TABLE III

Comparison of Glyceride Compositions (% mol.) Determined by Oxidation and Crystallization Methods with Values Calculated by Random and Restricted Random Distribution Hypotheses

	Oxidation					Crystallization				
	Sm	GS$_3$	GS$_2$U	GSU$_2$	GU$_3$	Sm	GS$_3$	GS$_2$U	GSU$_2$	GU$_3$
Lard										
Experimental	38.8	2.8	24.6	58.9	13.7	39.4	2.8	27.4	54.8	15.0
Restricted Random	......	2.8	32.4	43.1	21.7	......	2.8	33.4	43.0	20.8
Random	......	5.8	27.7	43.6	22.9	......	6.1	28.3	43.4	22.2
Chicken Fat										
Experimental	29.2	2.3	18.3	44.2	35.2	30.4	2.3	17.9	49.2	30.6
Restricted Random	......	2.3	18.4	43.9	35.4	......	2.3	20.0	44.2	33.5
Random	......	2.5	18.1	43.9	35.5	......	2.8	19.3	44.2	33.7
Palm Oil										
Experimental	51.2	9.4	47.4	30.5	12.7	54.6	9.4	48.1	39.3	3.2
Restricted Random	......	9.4	45.1	35.2	10.3	......	9.4	52.2	31.0	7.4
Random	......	13.4	38.4	36.6	11.6	......	16.2	40.6	33.8	9.4
Cottonseed Oil										
Experimental	24.6	0.0	13.0	47.7	39.3	26.7	0.0	14.5	51.0	34.5
Restricted Random	......	0.0	15.8	42.3	41.9	......	0.0	18.4	43.3	38.3
Random	......	1.5	13.7	42.0	42.8	......	1.9	15.7	43.0	39.4

culated as GSU$_2$, or conversely, in obtaining GU$_3$ by difference.

Summary

The glyceride composition of four dissimilar fats and oils was determined by two independent methods a) systematic fractional crystallization from acetone, and b) Kartha's modification of Hilditch's acetone permanganate oxidation method. Results by the two methods were in fair agreement for lard, chicken fat, and cottonseed oil but not for palm oil.

Calculations were also made of glyceride distribution according to the patterns of random and restricted (Kartha's hypothesis) distribution. The values calculated for either pattern however did not agree well with those obtained experimentally by either method, except for one of the four fats, chicken fat.

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Phase Relations Pertaining to the Solvent Winterization of Crude Peanut Oil in 85-15 Acetone-Hexane Mixture

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THE winterization of refined peanut oil requires the use of a solvent (1). Unless solvent refining is used, the production of a winterized oil from solvent-extracted peanut oil would involve complete removal of solvent twice, once before refining and again after winterization. Solvent winterization of the crude miscella would be advantageous in that one of these solvent-removal steps would be eliminated. The purpose of the present investigation was to determine, on a laboratory scale, the conditions under which solvent winterization of crude peanut oil is feasible.

Preliminary experiments with crude peanut oil showed that, as had been found (2, 4) for the refined oil, a mixture of 85 parts of acetone and 15 parts of hexane by weight is a preferred winterization solvent. When hexane is used as the solvent, the crystals which form present serious filtration difficulties. Satisfactory crystals are formed in acetone, but two liquid layers form at the required temperatures and oil-solvent ratios involved, interfering with the efficient removal of the solid from the liquid. By using the 85-15 acetone-hexane mixture as solvent, satisfactory crystals are formed and the separation into two liquid layers is avoided. Voogt and Seeles (5) used a mixture of acetone and benzene in the winterization of neat's-foot oil.

Materials. The commercial crude peanut oil used had the following characteristics: iodine value (Wijs), 93.9; free fatty acids as oleic, 1.14%; peroxide value, 2.7 millimoles per kg.; unsaponifiable matter, 0.41%; and moisture and volatiles, 0.07%. A commercial C. P. acetone was used. The commercial hexane was Skellysolve B.[2]

Procedure. The winterization procedure was the same as previously described in detail (2, 4). In brief, duplicate weighed samples of the desired concentrations were chilled in a constant temperature bath for a definite holding-time. The samples were then centrifuged in a refrigerated centrifuge for 30 minutes

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[2] The mention of the names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

at a speed corresponding to 700 times gravity at the bottom of the solutions. The clear supernatant liquid was quickly decanted and the residual solid fraction weighed. From the weights and oil contents of the supernatant and the solid fractions, the amount of solid which had separated could be calculated. The "percentage of solid removed" is reported as the percentage of the total oil in the original solution.

