A considerable portion of the savings can be attributed to omission of caustic. The caustic must saponify more oil than formerly suspected.

Part of the 0.89 lb. of crude oil saved results from the close operational control the 50 oil process provides. The dried lecithin is collected, measured, and sampled on a daily basis. The per cent acetone-insoluble is analyzed, and if this property is in the desired range, the refiner knows he is obtaining minimum losses. Also an excess of anhydride, unlike an excess of caustic, does not attack neutral oil and increase losses.

Advantages and Disadvantages

Based on the successful commercial experience of the 50 oil process in the Staley oil refinery the process can be evaluated as follows for a refiner and lecithin producer.

Advantages

0.89 lb. less of crude oil is required for 100 lbs. of finished deodorized product.

0.32 lb. additional lecithin is made.

The deodorization loss is lower than expected.

The flavor and stability of the deodorized oil are unchanged.

No acidulation plant is required with its attendant waste disposal problem.

Saponification of any neutral oil is eliminated.

The net savings of the process amount to some 10¢/cwt.

Disadvantages

The process is corrosive and requires 316 stainless-steel equipment and piping.

The process requires somewhat more care in deodorization.

Some highly colored vegetable oils present special problems for adaption to this 50 oil process.

Economic Significance of the 50 Oil Process

The 50 oil process has economic considerations for two classes of soybean oil refiners:

Class I: Oil producers and/or refiners who degum, refine, and sell finished oils and lecithin

For this category of refiner already established in the lecithin business the monetary advantage of the 50 oil process amounts to 10.6¢/cwt. of deodorized product. The following values were used: crude oil 11.5¢/lb., acid soapstock @ 5¼¢/lb., and lecithin @ 10.5¢/lb.

Class II: Oil refiners who refine only crude into finished oil.

For this category of refiners the lecithin would be acidulated at 72% AI into soapstock. The net savings per cwt. of refined oil are calculated to be 5.2¢/cwt. of deodorized product.

Summary

The 50 oil process has been demonstrated on a commercial scale to be physically possible and economically attractive to refiners of soybean oil. The flavor and stability characteristics of the finished oil are identical to the conventional caustic-refined product.

Acknowledgment

Special acknowledgment is made to the personnel of Podbielniak Inc., whose efforts aided materially in the success of this project.

REFERENCES

1. Freyer, E. B., and Shelburne, J., J. Am. Oil Chem. Soc., *29*, 403–408 (1952).
2. Hayes, L., and Wolff, Hans, J. Am. Oil Chem. Soc., *33*, 440–442 (1956).
3. Podbielniak, W. J., Gavin, A. M., and Kaiser, H. R., J. Am. Oil Chem. Soc., *33*, 24–26 (1956).

[Received October 1, 1956]

The Antioxidant Properties of Garden Cress (Lipidium Sativium) and Wild Mustard (Sinapsis Arvensis) Oils[1]

MOUSTAFA LOTFY, HUSSEIN AREF,[2] and ABDEL AZIZ HUSSEIN, Department of Agricultural Industries, Faculty of Agriculture, Cairo University, Giza, Egypt

LINSEED OIL is obtained from the seeds of the flax plant, *Linum usitatissimum*. Its production dates back to 259 B.C. when sesame, linseed, and castor oils were first recovered by pressing in Egypt (1). Although it contains a high percentage of unsaturated fatty acids, it is used as an edible oil on a rather large scale in Egypt. There is a general belief among its producers that the presence of foreign oils, particularly those of wild mustard *(Sinapsis arvensis)* and garden cress *(Lipidium sativium)*, increases its keeping quality and retards its rancidity. The presence of these foreign oils is attributed to the contamination of flax seeds with those of wild mustard and garden cress. The present work was undertaken to test this belief and to isolate and identify the stabilizers in these foreign oils.

