

TABLE I

Fractions	Wt./g.	B.P./ 2 mm.	I.V.	S.E.	Myristate	Palmitate	Stearate	Arachi- date	Lignocer- ate	Unsat. esters
S ₁	3.70	150-55°	1.02	256.86	<i>g.</i> 1.69	<i>g.</i> 1.98	<i>g.</i>	<i>g.</i>	<i>g.</i>	<i>g.</i> 0.03
S ₂	1.77	155-60°	1.52	280.28	1.10	0.65	0.02
S ₃	3.06	160-65°	2.51	308.81	1.78	1.22	0.05
S ₄	0.84	165-71°	2.69	311.21	0.42	0.41	0.02
S ₅	0.68	3.94	364.66	0.49	0.19
Loss.....	0.35
Total.....	10.40	1.69	3.08	2.85	1.63	0.49	0.31
% as esters.....	16.87	30.66	28.36	16.23	4.87	3.01
% as acids.....	16.87	30.66	28.36	16.23	4.87	3.01

(3) in conjunction with the qualitative examination data of the fractions, are given in Table I.

The unsaponifiable matter obtained prior to the liberation of the mixed fatty acids, when crystallized from methyl alcohol, gave colorless needles, m.p. 130-131°. This appears to be a sitosterol.

From the data obtained in the manner outlined, the composition of the total fatty acids in the seed oil of "White Todri" was calculated to be as follows:

Resin acids.....	7.40%
Saturated acids:	
Myristic.....	2.60%
Palmitic.....	4.73%
Stearic.....	4.37%
Arachidic.....	2.50%
Lignoceric (?).....	0.73%
Unsaturated acids:	
Oleic.....	32.17%
Linoleic.....	21.70%
Linolenic.....	10.70%
Erucic.....	13.10%

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The Selective Hydrogenation of Linolenic Acid¹

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The hydrogenated samples were analyzed by ultraviolet spectroscopy produced mostly nonselective hydrogenation. The variables of catalyst, catalyst concentration, solvent, temperature, and pressure had very little effect on the selectivity. Large differences were found in the relative reactivities of the three double bonds in methyl linoleate. It appears that the initial reaction strongly favors the 12 position assuming a limited amount of shifting of double bonds during hydrogenation. The solvent has an appreciable effect on this selectivity, but the other variables have only minor effects.

The hydrogenated samples were analyzed by ultraviolet spectroscopy. Efforts to identify the location of the double bonds by oxidative methods were unsatisfactory. Preliminary studies on the possible use of nuclear spin resonance as an analytical method in fatty acid analysis look promising.

THE OBJECT of this investigation was to find experimental conditions that would favor the conversion of linolenic acid (9,12,15-octadecatrienoic acid) to linoleic acid (9,12-octadecadienoic acid) with the limited formation of other unsaturated acids. Such a reaction would be expected to find

industrial application in the hydrogenation of several vegetable oils, such as linseed oil. To accomplish such a reaction it is necessary to find conditions which will favor the reaction of the number 15 double bond in linolenic acid over the 9 and 12 positions and also favor the hydrogenation of the trienoic acid over less unsaturated acids. Both of these aspects of selectivity are considered in the present investigation.

Each of the three double bonds in linolenic acid has been reported at one time or another to be the most reactive. Hilditch and Vidyarthi (9) reported (1929) that the rate of reduction of an ethylenic bond is greater the farther it is removed from the carboxyl group. This would indicate selectivity at the 15 position in linolenic acid. On the other hand, Bauer and Ermann (3) have claimed (1930) that linolenic acid is first reduced at the 9 position. van der Veen (20) (1931) and more recently (1946, 1949) Bailey and Fisher (1,2) find that the number 12 double bond is the first to be reduced.

