in the ohmmeter, the resistance of the fruit to the passage of the small direct current is read. The moisture content of the tung fruit is estimated from either a table or a curve.

The following table and curve give the correlation between the resistance of a tung fruit in ohms and its moisture content in percent:

Moisture in Percent	Resistance in Ohms
6.3	Infinity
11.2	10 million
11.5	5 million
12.5	1 million
13.7	600,000
14.4	325,000
17.0	105,000
19.3	60,400
27.9	43,000
31.3	24,000
35.0	21,000
37.2	16,000

REFERENCES

(1) J. D'A. Clark, Brit. Patent 275,741 (May 18, 1926).
(2) A. Allen, Brit. Patent 281,693 (December 2, 1926).
(3) E. J. Murphy and A. C. Walker, J. Phy. Chem. *32,* 1761 (1928).
(4) A. J. Stamm, Ind. Eng. Chem. *19,* 1021-5 (1927).
(5) M. E. Dunlap, U. S. Patent 1,690,672, November 6, 1929 (Public Service).
(6) E. G. Suits and M. E. Dunlap, Southern Lumberman *140,* No. 1782. 68-70 (1930).
(7) F. Schenk, Ger. Patent 571,117 (October 7, 1930).
(8) C. B. Limbrick, U. S. Patent 1,890,545 (December 13, 1933).
(9) W. L. Balls, Nature *129*, 505 (1932).
(10) Brabender Elekromaschiner, G.M.B.H., Ger. Patent 570,086 (May 1, 1931).
(11) C. D. Fisher, U. S. Patent 1,961,965 (June 5, 1934).
(12) N. E. Edlefsen, Agr. Eng. *14,* 243-4 (1933).
(13) M. C. Marsh and E. Earp, Trans. Faraday Soc. *29,* 173-93 (1933).
(14) Colombo Commercial Company, Brit. Patent 370,984 (April 15, 1932).
(15) B. Lampe, Z. Spiritusend *52,* 387-8 (1929).
(16) B. J. Eyers, U. S. Patent 2,043,241 (June 9, 1936).
(17) C. C. Baymiller and P. F. Nichols, Fruit Prod. J. *14,* 232, 237 (1935).
(18) E. A. Arnold, J. Inst. Fuel *10,* 418-19 (1937).
(19) F. A. Heinrici, Brit. Patent 502,525 (March 20, 1939).
(20) A. O. Store, Can. Patent 362,927 December 29, 1936).
(21) Ferranti Ltd. and Jack Dawson, Brit. Patent 454,438 (Sept. 30, 1936).

Elm Seed Oil II. Studies on Fatty Acid Separation

By R. G. ZEHNPFENNIG and H. A. SCHUETTE
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

THE DETERMINATION of solid and liquid acids, besides its applications to pure research, is of interest technologically for three reasons. These are the determination of saturated acids in oils containing linolenic acids, the determination of the composition of oils or fats having large amounts of unsaponifiable matter, and the determination of solid unsaturated acids in hydrogenated fats.

In the case of fats and oils containing no saturated acids lower than palmitic, nor solid unsaturated acids, the problem of separating solid from liquid acids has been solved by the Twitchell method[9] and its various modifications. Because of the use today of considerable amounts of fats and oils which contain myristic acid and its lower homologs, a method of separating them so that all saturated acids appear in the insoluble fraction would be of value.

Several attempts have been made in the past to solve this problem. Twitchell[7] used petroleum ether as solvent in the separation of the lead salts of lard fatty acids. The iodine numbers of the solid and the liquid acids revealed that the separation was improved by the substitution of this solvent for alcohol and ether. In addition, oxidation of the lead salts of the unsaturated acids, as indicated by the appearance of a yellow color, does not occur in petroleum ether. However, Twitchell found that the solid acids had higher iodine values when the lard fatty acids were not fresh.