Resistance of fats to oxidation derives from the presence of minute amounts of natural antioxidants, which inhibit oxidative processes (2, 3, 4, 5, 6). Vegetable oils are generally rich in such substances (*e.g.*, lecithin, tocopherol), but animal fats contain only insignificant quantities. Addition of antioxidants provides an important means of increasing stability to oxidative rancidity, but it has not proved successful in delaying flavor reversion in highly unsaturated fats.

Recently Lundberg *et al.* (7) examined the antioxidant properties of samples of 32 spices. Ground mustard exhibited an antioxidant effect on lard when tested by the active oxygen method at 98.6°C.

Materials and Methods

Flax seeds used in this work were obtained from the Ministry of Agriculture farm at Borg El-Arab. Wild mustard and garden cress seeds were procured from the University farm at Giza. Great care was taken to collect the seeds for each plant in as pure a manner as possible. Two methods were used for obtaining the oil from each seed: namely, solvent extraction and pressing.

Measurement of Keeping Quality. The onset and progress of rancidity in the different oils were determined and followed by the determination of the per-

[1] From a dissertation submitted by Moustafa Lotfy to Cairo University in partial fulfillment of the requirements for the Ph.D. degree, May 1954.
[2] Present address: Vice President, Cairo University, Giza, Egypt.

oxide value. Oxygen uptake by the oil at different stages was also determined by the Warburg manometric technique.

The technique of Lundberg *et al.* (8) for estimating the induction period by the peroxide value [3] method was adopted throughout the work. In this technique the end of the induction period is defined as the point at which the slope of the peroxide value curve rises sharply. In addition, the onset of rancidity was judged by odor. Results of the organoleptic tests agreed admirably with the peroxide values. For linseed oil, preliminary experiments showed that the rapid increase in the peroxide formation occurred at a value of three, or 30 cu./mm. of absorbed oxygen per gram of oil in the case of Warburg technique.

Determination of Tocopherol Content. The method of Karrer and his co-workers using auric chloride was adopted (9).

Separation of Unsaponifiable Matter. The method outlined in the A.O.A.C. Official Methods (10) was used with the following modifications. To help saponification, the mixture was left for 24 hrs. at room temperature under an atmosphere of CO_2 instead of heating for half an hour. Also petroleum ether of a boiling point of 50–70°C. was substituted for ether. The extract was dried with anhydrous sodium sulphate. The petroleum ether was distilled off under vacuum and in an atmosphere of CO_2 at a temperature not exceeding 30°C.

Solvent Fractionation of Unsaponifiable Matter, Preparation of Allophonates, and Isolation of Antioxidants. The method of Herbert *et al.* (3) was used.

Spectrophotometric Analysis. The examination was carried out on a 0.1% solution in absolute ethanol, using the Unicam Spectrophotometer. Fraction J allophonates from both garden cress and wild mustard oils were examined spectrophotometrically. Check determinations were made on pure α-tocopheryl acetate for comparison.

Results and Discussion

The Induction Period of Linseed, Wild Mustard, and Garden Cress Oils. The peroxide value-time relationship was established for the three oils. Figure 1 shows that expressed and extracted linseed oil, garden cress oil, and wild mustard oil have induction periods of 6, 12, 48, and 48 hrs., respectively. It is apparent that garden cress and wild mustard oils are more stable than linseed oil and extracted linseed oil contains more of the natural antioxidants than does expressed linseed oil. This finding agrees with data on wheat germ oil and butter oil (11, 12).

[3] The peroxide value was expressed as millimoles of peroxides per 1,000 g. of oil.