A modification (4) of the A.O.C.S. Official Method Cc 11-42 Cold Test was used. It was found in the preliminary experiments that a refining step was necessary after winterization of the crude peanut oil to obtain a significant cold test. For example, one winterized crude peanut oil sample, 4.5% solid removed, failed a one-half-hour cold test before refining, but after a standard alkali refining treatment it had not failed in 90 hours when the test was terminated.

Effect of Oil-Solvent Ratio and Temperature (3-Hour Holding-Time). Bench-scale winterizations in the mixed solvent were carried out, using oil concentrations of from 20 to 60% by weight at temperatures of —6.5°, —8°, —10°, and —12°C. The resulting data, plotted in Figure 1, indicate that the percentage of solid removed increases slightly as the oil concentration is increased or as the chilling temperature is lowered. For a comparison, the —8° and —10°C. curves for the refined oil (2) are included in Figure 1 as broken lines. It is evident that changes in the percentage of solid removed, as either the oil concentration or chilling temperature varies, is a little greater for the crude peanut oil than for the refined oil.

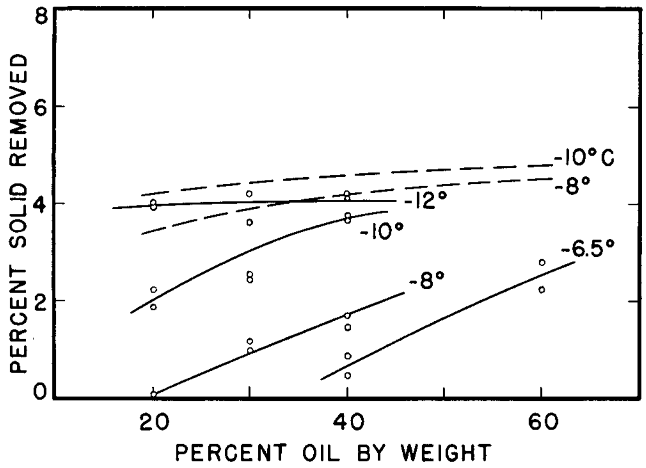

FIG. 1. Solvent winterization data for peanut oil in 85-15 acetone-hexane mixture (3-hour holding-time): ————————, crude oil; — — — — —, refined oil (2).

The centrifugal separation of the solid glycerides from the crude peanut oil solutions was, in general, less efficient than for the refined oil. This was particularly evident for the 60% crude oil solutions at —8°C. or below. Here, though only about 4% or less of the oil had crystallized, the crystals were of such a nature that there was little or no clear supernatant liquid after centrifuging.

To determine the effect of holding-time upon the percentage of solid separating, 40% oil concentrations were chilled at —10°C. for holding-times of 0.5, 1, 2, and 3 hours. The results showed 3.5, 4.0, 4.2, and 4.1% solid removed, respectively. This indicates that crystallization did not reach completion until some time between one-half and one hour. Crystallization in the refined peanut oil solutions, on the other hand, reached completion within 30 minutes (2).

Cold Tests. Since the majority of the winterized crude peanut oil samples were too small to be given a standard refining treatment, the oils were refined by a modification of the chromatographic method (3), which was found experimentally to result in the same cold test. A 20-g. portion of the oil was diluted to 50 ml., with the 85-15 acetone-hexane mixed solvent, and put through a 40-g. column of 200-mesh ignited aluminum oxide (16 mm. diameter and about 20 cm. in length). The column was eluted with 200 ml. of acetone and the recovered oil stripped of solvent. The cold test procedure was then the same as previously described. For the crude peanut oil used, removal of 3% of solid was sufficient for the oil to pass a 6-hour cold test.

Discussion

The results indicate that the solvent winterization of crude peanut oil in 85-15 acetone-hexane mixture is feasible on a laboratory scale. More satisfactory crystals are formed from lower oil-solvent ratios and at lower temperatures. From a practical point of view the winterization can best be carried out on a 35% oil solution in the above solvent at —12°C. with a one-hour holding-time. Judging from the results on cottonseed oil (4) these conditions should be satisfactory for peanut oils having a fairly wide range of iodine values. The winterization temperature does not seem to be very critical. For example, a variation of one degree would result in only a few-tenths of a unit change in the percentage of solid removed. Slightly lower winterization temperatures would favor shorter holding-times. The conditions for solvent winterization of crude peanut oil are thus very similar to those for refined peanut oil in the same solvent (2), except that a slightly lower temperature is required and that the crystals form a little more slowly at a given temperature and do not settle out as readily.