Several modifications of the Twitchell lead salt-alcohol method have been proposed to decrease the solubility of the lead salts of the lower acids. The limitations of these methods have been discussed by Stillman and Andrews.[6]

In the course of further studies[5] on elm seed oil, it was found desirable to make a separation of the saturated from the unsaturated acids. The oil, obtained by petroleum ether extraction of seeds produced in the spring of 1937, had the following constants: d 25°/25°, 0.9305; n^{25°, 1.4574, saponification number, 274.6; iodine number, 25.32; thiocyanogen number, 17.18; Reichert-Meissl Number, 2.79; Polenske Number, 34.51; acid number, 1.49; and unsaponifiable matter, 1.45 per cent. By means of ester fractionation the percentage acid composition of the oil used was found to be as follows: caprylic, 4.8; capric, 55.5; lauric, 5.3; myristic, 4.2; palmitic, 2.6; oleic, 10.0; linoleic, 8.1 and linolenic, a trace.

The usual Twitchell method[9] was found to be entirely inapplicable to this oil. It was therefore necessary to search for a combination of salt and solvent which would permit the precipitation of the capric and caprylic acids.

From a consideration of theoretical solubility relations, it is evident that any compound will be most soluble in that solvent to which it is most nearly related in composition and structure. Thus, the unsaturated compounds should be highly soluble in unsaturated solvents, while the corresponding saturated compounds would show a decreased solubility.

A review of the properties of unsaturated liquids reveals that few are suitable with respect to boiling point and to stability toward the reagents required in the separation process. Amylene was deemed to be such a solvent. This substance is available as mixed amylenes, consisting of approximately equal parts of trimethyl ethylene and pentene-2, and as pentene-2 of 90 per cent purity. Both these solvents are water-white liquids of characteristic odor, boiling over a range of approximately 34° to 40°. Portions of these solvents, shaken with a mixture of hydrochloric acid (2 + 1) and lead chloride, showed no change in boiling range or color.

Accordingly, an attempt was made to separate the acids of elm seed oil by means of the lead salts, using as solvents mixed amylenes, pentene-2 and low-boiling petroleum ether. The results obtained follow (Table 1):

TABLE I.

Efficiency of Separation of Lead Salts by Petroleum Ether and Amylenes.

Solvent	Solid Acids Yield Pct.	Solid Acids Iodine No. (Wijs)	Liquid Acids Yield Pct.	Liquid Acids Iodine No. (Wijs)
Petroleum ether	72.68	21.11	11.32	67.90
Mixed amylenes	65.55	9.92	43.44	....
Pentene-2	68.01	9.58	20.20	67.93

It will be observed, in the case of the two amylenes, that the sum of the solid and liquid acids is greater than the amount of total acids (91.56 per cent) in the original oil. The liquid fraction had a strong odor similar to that of burning oil. On conversion of the liquid acids to soaps and extraction with petroleum ether, the weight of the fraction was greatly reduced. Apparently the lead soaps catalyze the polymerization or oxidation of the amylenes to non-volatile compounds. No oxidation was apparent in the case of the petroleum ether separation, and the amount of total acids recovered was more nearly equal to the amount actually present.

In the next set of experiments, the free fatty acids were dissolved in amylene, and ammonia gas was passed into the solution. In this manner the ammonium salts were formed under anhydrous conditions, and the possibility of double salt-formation eliminated by the use of a monovalent ion. The resulting flocculent precipitate held up a considerable amount of the solvent. The degree of separation seemed to be better than that obtained with petroleum ether, but was not as good as that obtained with either of the amylenes with lead salts (Table 2).

TABLE II.

Separation of Ammonium Salts by Amylenes.

Solvent	Solid Acids Yield Pct.	Solid Acids Iodine No.	Liquid Acids Yield Pct.	Liquid Acids Iodine No. (Wijs)
Pentene-2*	67.00	16.39	22.39	59.29
Mixed amylenes**	63.90	....	28.31	....

*50 cc. cooled to 0°.
**100 cc. cooled to —15°.

By the use of calcium salts, a solid fraction was obtained having an iodine value of 18.09 and a liquid fraction having an iodine value of only 50.93.