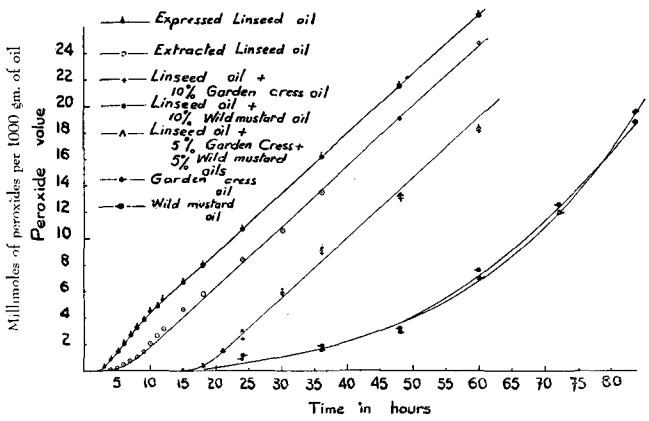


FIG. 1. Stability of expressed and extracted linseed oils, garden cress and wild mustard oils, and the effect of garden cress and wild mustard oils on expressed linseed oil.

El-Rafey *et al.* (11) attributed the greater stability of the extracted oil to the formation of sulfhydryl groups during the heat treatment. An experiment was conducted to test this hypothesis by adding cysteine and glutathione to expressed and extracted linseed oils. There was no difference between the –SH treated and the untreated oils. Experiments conducted to test the effect of moisture, postulated by El-Rafey *et al.* (11), proved that this factor was not important.

Tocopherol Content of Expressed and Extracted Linseed Oil. Widely different values for the tocopherol content in linseed oil have been reported, 250 γ/g. (9) and 1130 γ/g. (12).

So that the cause of the differences in stability might be determined, tocopherol contents were estimated in extracted and expressed linseed oils and the oil was extracted from previously expressed meal. The values obtained were 190, 115, and 265 γ/g. of oil, respectively. These results might explain the better quality of the extracted linseed oil.

Stabilizing Effect of Garden Cress and Wild Mustard Oils on Linseed Oil. Induction Period. Three different mixtures with expressed and with extracted linseed oil were studied:

Linseed oil (90 ml.) + garden cress oil (10 ml.)
Linseed oil (90 ml.) + wild mustard oil (10 ml.)
Linseed oil (90 ml.) + 5 ml. each of garden cress and wild mustard oils

The peroxide value *vs.* time relationship shown in Figure 1 demonstrates that both garden cress and wild mustard oils have a definite stabilizing effect on linseed oils. No synergistic effect was observed. The two oils probably contain the same antioxidants in approximately the same concentrations.

Using a peroxide value of 3 to establish the end of the induction period, Lundberg (12) estimated the protective value as follows:

$$\text{Protective value} = \frac{\text{Keeping time (stability) of antioxidant + control}}{\text{Keeping time (stability) of control}}$$

When added to expressed linseed oil, wild mustard oil, garden cress oil, and their mixture had a protective value of 4. But in the extracted linseed oil the protective value of these additives was only 2. However the induction period for both the treated extracted and expressed linseed oils was the same.

Oxygen Absorption. In order to ascertain the antioxidant activity of garden cress and wild mustard oils, the oxygen absorption of linseed oil was measured in their presence and absence, using the above mentioned concentrations. The results as presented in Figure 2, show that the garden cress and wild mustard oils were effective in retarding the O_2 absorption of expressed linseed oil. Consequently the induction period was prolonged four-fold as compared with that of the untreated expressed linseed oil.

When added to extracted linseed oil, wild mustard oil, garden cress oil, and their mixture had a protective value of 2. However the induction period for