It has been established that under the conditions of hydrogenation the double bonds in linolenic acid do not remain stationary but rather migrate to ad-

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jacent carbon atoms to some extent. Lemon (12, 13) was the first to recognize that the double bonds in isolinoleic acid were separated by more than one methylene group. Feuge *et al.* (7) have shown that, in the hydrogenation of methyl linoleate, the first reaction generally is one of conjugation to produce a system possessing enhanced reactivity. Boelhouwer *et al.* (6) found that, during the hydrogenation of methyl esters of oleic, elaidic, petroselinic, and linoleic acids, large amounts of position isomers were formed.

Rebello and Daubert (18, 19) studied the hydrogenation of methyl linolenate with the object of determining the relative reactivities of the various polyunsaturated acids. They found that the residual double bonds migrated, at least to some extent, to produce isomers of linoleic acid. They found that linolenic and linoleic acids were about equally reactive, and both were about five times as reactive as isolinoleic acids in the presence of palladium black catalyst.

Major contributions have been made in the past 20 years in the field of fatty acid analysis. Of most use to this study has been the adaptation of ultraviolet spectroscopy to the analysis of mixtures of oleic, linoleic, and linolenic acids (4,16,17). Progress has been reported in the use of wet oxidation of these unsaturated acids as a means of identifying the positions of the double bonds (10,11). Partition chromatography has been employed for the quantitative measurement of the dicarboxylic acids resulting from the oxidation (5,10). In the present investigation extensive efforts were made to analyze the hydrogenated products by periodate-permanganate oxidation, followed by chromatographic analysis of the dicarboxylic acids. Experimental conditions were never found for the quantitative oxidation of the double bonds in methyl linolenate, and, in the end, this analytical method was not used. Similarly, extensive efforts were made to analyze the hydrogenated products by oxidation with permanganate in acetone, employing gas chromatography to identify the monocarboxylic acids. The evidence indicated that the propionic acid, and possibly caproic acid, were further oxidized to carbon dioxide, and conditions were never found that would permit this technique to be useful.

An investigation was made of the possible usefulness of high resolution nuclear spin resonance in fatty acid analysis. The results are promising. Using a Varian Model V-4300C NSR Spectrometer, patterns were recorded of pure samples (from the Hormel Institute) of methyl linolenate, methyl linoleate, methyl

oleate, and methyl stearate. The various peaks can be related to certain atomic groups, and significant differences appear among the samples. This new technique of fatty acid analysis will require considerable development before it will be useful, but the fact that it shows possibilities is encouraging.

Methods and Materials

The methyl linolenate used in these studies was obtained from the Hormel Institute; it was 99+% methyl 9,12,15-octadecatrienoate (iodine number = 261.8). One-gram samples of the ester in 15 milliliters of solvent were hydrogenated in a low-pressure Parr shaker. The course of the reaction was followed with a gas burette kept at constant pressure by a mercury levelling bulb. The experimental variables investigated include catalyst and catalyst concentration, solvent, temperature, and pressure. Attempts were made to continue the reaction until the absorption of one equivalent of hydrogen had taken place. When this stage was reached, as estimated by the volume of hydrogen absorbed, the heat was turned off and the hydrogen was replaced with nitrogen. The catalyst was removed by filtration, and the exact amount of hydrogenation that had occurred was calculated from the iodine number of the filtered sample. Another portion of the filtered sample was analyzed for linolenic and linoleic acids, using UV spectroscopy, A.O.C.S. Tentative Method Cd 7-48. This method reports as linoleic acid those dienoid acids which contain conjugated double bonds or which can isomerize to a conjugated system under the conditions of the isomerization reaction. This includes numerous dienoid acid isomers, all of which can result only from the hydrogenation of double bonds which were originally in the 9 or 15 position. The hydrogenation of the double bond which was initially in the 12 position can lead only to dienoid acids which are nonconjugatable. From these two measured quantities, linolenic acid and conjugatable dienoid acids, and from the iodine number of the product it is possible to calculate within limits the amounts of a) nonconjugatable dienoid acids, b) monoenoic acids, and c) stearic acid. Nonconjugatable dienoid acids can result from the hydrogenation of any one of the three double bonds in linolenic acid in view of the fact that the double bonds can shift to adjacent carbon atoms.