The low-temperature crystallization procedure of DeGray and DeMoise[3] was also tried, using both petroleum ether and pentene-2, at —50° and at —70° (Table 3).

TABLE III.

Low Temperature Crystallization of Fatty Acids.

Solvent	Temperature °C.	Solid Acids Yield Pct.	Solid Acids Iodine No. (Wijs)	Liquid Acids Yield Pct.	Liquid Acids Iodine No. (Wijs)
Petroleum ether	—50°	37.29	....	59.74	....
Pentene-2	—50°	45.15	....	53.57	....
Petroleum ether	—70°	77.40	13.68	21.12	76.26
Pentene-2	—70°	49.13	5.54	47.25	50.49

The use of the DeGray method at a temperature of —70° yielded high results for the recovery of saturated acids, but is not applicable at —50° for the determination of saturated acids in oils containing capric acid and lower fatty acids. After subtracting the unsaturated acids from the solid-acid fraction, the recovery of saturated acids was 62.2 per cent, which is 10.0 per cent less than the known amount.

The use of chemical methods of separation has not found great favor, because the unsaturated acids either are destroyed or their structure is changed so that they are not available for further examination or identification.

By the method of Bertram[2], the most satisfactory from a quantitative standpoint, the saturated acids are oxidized to dibasic acids and lower monobasic acids. These are eliminated by the solubility of their magnesium salts in water. The method is sufficiently sensitive for the detection of the presence of 0.5 per cent saturated acids. However, in the presence of saturated acids lower than lauric acid, or of unsaturated acids which yield lauric or higher acids on oxidation, the method is not applicable.

The reaction of sulfuric acid with unsaturated acids was used by Twitchell,[8] who found that the reaction product is insoluble in petroleum ether. On treatment of the reaction product with water, a part of the sulfonated acid is converted to material soluble in petroleum ether. Twitchell therefore used 85-per cent acid, and extracted the reaction mixture without further dilution. No constants were given for the recovered saturated acids, but the melting points indicated a mixture of stearic and palmitic acids. Lewkowitsch,[4] however, criticized the method adversely claiming that the amount of reaction is influenced by the time of contact of the fatty acids with the acid. Again, no constants were given in support of the conclusions.

Alessandri[1] and co-workers reported that nitroso compounds add to unsaturated compounds. If *p*-nitrosodimethylaniline would react in such a manner with the unsaturated acids, it should be possible to introduce the basic amino group into the molecule, and thus make possible extraction of the product by dilute acid. Attempts were made to carry out this reaction on a quantitative basis, but the reaction product was found to be insoluble in dilute acid.

Summary

None of the procedures tried gave quantitative recoveries of saturated acids. The results obtained by the lead salt-amylene mthod were better than those obtained with lead salts and petroleum ether. Unsaturated acids could not be determined by the amylene procedure, because of the formation of non-volatile polymerization products from the solvent. The use of ammonium and calcium salts did not lead to a successful separation. An attempted chemical separation by means of *p*-nitrosodimethylaniline was unsuccessful because of the insolubility of the reaction product in dilute acid.

REFERENCES

(1) Alessandri, L., Gazz. chim. ital., *51*^{2}, 129 (1921).
(2) Bertram, S. H., Z. Unters. Lebensm., *55*, 179 (1928).
(3) DeGray, R. J. and DeMoise, A. W., Ind. Eng. Chem., Anal. Ed., *13*, 22-4 (1941).
(4) Lewkowitsch, J., Analyst, *25*, 54 (1900).
(5) Schuette, H. A. and Lunde, C., Oil and Soap, *13*, 12-13 (1936).
(6) Stillman, R. C. and Andrews, J. T., Oil and Soap, *14*, 257 (1937).
(7) Twitchell, E.. J. Am. Chem. Soc., *17*, 289-295 (1895).
(8) Twitchell, E., J. Soc. Chem. Ind., *16*, 1002 (1897).
(9) Twitchell, E., Ind. Eng. Chem., *13*, 806-07 (1921).