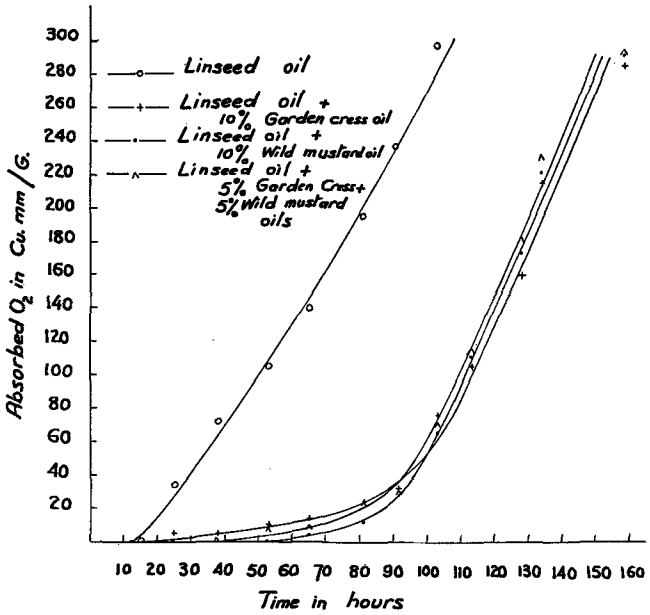


FIG. 2. Effect of garden cress and wild mustard oils on the oxygen absorption of expressed linseed oil.

the treated expressed and extracted linseed oils was the same.

Effect of Varied Quantities of Stabilizing Oils on the Keeping Quality of Linseed oil. Several factors seem to influence the action of an antioxidant, among which may be mentioned the concentration of the antioxidant and the type of substrate. There seems to be an optimum concentration for each antioxidant, limiting its use for edible purpose, which depends upon its potency, toxicity, and the products of its oxidation (8). Lecithin, for example, in concentrations higher than 0.05–0.1% leads to noticeable darkening of the product (13). There is also a maximum concentration for each antioxidant, above which no further increase in the stability of the oil or fat is achieved (8).

Various concentrations, namely 10, 15, 20, 25, and 30% each of wild mustard oil and garden cress oil in linseed oil were tested by both the peroxide value method and the Warburg manometric technique in order to determine the levels which gave satisfactory protection without undesirable side-effects. Using these concentrations, the protective factors for both wild mustard and garden cress oils were 1.8, 2.0, 2.2, 2.4, 2.6, and 2.6, respectively, when extracted linseed oil was used as substrate, and 3.7, 4.0, 4.2, 4.4, 4.5, and 4.5, respectively, using expressed linseed oil. The results also showed that the optimum and maximum stabilizing concentrations for both garden cress and wild mustard oils in linseed oil were 10 and 25%, respectively.

In concentrations exceeding 10% there was little difference in the stabilizing effect of the two additives on either expressed or extracted linseed oil. Thus from a commercial point of view the preferred concentration of the additive is around 10%. Higher concentrations did not increase the keeping quality of linseed oil and might raise the cost of production and give a distinctive sharp taste and odor to linseed oil.[4]

[4] Samples of edible linseed oil taken from the Egyptian market were found to contain oils of garden cress and wild mustard in concentrations around 10%.

Effect of Other Antioxidants on Linseed Oil. The following antioxidants were tested: glutathione, cysteine, hydroquinone, and ascorbic acid. The concentration used was 0.05% for each, except 0.4% for ascorbic acid, as these were the recommended optimums (11, 12, 14). Garden cress and wild mustard oils were also included in the test in 10% concentrations. Both expressed and extracted linseed oils were subjected to this experiment. The results for expressed linseed oil are summarized in Table I. With

TABLE I
Effect of Different Antioxidants on the Induction Period of Expressed Linseed Oil

	Peroxides Values[a]						
Time (hours)	00	12	24	36	48	60	72
Linseed oil							
Original	0.0	6.0	10.5	15.3	19.3	24.0	28.5
With 0.05% glutathione	0.0	3.3	7.5	12.9	18.1	22.3	27.1
With 0.05% cysteine	0.0	3.4	8.8	13.2	17.9	23.5	28.8
With 0.05% guaiacum + 0.002% H_3PO_4	0.0	0.0	7.2	12.4	17.9	23.5	28.8
With 10% garden cress oil	0.0	0.0	3.15	8.2	13.3	18.3	22.9
With 10% wild mustard oil	0.0	0.0	3.05	8.1	13.1	18.3	23.4
With 0.05% hydroquinone	0.0	0.0	0.6	5.3	9.6	13.7	18.1
With 0.04% ascorbic acid	0.0	0.0	0.0	0.3	7.0	12.2	18.2

[a] Millimoles of peroxides per 1,000 g. of oil.

a peroxide value of 3.0 taken as an indication of the development of perceptible rancidity, the induction period for the tested antioxidants ranged between 11–41 hrs., ascorbic acid in 0.4% concentration being the most efficient one. Moreover there was no significant difference observed between expressed and extracted linseed oil.

