

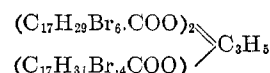
means of separating oil bromides from the reaction mixture, and the volatility of ether proved no drawback.

2—Alcohol (sp. gr. 0.820) used as a final wash liquor removes ether, and yields oil bromides as a loose granular powder when dried.

3—The Stepanow-Bacon method was found to be the most satisfactory and accurate of the methods tried for the estimation of bromine in oil bromides.

4—The properties of the crude oil bromide are summarized,

and its composition is suggested to be mainly dillinenin-linolin bromide



5—A method is given, based on the results of this investigation, which should ensure a maximum yield of oil bromide of maximum purity, and with small experimental error.

The Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution¹

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If a hot alcoholic solution of a mixture of fatty acids, such as is obtained from an ordinary fat or oil, is treated with an alcoholic lead acetate solution, also hot, there is no precipitation at first; but on cooling, the lead salts of the solid acids precipitate in a crystalline form, which can be filtered with great rapidity and ease. This simple method of direct precipitation of solid fatty acids was long ago employed by Jean to separate a portion of the liquid acids and to obtain their iodine value in the examination of lard. It does not seem to be commonly used to separate and estimate the solid fatty acids. The present author, however, much prefers it to the well-known lead-salt-ether method, and has briefly referred to it in some previous publications.

SOLUBILITIES OF LEAD PALMITATE AND MYRISTATE

The following experiments were made to test the accuracy of the results obtained by this method:

A solution of pure palmitic acid in hot 95 per cent alcohol was treated with an excess of lead acetate dissolved in hot alcohol. This precipitated on cooling and was allowed to cool further over night to a temperature of 16.5°C. It was then filtered and washed with 95 per cent alcohol. From the precipitate 98.8 per cent of the palmitic acid was recovered.

One hundred cc. of the filtrate, on decomposing with dilute nitric acid and collecting with ether, yielded 0.010 g. of palmitic acid; and 100 cc. of the washings, 0.004 g. of palmitic acid. This shows a sufficient insolubility of lead palmitate, for analytical purposes, in the filtrate, which contains lead acetate and acetic acid, and in the washings, which consist of 95 per cent alcohol.

The same experiment with pure myristic acid showed a solubility of lead myristate at 12°C., corresponding to 0.0175 g. of myristic acid in 100 cc. of the filtrate, and of 0.0110 g. in 100 cc. of the washings.

A slight impurity of the palmitic and myristic acid would have a considerable effect on the above results, so the solubility found in this way must be considered as a maximum.

The solubilities of lead laurate, eruceate, or iso-oleate have not been determined in this manner; but in most fats and oils palmitic acid would be the solid acid forming the most soluble lead salt, those of the higher saturated acids being less soluble.

EFFECT OF LIQUID FATTY ACIDS

As it seemed possible that the solubility of lead palmitate might be considerably increased by the presence in the solution of the liquid acids found in most fatty acid mixtures, and as the author knew of no way to prove directly the presence or absence of small quantities of solid fatty acids in the liquid acids of the filtrates, the following indirect method was used:

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The fatty acids of cottonseed oil contain about 25 per cent of a solid acid, which is almost pure palmitic acid. A hot alcoholic solution of the cottonseed oil fatty acids was precipitated as above with lead acetate *insufficient* to combine with all the palmitic acid. On cooling to 22°, filtering, and adding to the filtrate a few drops of a dilute alcoholic solution of sulfuric acid, a mere trace of lead was found, while the filtrate obtained after cooling the liquid to 16° contained no lead that could be detected with alcoholic sulfuric acid, showing that, with palmitic acid in excess, lead palmitate is practically insoluble at 16° in 95 per cent alcohol containing liquid fatty acids, palmitic acid, and a small amount of acetic acid; and it seems probable that, with lead acetate in excess, the lead palmitate would be equally insoluble.