It is the regular practice in a number of peanut mills to remove a large portion of the oil by prepressing and then recover the residual oil in the press cake by solvent extraction with hexane. On the basis of the above results a process for winterizing crude peanut oil could be visualized which would involve mixing the proper proportions of the concentrated crude hexane miscella and acetone to make up a winterizable mixture of 35% by weight of oil in an 85-15 acetone-hexane mixture. Such a composition could be arrived at, for example, by adding approximately 55 parts by weight of acetone either to 45 parts of a 78% hexane miscella or to a mixture of 25 parts of prepressed crude peanut oil and 19.5 parts of a 50% hexane miscella. Performing the winterization step at this stage, before refining, bleaching, and deodorizing, would result in a fully winterized salad oil and thus eliminate subsequent readdition of solvent and restripping.

Summary

Fundamental phase relation data have been obtained on a laboratory scale which show that solvent winterization of crude peanut oil is feasible in a solvent consisting of 85 parts by weight of acetone and 15 parts of commercial hexane. The results show the effect of oil-solvent ratio, chilling temperature, and

holding-time upon the percentage of solid removed. The behavior of crude peanut oil is very similar to that of the refined oil in the same solvent except that a slightly lower chilling temperature is required and that the crystals tend to form a little more slowly and do not settle out as readily. The advantage of winterizing hexane-extracted peanut oils before refining is discussed.

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Letter to the Editor

Effect of X-ray Irradiation on Seasamum Seeds

JACOB and his group (1) are carrying out extensive studies on the effect of X-ray irradiation on seasamum seeds with the idea of getting an active mutant strain which will have earlier flowering time with greater yield of fruit. We have analyzed some of these X-ray irradiated seeds for their oil content as well as the lipase and esterase activities, and we wish to record the results in this note.

Seasamum Indicum control T12, T12.140 (irradiated with 140 m.a.H.), T16 control T16.36 (irradiated with 36 m.a.H.), T.16.50 (irradiated with 50 m.a.H.) were used for the experiments. The oil was extracted from these seeds, using the soxhlet ether extraction method, and analyzed. Crude powder possessing lipase and esterase activities was prepared by the usual method, and the lipase and esterase activities were determined, using fresh peanut oil as the substrate in the former case and ethyl butyrate as substrate in the latter case (2). The results are given in Table I.

TABLE I

Type	Free acid,%	Saponification value	Iodine value	Peroxide value	Oil obtained, %	Difference in cc. of N/10NaOH between the sample and blank	
						Lipase activity	Esterase activity
T.12.control	0.08	185.6	106.1	5.04	37.0	1.1	1.0
T.12.140.m.a.H	0.20	186.6	105.7	5.90	35.0	0.7	1.3
T.16.control	0.05	187.1	103.6	5.86	36.0	0.7	1.0
T.16.36.m.a.H	0.05	185.8	105.0	5.78	36.0	0.7	1.0
T.16.50.m.a.H	0.05	186.3	105.2	2.05	36.0	0.9	1.0

From Table I it appears that oil extracted from T.16.50.m.a.H. has low peroxide value. The field experiments showed that seeds T.16.50.m.a.H. have earlier flowering time and yield more fruit.

It is found that in the case of T.12.140.m.a.H., the lipase activity is less and the esterase activity is more, which indicates the possibility that by studying the irradiation process in greater detail a strain devoid of one of these enzymes may be secured and this would help us to separate these two groups of enzymes.

A detailed study of this problem may yield interesting results.

The authors wish to thank the government of West Bengal for having kindly supplied the control seeds; M. Chakravarthy, lecturer in oil technology, University of Calcutta, for analyzing the oil samples; and D. M. Bose, director, for the keen interest he has shown in the problem.

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ABSTRACTS . . . . E. S. Lutton, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor

Characterization of selectivity of the process of fat hydrogenation. B. N. Tyutyunnikov and B. Fraĭer (Kharkov Polytech. Inst.). *Masloboĭno Zhirovaya Prom.* 18(2), 14-18(1953). It is suggested that the index for the determination of selectivity of hydrogenation be the amount of H utilized under specified conditions for saturation of 1 double bond in linoleic, or generally highly unsaturated acid; this amount is expressed as a percentage of total consumption of H needed for saturation of the oil or fat specimen. At fully selective conditions all H (100%) is utilized for saturation of a particular acid. (*C. A.* 47, 7233)

A method of examining oils. A specific reaction of rapeseed oil. Jean Vizern and Leon Guillot. *Compt. rend.* 236, 813-4(1953). Methods are given for detecting additions of other oils to peanut oil. Copra oil can be detected by examining the traces of fatty acids on the surface of the distillate in the determination of volatile soluble and insoluble acids; in the absence of copra oil these acids crystallize at 22°, and in the presence of 2.5% or more copra oil crystallization does not occur at 22°. The K salts from various samples of peanut oil yield approx. the same quantity of precipitate in acetone containing 10% water