Effect of Garden Cress and Wild Mustard Oils on Rancid Linseed Oil. Batches of linseed oil having initial peroxide values of 2.3, 3.0, 4.85, 7.35, and 10.9 were treated with garden cress and wild mustard oils in 10% concentration. Results shown in Table II indicate that once the perceptible rancidity sets in, the addition of antioxidants did not affect the progress of deterioration.

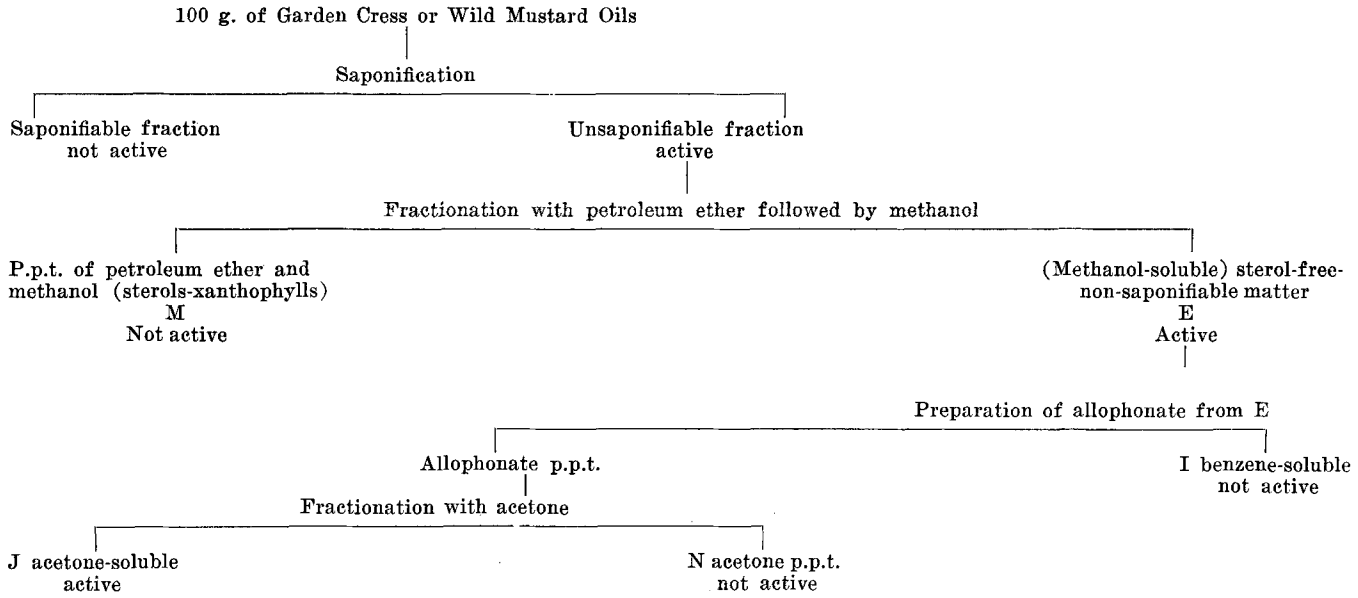
TABLE II
Effect of Addition of Garden Cress Oil on the Induction Period of Extracted Linseed Oil Having Different Original Peroxide Values