Discussion

In Table I are listed the conditions and the results of several experiments in which methyl linolenate was hydrogenated in the presence of Rufert nickel

TABLE I
Hydrogenation Results, Using Rufert Nickel Catalyst

Run No.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature, °C.....	85	100	115	145	160	175	115	115	115	175	175	175	115	115
Catalyst concentration, %.....	10	10	10	0.2	0.2	0.2	1.0	0.4	0.2	0.1	0.3	0.4	0.4	0.4
Pressure, inches of mercury, gauge.....	2	2	2	2	2	2	2	2	2	2	2	2	10	20
Solvent.....	Lorol	Lorol	Lorol	Tetra- glyme	Tetra- glyme	Tetra- glyme	Lorol	Lorol	Lorol	Tetra- glyme	Tetra- glyme	Tetra- glyme	Lorol	Lorol
H ₂ absorbed, equivalents.....	0.962	0.869	0.930	0.68 ¹	1.43	1.65	0.981	1.045	0.750 ¹	0.479 ¹	1.354	1.370	0.994	0.968
Methyl linolenate reacted, %.....	69.4	51.8	71.2	43.2	98.0	84.2	70.1	84.2	49.7	18.3	87.9	87.9	79.0	70.1
Linolenic acid, %.....	29.0	45.8	27.4	54.1	1.8	15.0	28.4	15.0	47.9	77.8	11.5	11.5	19.9	28.4
Conjugatable dienoid acids, %.....	5.8	8.8	4.7	0.0	0.0	0.0	13.8	9.6	6.5	0.0	0.0	0.0	10.8	10.8
Nonconjugatable dienoid acids, %.....	30.4	31.1	37.9	14.2	43.8	0.0	21.7	46.3	13.1	0.0	32.4	40.4	40.4	26.0
Monoenoic acids, %.....	45.4	21.8	50.5	27.7	68.6	37.8	37.4	58.4	27.0	2.1	58.1	62.1	52.4	41.0
Stearic acid, %.....	<30.0	<37.5	<25.2	<26.9	<49.6	<87.8	<31.3	<24.3	<27.7	<30.6	<51.3	<43.3	<24.1	<30.0
Ratio of nonconjugatable to con- jugatable dienoid acids.....	<15.0	<18.8	<12.6	<13.4	<24.8	<42.4	<15.6	<12.2	<13.8	<15.3	<25.6	<21.6	<12.0	<15.0
	5.2:1	0.4:1	8.1:1	inf- nite	inf- nite	inf- nite	1.6:1	4.8:1	2.0:1	inf- nite	inf- nite	inf- nite	3.7:1	2.4:1
	7.8:1	2.5:1	10.8:1				2.7:1	6.1:1	4.1:1				4.8:1	3.8:1

¹ Hydrogenation would not proceed further under these conditions.

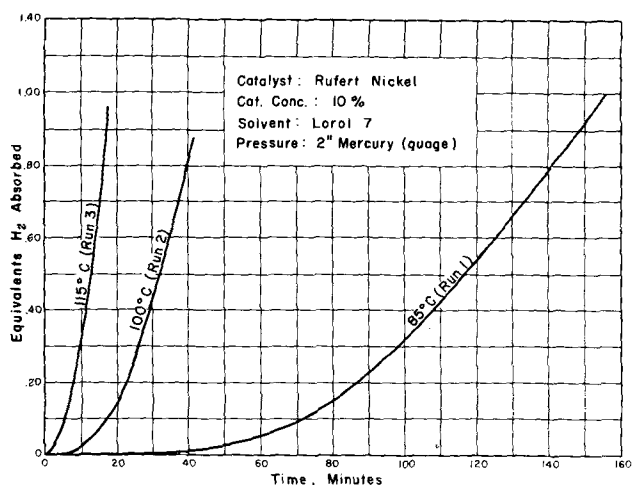


Fig. 1. Effect of temperature on reaction rate.

catalyst. Referring to the data in this table, the equivalents of hydrogen absorbed, the percentage of linolenic acid, and the percentage of conjugatable dienoic acids were determined by analysis. The remainder of the data relating to the composition of the hydrogenated samples were calculated from these values.

