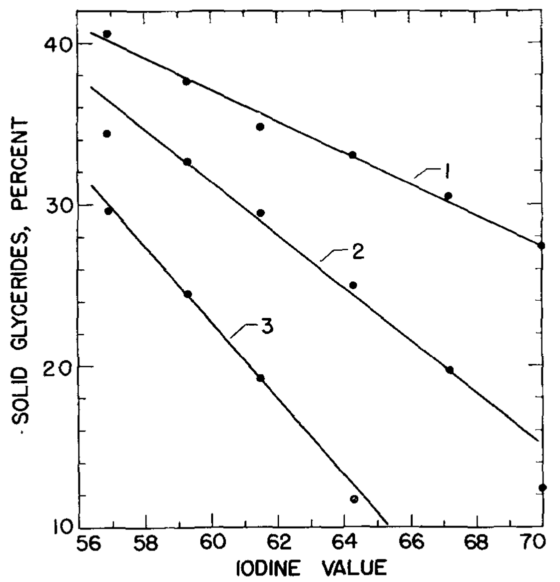

FIG. 3. Effect of hydrogenation on the content of solid glycerides of peanut oil at different temperatures: (1) 20°C.; (2) 25°C.; (3) 30°C.

Summary

1. The heat contents of hydrogenated and unhydrogenated peanut oils have been measured over a temperature range within which the glycerides of the oils changed from a completely solid state to a completely liquid one.

2. The specific heats of the oils in both solid and liquid states have been determined, and the heats of fusion have been calculated to be 21.7 cals./g. and 24.7 cals./g. for unhydrogenated and hydrogenated peanut oils, respectively. Equations were developed for expressing the specific heats of these oils (Cp, cals./g.), in terms of temperature (degrees C.):

Unhydrogenated, solid state (—163.16° to —33.16° C.): $Cp = 0.5042 + 0.00195t$

Unhydrogenated, liquid state (26.84° to 56.84°C.): $Cp = 0.4914 + 0.0004t$

Hydrogenated, solid state (—189.16° to —43.16° C.): $Cp = 0.4418 + 0.00159t$

Hydrogenated, liquid state (46.84° to 76.84°C.): $Cp = 0.4715 + 0.00117t$

3. The relative amounts of solid and liquid glycerides in hydrogenated and unhydrogenated peanut oils at different temperatures over the melting ranges of the respective oils have been estimated from calorimetric data.

4. The relationship between the content of solid glycerides in hydrogenated peanut oil and consistency, as determined by micropenetrations, has been established.

5. From previous determination of the micropenetration of hydrogenated peanut oils and present data, the correlation between the content of solid glycerides and the iodine values of progressively hydrogenated peanut oils has been established. Within the plastic range it is estimated that the reduction of iodine value by 1 unit increases the content of solid glycerides of progressively hydrogenated peanut oil by approximately 2%.

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ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

COMPOSITION OF THE SEED OIL OF *Xanthium riparium*. J. Tischer and A. Patzenhauer. *Fette u. Seifen* **52**, 137-40(1950). The dried seeds of *Xanthium riparium* contain about 36% oil and 41% protein. The oil has an acid no. 2.6, saponification no. 190.1, hydroxyl no. 8.6, iodine no. 143, and unsaponifiable 0.61%. The fatty acids have an acid no. 195.7, saponification no. 197.6, hydroxyl no. 13.1, iodine no. 151.2, average molecular weight 283.9, hexabromide no. 0.04, saturated fatty acids 7.3%. From these data the oil is calculated to contain oleic acid 24.5, linoleic acid 63.6, higher saturated acids 6.9, glycerol residue 4.3, and unsaponifiable 0.6%. The possibilities of industrial use are discussed. (*Chem. Abs.* **44**, 7569)

SOUTH AFRICAN FISH PRODUCTS. XXX. SEASONAL CHANGES IN THE COMPOSITION OF THE PILCHARD *(Sardinia Ocillata Jenyns)*. M. M. Black and H. M. Schwartz (Dept. of Chemistry, U. of Capetown). *J. Sci. Food and Agr.* **1**, 182(1950). Results of a 4-year study of seasonal changes in the yield and composition of the oil of pilchards from the west coast of South Africa indicate that in March or April the fish contain 10-15% oil, in May or June the oil content rises to 16-17% (the maximum), and by September or October it falls to a minimum (2-4%). The iodine value ranges from 172 to 203 and does not show any regular variation with the fat content of the fish. Water, protein, and P contents of the fish are also reported.

COMPOSITION OF KAPOK-SEED OIL. H. Nobori (Kao Soap Co. Ltd., Tokyo). *J. Soc. Chem. Ind., Japan* **44**, Suppl. binding 227-9(1941). The oil is an orange-yellow liquid; acid value, 11.8; saponification value, 194.1; iodine value (Wijs), 95.4; n_D^{20}, 1.4718. The composition was as follows: palmitic acid 10.1; stearic acid 4.6; oleic acid 52.9; and linoleic acid 25.9%. C_{20} acids were not isolated but are probably present. There is no linolenic acid or higher homologs. There is a small amount of phytosterol. (*Chem. Abs.* **44**, 8138)

THE CONSTITUENTS OF CHANA *(Cicer arietinum, Linn.)*. III. CHEMICAL EXAMINATION OF THE FIXED OILS FROM CHANA AND KABULI CHANA (ORDINARY AND WHITE VARIETIES). P. R. Bhandari, J. L. Bose, and S. Siddiqui (Council of Sci. & Ind. Res. Delhi). *J. Sci. Ind. Research (India)* **9B**, (3), 60-3(1950). Chana (chick-pea) and K. Chana (white chick-pea) were found to contain 4.1 and 5.0% oil respectively. The properties of these oils were about the same: n_D^{38} 1.4845; saponification value, 184.6; acid value, 2.4; iodine value (Wijs), 111.7; unsaponifiable matter, 4.0%. The composition of the fatty acids derived from these oils is: oleic acid, 52.1; linoleic acid, 38.0; myristic acid, 2.52; palmitic acid, 4.69; stearic acid, 1.87; arachidic acid, 0.06%. (*Chem. Abs.* **44**, 7570)

INVESTIGATION OF RICE OIL AND ITS UTILIZATION. IX. REFINING OF RICE OIL OF EXTRAORDINARILY HIGH ACID VALUE. S. Ueno (Imperial Univ. Osaka). *J. Soc. Chem. Ind., Japan* **44**, Suppl.