Time in hours	Peroxide Value[a]									
	2.3		3.0		4.85		7.35		10.9	
	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B
00	2.3	2.1	3.0	2.7	4.85	4.45	7.35	6.65	10.9	9.8
5	4.2	3.0	5.6	5.4	7.3	7.1	9.3	9.2	12.8	12.5
12	7.3	5.5	8.5	8.3	11.5	11.4	12.8	12.6	15.0	14.8
24	12.5	10.2	13.4	13.3	16.8	15.8	18.2	16.8	20.2	19.9
36	18.2	16.2	18.6	17.9	21.7	20.6	23.9	22.6	26.1	25.4
48	24.1	20.9	23.4	22.9	27.2	26.2	29.2	27.9	31.0	30.05
60	29.9	24.9	29.1	28.5	32.8	31.2	35.9	32.2	36.4	35.5

A = Linseed oil.
B = Linseed oil plus 10% garden cress oil.
[a] Millimoles of peroxides per 1,000 g. of oil.

The Isolation and Identification of the Antioxidant in Garden Cress and Wild Mustard Oils. Several methods have been devised for isolating antioxidants from their natural sources (2, 3, 12). The method of Herbert *et al.* (3) was followed.

The different fractions obtained were subsequently tested for their antioxidative power, using both O_2-uptake and peroxide value techniques. Tests were made, using the equivalent quantities of 10% of the oil of the different fractions. The activity of fraction J closely corresponded to that of the protective oil. It is worthy of note that the fractions in both



Fractionation of fraction J allophonate by several recrystallizations in methanol and washings with petroleum ether.

Yield: 182 mg. in case of garden cress oil
171 mg. in case of wild mustard oil

garden cress and wild mustard oil were quite similar, if not completely identical.

Fraction J obtained from both garden cress and wild mustard oil was identified as α-tocopheryl allophonate. Repeated recrystallizations yielded a constant melting-point product (159°C.). Ultraviolet spectrophotometric examinations of α-tocopheryl acetate and fraction J of garden cress oil showed that both exhibit maximum absorption at 290 mμ (Figure 3). Fraction J of wild mustard oil showed also the same maximum absorption.

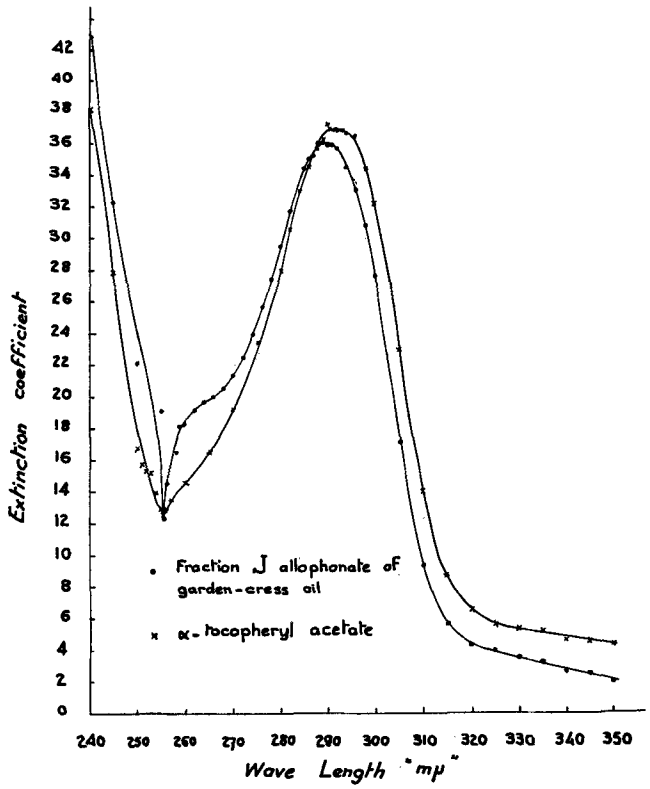


FIG. 3. Ultraviolet absorption spectra of α-tocopheryl acetate and fraction J of garden cress oil in ethyl alcohol.