For an interpretation of these data from the point of view of selectivity, consider Run 1 for the purpose of discussion. Approximately 69.4% of the methyl linolenate reacted during the absorption of 0.962 equivalent of hydrogen. If the reaction had been completely selective toward the linolenate radical, 96.2% of the methyl linolenate would have reacted. If the reaction had been completely selective toward less unsaturated acids, 32.1% (one-third of 96.2) of the methyl linolenate would have reacted. A comparison of the percentage of methyl linolenate that reacted with the two extremes of selectivity gives a relative measure of the selectivity of the reaction, that is, toward the linolenate radical.

Next, consider the selectivity of the reaction as defined on the basis of the relative reactivities of the 9, 12, and 15 double bonds. The ratio of nonconjugatable to conjugatable dienoic acids has only a vague meaning when it is remembered that the double bonds can shift to adjacent carbon atoms during hydrogen-

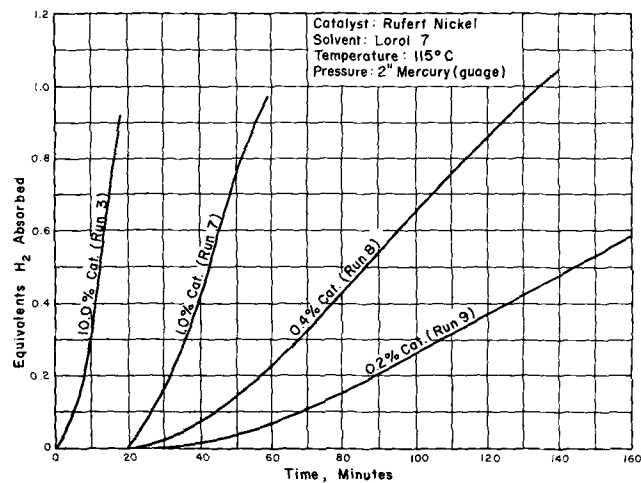


Fig. 2. Effect of catalyst concentration on reaction rate.

ation. The nonconjugatable dienoic acids can result from hydrogenation of any one of the three double bonds in methyl linolenate, and the conjugatable dienoic acids can result only from hydrogenation of a double bond which was originally in either the 9 or 15 position. If however the shifting of double bonds during hydrogenation is very limited, then the ratio under discussion becomes a measure of the relative reactivity of the number 12 double bond. This does not take into account those molecules which absorb more than one equivalent of hydrogen. In the example of Run 1, the ratio of nonconjugatable dienoic acids to the conjugatable dienoic acids lies between 5.2 and 7.8 to 1. This indicates that the reaction is highly selective toward the 12 position, assuming limited shifting of double bonds.

Two sets of experiments were carried out to evalu-

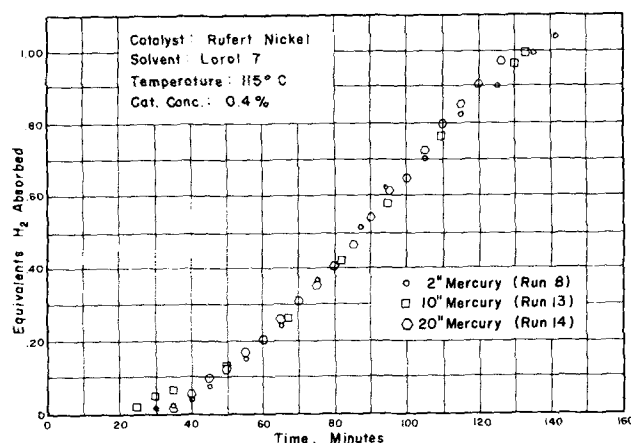


Fig. 3. Effect of pressure on reaction rate.