The same experiment was performed with fatty acids containing iso-oleic acid. Sufficient lead acetate was used to combine with all the stearic and palmitic acids, but not enough to combine with all the iso-oleic acid. At 13° the filtrate contained the merest trace of lead, showing that lead iso-oleate is practically insoluble under these conditions.

Though the liquid fatty acids can be separated fairly free from solid acids, it has hitherto been found impossible to obtain the solid acids free from liquid acids, either by the method herein described or by the old lead-salt-ether method. Lewkowitsch¹ states that the iodine value of the solid fatty acids obtained by the latter method will, as a rule, be in the neighborhood of 10, provided there is no erucic acid, etc., present, and he quotes a table of Tortelli and Fortini, in which the solid acids of cottonseed oil are given as having an iodine value of 19! If our object were only to determine the amount of solid acids in a mixture, a rough correction might be made for this iodine value; but it is generally very desirable to obtain the solid acids in a pure state so that, for instance, their neutralization value (mean combining weight) can be exactly determined, also their melting points, etc., and finally so that if they have an iodine value this shall indicate not an imperfect separation of liquid acids, but shall prove the presence of *unsaturated solid fatty acids*.

It has been found in using the method described in this paper that the solid acids separated from the lead salt precipitate will have an iodine value generally ranging from 3 to 10 per cent, and no amount of washing of the precipitate will lower this figure. Even ether, in which lead oleate, linolate, etc., are soluble, will wash practically nothing from the precipitate which has been exhausted with alcohol. Evidently there is formed a lead salt containing liquid fatty acid which is quite insoluble in alcohol containing acetic acid and in ether.

¹ "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed. 1, 552.

This residue of liquid acids can, however, be removed from the solid acids by dissolving the latter in alcohol and reprecipitating with lead acetate; or more simply by removing the washed first precipitate from the filter, dissolving in boiling alcohol containing about 0.5 per cent of acetic acid and allowing this to cool, and precipitating again. Two precipitations in all are generally sufficient to reduce the iodine value of the solid fatty acids to 1 per cent or under, a trifling figure.

ANALYTICAL PROCESS IN DETAIL

Weigh in a beaker as much of the fatty acid as is estimated to contain 1 to 1.5 g. of solid acids. In the case of a very liquid oil this amount will be about 10 g., while in the case of tallow it will be only 2 or 3 g. Dissolve in 95 per cent alcohol. Dissolve 1.5 g. of lead acetate in 95 per cent alcohol. The total alcohol for the two solutions should be about 100 cc. Heat both solutions to boiling and pour the lead acetate solution into the solution of fatty acid. Allow to cool slowly to room temperature, and then for several hours, preferably over night, to about 15°C. Filter and test the filtrate for lead with a few drops of an alcoholic solution of sulfuric acid. If there is no precipitate, showing that lead is not in excess, the analysis must be repeated, using less fatty acid or more lead acetate. Wash the precipitate with 95 per cent alcohol until a sample of the washings diluted with water remains clear. Transfer and wash the precipitate from the filter back into the beaker, using about 100 cc. of 95 per cent alcohol. Add 0.5 g. of acetic acid and heat to boiling. The precipitate will slowly dissolve. Allow to cool to room temperature and then to 15°C. as before. Filter and wash with 95 per cent alcohol as before. Transfer the precipitate by washing the filter paper with ether into the beaker. Add sufficient dilute nitric acid to decompose the lead salts. Pour and wash the whole mixture into a separatory funnel and shake. Wash with water until the washings are no longer acid to methyl orange. If a trace of nitric acid should remain with the ethereal solution it will act on the fatty acids in the subsequent drying. Transfer the ethereal solution to an evaporating dish, evaporate, dry, and weigh.

If desired larger quantities of material than those given above can easily be handled.

RESULTS OBTAINED BY METHOD

The figures of the following table are in accordance with the above directions. In each case two precipitations were made as described.