Using the auric chloride potentiometric method of Karrer *et al.* (9), the amounts of α-tocopherol in fraction J of both garden cress and wild mustard oils were determined. The values were 1,830 and 1,909 micrograms per gram of oil, respectively.

Effect of Added α-Tocopheryl Acetate on the Stability of Extracted Linseed Oil. Peroxide value and oxygen-uptake experiments were conducted on linseed oil in the absence and the presence of added chemically pure α-tocopheryl acetate. The protective values of 0.01, 0.02, 0.03, 0.04, 0.05, and 0.06% α-tocopheryl acetate were 1.7, 2.0, 2.2, 2.4, 2.5, and 2.5, respectively. The optimum and maximum concentrations were obtained at 0.02 and 0.05%, respectively.

The antioxidant effect and protective factors obtained from the addition of these concentrations of chemically pure α-tocopheryl acetate were the same as those obtained by adding the same concentrations of α-tocopheryl allophonate present in garden cress and wild mustard oils (fraction J). The optimum and maximum concentrations were also the same.

Summary and Conclusion

Data obtained in the present work confirm previous reports of the presence of tocopherol in linseed oil. However the amount of tocopherol found in this work was 5 to 10 times less than the figures reported by Lange (12). One possible reason for this difference may be the variety of seeds used. Our results on extracted linseed oil agree quite closely with those reported by Winton and Winton (9).

Solvent extraction yielded a more stable linseed oil than did expressing. More tocopherol was found in the extracted oil than in the expressed oil, 190 and 115 γ/g., respectively. This difference seems ample enough to account for differences in the stabilities of the two oils. Although other workers have suggested

that stability differences might be accounted for by the larger amount of moisture in the expressed oil and/or the presence of more free sulfhydryl groups in the extracted oil (11), these factors were found to be without effect.

The oils of garden cress and wild mustard seeds, when added to linseed oil, were effective in delaying its oxidation. The optimum stabilizing concentration for both additives was found to be 10%. In each case above 25% no further increase in the stability was achieved. The addition of 10% garden cress or wild mustard oil to linseed oil showed a protective value of 2 for the expressed linseed oil and 4 for the extracted one. However the induction periods for both extracted and expressed linseed oils were the same. This could be explained on the basis that garden cress and wild mustard oils contain approximately the same concentration of α-tocopherol per gram of oil, which is higher than its maximum effective concentration (183 γ/g. for wild mustard oil and 190 γ/g. for garden cress oil). The smaller protective value could be explained on the basis that the extracted linseed oil contains more tocopherol than the expressed oil (150 γ/g. for expressed and 190 γ/g. for extracted linseed oil). No synergistic effect was observed when the two oils (garden cress and wild mustard) were added together since α-tocopherol was the only antioxidant that could be detected in the three oils.

Fraction J of the unsaponifiable matter of both wild mustard and garden cress oils was identified as α-tocopheryl allophonate. The melting point of the two fractions, 159°C., corresponded to the reported one for α-tocopheryl allophonate, which was between 158–160°C. (3). The spectrophotometric examination of these two fractions and that of α-tocopheryl acetate showed the same selective absorption in the ultraviolet region of the spectrum with a maxima at 290 mμ and a minima at 225.5 mμ approximately.

Several experimental results indicated that α-tocopherol was the only active antioxidant present in both wild mustard and garden cress oils. All the fractions M, I, and N, with the exception of fraction J, showed no antioxidation effect. Furthermore, upon the separation of α-tocopheryl allophonate from the acetone solution, the residue was inactive. The antioxidation effect obtained from the addition of different concentration of the α-tocopherol present in garden cress and wild mustard oils were the same as those obtained from the addition of chemically pure α-tocopheryl acetate.