ate the effect of temperature on selectivity. The first set consists of Runs 1, 2, and 3 in Table I, carried out at 85, 100, and 115°C., respectively. The solvent used in these experiments was Lorol 7, a commercial product consisting chiefly of lauryl alcohol. The data show that the effect of temperature as such on selectivity is not clearly defined. In all cases the reaction was selective toward the number 12 double bond, assuming limited shifting of double bonds.

The reaction rates of these three experiments are shown in Figure 1. The effect of temperature on the rate of reaction is about what would be expected. It was thought that a slow reaction would afford a better chance of achieving selectivity, and, throughout this study, the variables of catalyst concentration and temperature were chosen so as to produce slow reactions.

The second set of experiments designed to evaluate the effect of temperature on selectivity consists of Runs 4, 5, and 6 in Table I. The solvent was tetraglyme (dimethyl ether of tetraethylene glycol), and the temperatures were 145, 160, and 175°C., respectively. The reaction was highly selective toward the number 12 double bond at all temperatures, assuming limited shifting of double bonds. The effect of temperature as such is not clear.

The effect of catalyst concentration on selectivity was studied in each of the two solvents mentioned above. Runs 3, 7, 8, and 9, Table I, represent this study of catalyst concentration in Lorol 7, and the reaction rates of these runs are shown in Figure 2.

Decreasing the catalyst concentration decreased the reaction rate. When the concentration was reduced to a certain critical level, the reaction would stop before one equivalent of hydrogen was absorbed. This phenomenon was observed in several cases. When slower reactions were obtained by using less catalyst, a concentration was reached which would not produce the level of hydrogenation sought. It was then necessary to increase the catalyst concentration until the absorption of one equivalent of hydrogen was possible, then vary the temperature to find conditions that would give a slow reaction.

Referring to the data in Table I (Runs 3, 7, 8, and 9) it appears that a low catalyst concentration possibly favors selectivity toward linolenic acid. This effect is not pronounced if indeed it is real. The effect of catalyst concentration on the selectivity of the various double bonds in methyl linoleate is not clear. In all cases the reaction strongly favors the 12 position, assuming limited shifting of double bonds.

The effect of catalyst concentration on selectivity in the solvent tetraglyme is represented in Runs 6, 10, 11, and 12, Table I. The absence of conjugatable dienoic acids in this solvent is conspicuous. This means that the reaction is highly selective toward the 12 position, assuming limited shifting of double bonds. As mentioned earlier, the possibility exists that some of the reaction could start at the 9 or 15 position and form products that react further. These four runs show that the catalyst concentration as such, has no effect on the selectivity, either on the linolenic acid or the various double bonds in the linolenate radical.

The effect of pressure on selectivity is shown in the results of Runs 8, 13, and 14 in Table I. Within the range of pressures shown, 2 to 20 in. of mercury gauge, there was essentially no variation in reaction rate (Figure 3). The lower pressures however did favor the selectivity of the methyl linolenate in preference to less unsaturated esters. The effect of pressure on the relative rates of the three double bonds was that lower pressures increased the relative reactivity of the 12 position.

In view of the finding that low pressures favor selectivity toward the linolenate radical, three experiments were made at an absolute pressure of one-half atmosphere in an attempt to improve further this selectivity. These results are shown in Table II, Runs 22, 23, and 24. Palladium-lead (14) and Rufert nickel catalysts were used. The selectivity was rela-

TABLE III
Hydrogenation of Raw Linseed Oil

	Starting material	Run 25	Run 26	Run 27
Iodine No.	184.9	147.0	157.5	129.6
H ₂ absorbed, equivs.		0.96	0.70	1.40
Oleic acid, %	24.4	83.0	50.6	95.6
Conjugated dienoic acids, %	11.0	7.9	7.1	9.2
Linolenic acid, %	51.4	20.6	34.6	9.3