SAMPLE OILS	Weight Fatty Acid Grams	Lead Acetate Grams	Alcohol for Each Precip. Cc.	Weight Solid Fatty Acids Grams	Per Cent	Iodine Value of Solid Fatty Acids
No.						
1. Cottonseed	5	1.5	100	1.1565	23.13	0.72
2. Soy-bean	10	1.5	100	1.7010	17.01	0.85
3. Olive	10	1	100	1.0935	10.93	1.75
4. Peanut	20	3.5	300	3.3165	16.58	0.80
5. Cottonseed	20	4	200	4.8680	24.34	0.56
6. Lard	3	1.25	100	1.2005	40.02	0.58
7. Partly hydrogenated cottonseed	2.5	1.5	100	1.2655	50.62	42.21
8. Tallow	3	1.5	100	1.6085	53.62	4.38

The solid fatty acids of most of the fats and oils in this table have iodine values below 1 per cent.

Sample 7 is a partly hydrogenated cottonseed oil which would contain iso-oleic acid.¹ The iodine value of its solid fatty acids, 42.21, shows a large amount, $\frac{100 \times 42.21}{90} = 46.9$

per cent of an unsaturated solid fatty acid (iso-oleic acid). To confirm this figure, the solid acids were redissolved in alcohol and reprecipitated with lead acetate as before. The iodine value of the resulting solid acids was 40.07, only slightly below the value found above.

Sample 8 is a sample of beef tallow, the solid fatty acids of which have the comparatively high iodine value of 4.38. On redissolving these solid fatty acids in alcohol and reprecipitating, their iodine value was reduced only to 3.89. This would indicate the presence in tallow of a small amount of an unsaturated solid acid, of which, however, we have no other proof.

If in the above process insufficient lead acetate is used to precipitate all of the solid acids, the precipitation is fractional, and the solid saturated fatty acids of higher molecular weight come down first. In this case liquid acids are not carried down with the solid and a second precipitation is not required. For example:

Thirty g. of peanut-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 12°, yielded 1.6935 g. of solid acids having a mean combining weight of 317.

Thirty g. of olive-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 11°, yielded 1.3770 g. of solid acids having a mean combining weight of 266 and an iodine value of 0.79.

ORGANIZATION OF CHEMICAL SALESMEN

A movement to organize a national association of chemical salesmen was started at a recent meeting of sales representatives of every branch of the chemical industries held at the Chemists' Club. It was felt that there is a broad field for service for an organization composed of members of the sales and advertising staffs, manufacturer's sales agents and executive sales officers of companies in every branch of the chemical industry. It was the unanimous opinion of those present that such an organization should concern itself with the broad commercial problems whose solution would react to the benefit of the entire industry, and that the questions of prices or sales policies of individual companies should not be included. An Organization Committee was appointed, to arrange for a general meeting at the time of the Exposition. This committee was composed of the following: Fred E. Signer, chairman, Butterworth-Judson Corporation; William Haynes, secretary, Drug & Chemical Markets; C. F. Abbott, National Aniline & Chemical Co.;

The Technical Committee on Standardization of Petroleum Specifications held a meeting at the Bureau of Mines in Washington recently to consider a number of changes in the specifications used by the Government for the purchase of kerosene, gasoline, fuel and lubricating oils. Dr. N. A. C. Smith of the Bureau of Mines was chairman of the meeting, and Dr. T. G. Delbridge of the American Society for Testing Materials and the American Petroleum Institute represented the several engineering societies constituting the Advisory Board. It was decided to give further study to the new methods which have been approved by the American Society for Testing Materials before deciding upon their adoption. The methods include the following tests: corrosion, flash, distillation, sulfur, cloud and pour, saponification in place of fatty oil, water and sediment, precipitation, viscosity, and melting point.

¹ Moore, *J. Soc. Chem. Ind.*, 38, (1919), 3201