REFERENCES

1. Kirschenbauer, H. G., "Fats and Oils, an Outline of Their Chemistry and Technology," Reinhold Publishing Corporation, pp. 122 (1944).
2. Budowski, P., J. Am. Oil Chemists' Soc., *27*, 264–7 (1950).
3. Herbert, M. E., Oliver, H. E., and Gladys, A. E., J. Biol. Chem., *113*, 319–32 (1936).
4. Herbert, M. E., Oliver, H. E., Gladys, A. E., and Mohamed, A., J. Biol. Chem., *122*, 99–107 (1937).
5. Mourea, C., and Dufraisse, C., Chem. Rev., *3*, 113 (1926).
6. Mourea, C., and Dufraisse, C., Chemistry and Industry, *47*, 819 (1928).
7. Chipault, J. R., Mizuno, G. R., Hawkins, J. M., and Lundberg, W. O., Food Research, *17*, 46–55 (1952).
8. Lundberg, W. O., Halverson, H. O., and Burr, G. O., Oil and Soap, *21*, 33–35 (1944).
9. Winton, A. L., and Winton, K. B., "The Analysis of Foods," John Wiley and Sons Inc., pp. 386–7 (1945).
10. Association of Official Agricultural Chemists, "Official Methods of Analysis," pp. 430, 441, and 442 (1950).
11. El-Rafey, M. S., Richardson, G. A., and Henderson, J. L., J. Dairy Sci., *27*, 807–20 (1944).
12. Lange, W., Oil and Soap, *27*, 418–21 (1950).
13. Lundberg, W. O., "A Survey of Present Knowledge of Researches and Practices in the United States Concerning the Stabilization of Fats," University of Minnesota, Minneapolis, Minn., No. 20, 1–39 (1947).
14. Jacobs, M. B., "The Chemistry and Technology of Food and Food Product," Interscience Publishers Inc., vol. 2, ch. 13, pp. 410–1 (1944).

[Received December 28, 1955]

Synthetic Detergents from Animal Fats. IX. Triethanolammonium, Lithium, Alkaline Earth, and Other Salts of α-Sulfonated Fatty Acids[1]

J. K. WEIL, R. G. BISTLINE JR., and A. J. STIRTON, Eastern Regional Research Laboratory, Philadelphia, Pennsylvania [2]

α-Sulfopalmitic acid and α-sulfostearic acid have aqueous solubility in excess of 10% at room temperature. In contrast, the sodium salts, $RCH(SO_3Na)CO_2H$ and $RCH(SO_3Na)CO_2Na$, which have detergent properties (9) and show promise as components in detergent mixtures (7), have limited solubility except at higher temperatures. Difference in solubility may be related to the fact that aqueous solutions of the "diacids" $[RCH(SO_3H)CO_2H]$ contain micelles, while the sodium salts do not form micelles, at room temperature (11).

Properties of a variety of salts of α-sulfonated acids have been reported only in the case of the lower fatty acids, for example, salts of α-sulfobutyric and α-sulfovaleric acids (1, 2). Triethanolammonium α-sulfopalmitic acid has been shown to be exceedingly soluble (8); and the detergent and foaming properties of the sodium salts of α-sulfopalmitic and stearic acids can be favorably affected by the presence of the Ca^{++} and Mg^{++} ions of hard water. These considerations suggest there may be considerable differences in the solubility and surface-active properties of different salts of α-sulfonated higher fatty acids. Accordingly ammonium, triethanolammonium, lithium, sodium, potassium, silver, magnesium, calcium, barium, zinc, copper, aluminum, and iron salts of α-sulfopalmitic acid and α-sulfostearic acid were prepared. Most of the salts were made from aqueous solutions of the isolated diacids (10). Where solubility and purity of the salts permitted, detergent and other surface-active properties were measured.

Preparation of Salts

Ammonium, Lithium, Sodium, Potassium, and Silver. Acid ammonium, sodium, and potassium salts $[RCH(SO_3M)CO_2H]$ were prepared from the diacid

[1] Presented at the meeting of the American Oil Chemists' Society, Chicago, Ill., September 24–26, 1956.
[2] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.