Run No.	Catalyst	Catalyst conc., %	Temp., °C.	Pressure	Solvent
25	Rufert Ni	0.4	145	2-in. Hg gauge	Tetraglyme
26	Rufert Ni	0.3	145	2-in. Hg gauge	Tetraglyme
27	Pd-Pb	8.0	145	2-in. Hg gauge	Tetraglyme

tively good at this pressure, particularly in Run 23, but not better than in Runs 8 and 13 at slightly higher pressures. (A measure of this selectivity is the ratio of methyl linolenate reacted to equivalents of hydrogen absorbed. However for two experiments to be compared precisely with each other by this ratio, the equivalents of hydrogen absorbed must be the same.)

In Table II are listed numerous other catalyst systems studied in attempts to find conditions that would influence selectivity of the reaction. These include reduced nickel oxide, reduced nickel oxide poisoned with cupric acetate, copper chromite and palladium-lead catalysts. In addition, there is included one hydrogenation experiment carried out in the presence of cobalt 60 radiation (8 x 10⁴ R/hr.). These catalysts had various effects on the reaction rate but not much effect on the selectivity. The gamma radiation from cobalt 60 had no apparent effect.

In Table III are shown the results of three experiments in which samples of raw linseed oil were hydrogenated. Here an attempt was made to stop the reaction after absorption of one equivalent of hydrogen based on the linolenic acid content. Ideal selectivity would have resulted in the disappearance of the linolenate radical with the formation of the equivalent amount of dienoic acids. In Run 25, which was stopped very close to the absorption of exactly one equivalent of hydrogen based on the linolenic acid, 60% of this acid disappeared. However there was no build-up in the concentration of the conjugatable dienoic acids but rather in the oleic acid content. This indicates that the dienoic acids are more readily hydrogenated than the linolenic acid under these conditions. The analytical data are not complete enough to permit an evaluation of the relative reac-

TABLE II
Hydrogenation Results, Using a Variety of Catalysts

Run No.	15	16	17	18	19	20	21	22	23	24
Catalyst	Reduced NiO	Reduced NiO + Cu acetate	Reduced NiO + Cu acetate	Cu chromite	Rufert Ni + radiation from Co 60	Pd-Pb	Pd-Pb	Pd-Pb	Pd-Pb	Rufert Ni
Catalyst concentration, %	4.2	4.2	2.0	4.0	1.0 and 8 x 10 ⁴ R/hr.	10	5	7	10	0.3
Temperature, °C.	175	175	175	175	94-131	145	160	145	145	145
Pressure, inches of mercury, gauge.	2	2	2	2	2	2	2	½ atm., ab.	½ atm., ab.	½ atm., ab.
Solvent	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme	Tetraglyme
H ₂ absorbed, equivs.	1.31	1.22	0.39 ¹	0.63 ¹	1.26	1.24	0.88	0.77 ¹	1.16	0.81
Methyl linolenate reacted, %	87.7	83.6	17.0	35.9	89.0	94.0	69.6	58.2	90.4	55.1
Linolenic acid, %	11.7	15.5	79.0	61.0	10.4	5.7	28.9	39.8	9.0	42.7
Conjugatable dienoic acids, %	4.8	3.7	0.0	0.0	6.8	6.5	6.4	5.8	8.0	3.1
Nonconjugatable dienoic acids, %	31.2	33.7	0.0	5.4	36.8	48.5	38.2	28.0	48.4	20.9
Monoenoic acids, %	54.9	54.8	4.8	19.8	64.2	72.3	55.5	38.8	63.3	35.2
Stearic acid, %	<47.5	<42.3	<22.8	<28.8	<41.2	<34.5	<21.7	<21.6	<29.8	<28.5
Ratio of nonconjugatable to conjugatable dienoic acids, %	<23.8	<21.2	<11.4	<14.4	<20.6	<17.2	<10.8	<10.8	<14.9	<14.2
Ratio of nonconjugatable to conjugatable dienoic acids, %	6.6:1-11.5:1	9.2:1-15.0:1	infinite	infinite	5.4:1-9.5:1	7.4:1-11.1:1	5.9:1-8.6:1	4.8:1-6.7:1	6.0:1-7.9:1	6.8:1-11.4:1

¹ Hydrogenation would not proceed further under these conditions.

tivities of the 9, 12, and 15 double bonds. Comparing Run 26 with Run 25 in Table III, it can be shown that the absorption of 73% as much hydrogen caused the disappearance of only 54% as much linolenic acid. The only difference in the conditions of these two runs was in the amount of catalyst. It is concluded that a higher Rufert nickel catalyst concentration favors hydrogenation of linolenic acid in preference to less unsaturated acids.

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The Production of Salad Oil by Fractional Crystallization With Solvents

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A fractional crystallization method for the winterization of cottonseed oil with solvents was developed in our laboratories and pilot plant.

Small amounts of solvent (*e.g.*, 10% by weight of acetone) were mixed with the oil. This mixture was rapidly chilled to 0°C. and kept at this temperature for 3-4 hrs.; the liquid portion was separated from the solids.

After solvent evaporation a salad oil of good quality was obtained. The yield is equal to or better than that obtained with conventional methods.

The method is suitable for a continuous operation since rapid chilling can be used, and only a short over-all time is necessary. Great advantages of the process are the use of low amounts of solvent and of a refrigeration system not requiring temperatures below 0°C.

THE HIGHER-MELTING GLYCERIDES in cottonseed oil crystallize out at refrigerator temperature and therefore have to be removed in order to obtain a salad oil. This is usually done by the well-known winterization process, in which the oil is slowly cooled to facilitate a partial crystallization, and the crystallized portion is separated from the liquid oil by filtration.

With this conventional winterization method it is difficult to obtain good-sized, easily-filterable crystals, and the rate of cooling as well as the rate of filtering is quite slow. "Because of the slowness of the operation and the poor separation obtained, ordinary winterization is one of the least satisfactory of present oil-processing methods" (1).

Efforts have been made by many workers to improve this conventional method, and the most promising ways seem to be the use of crystal modifiers (13) and solvents.

The great advantage of using a solvent-oil mixture for fractional crystallization lies in the fact that "equilibrium between the solid and liquid phases is

established much more rapidly, large easily-separable crystals are produced even at relatively-high cooling rates, and the viscosity of the liquid phase is reduced so that separation of the crystals by filtration or other means is more rapid" (1).

Previously-reported solvent crystallization methods employ large amounts of solvents (the average oil: solvent ratio is 1:3) at relatively low temperatures (from -3° to -60°C.). Methods have been developed for a variety of fatty substances (*e.g.*, fatty acids, lard, tallow), including peanut oil and cottonseed oil (2,3,4,5,6,14).

The solvent winterization method developed in our laboratories is different from previously described methods in that it uses very small amounts of solvent (in the order of 10%). The small amount of solvent is a major advantage of this method since it eliminates the need for large-scale solvent handling equipment and reduces solvent losses markedly. A wide variety of solvents was found to be useful.

Even with this small amount of solvent however, a fast chilling of the oil-solvent mixture in a Votator type of heat exchanger is possible, and the temperature desired for further crystallization (around 0°C.) can easily be maintained with regular refrigeration equipment. Contrary to our expectation, these conditions do not result in the formation of an unmanageable gel but produce large-sized, easily-filterable crystals. The necessary crystallization time at about 0°C. is only 3-4 hrs. as compared with 1-2 days for regular winterization. This eliminates the need for large-capacity refrigerated tanks and opens the way for a continuous winterization process.

One commercially-used continuous solvent winterization method (6,7) usually employs 50-60% hexane. It takes advantage of the fact that the oil is already