

insolubility in water and in alcohol, which makes the titration tedious. As an improvement on this, it seemed that an analogous compound might be more convenient as regards solubility, and the acid phthalates appeared worthy of examination.

The acid phthalate of potassium has not apparently been described. It is readily obtained by half-neutralization of a solution of phthalic anhydride and crystallizes nicely in hexagonal plates.

ACID POTASSIUM PHTHALATE

PREPARATION—50 g. resublimed phthalic anhydride are dissolved in about 200 cc. of water. The solution is exactly neutralized with a solution of about 60 g. of pure potassium hydroxide in an equal amount of water; 50 g. more of anhydride are then added, and the heating continued until all crystals are dissolved. The solution is now made up to about 550 g. with water, filtered hot, if necessary, and let cool, with continuous agitation to promote the formation of small crystals. When cold, the latter are filtered by suction or centrifuge. The yield is about 125 g. The product is recrystallized from 300 cc. of hot water and dried at 110°.

The salt is anhydrous $\text{KHC}_8\text{H}_4\text{O}_4$ with mol. wt. 204. It is soluble in 10 to 11 parts of water at ordinary temperatures, and in about 400 parts alcohol.

This compound seems to approximate the ideal substance, as shown by the following facts:

1—As regards purity, the sublimed anhydride is an admirable raw material and not expensive. Recrystallization of the salt is hardly necessary as the impurities derived from the alkali used should be minimal.

2—The salt is stable, anhydrous, not hygroscopic.

3—The solubility in water is sufficient.

4—The molecular weight is higher than that of any compound so far proposed, except picric acid.

5—It behaves like a monobasic acid, and can be titrated with all desirable sharpness.

6—It is colorless.

7—The writer has found it to work well in practice.

The acid phthalate of sodium was obtained by Wislicenus¹ as a by-product, and described as glassy, prismatic crystals, containing $2\text{H}_2\text{O}$. Salzer,² however, reports the salt as anhydrous. It is easily prepared in the manner described for the potassium salt, substituting sodium hydroxide or carbonate. In all cases, however, the writer found the fine transparent prisms to contain $\frac{1}{2}\text{H}_2\text{O}$. The salt is soluble in about 9 parts water at 25° and analyzed for moisture as follows:

Wt. of salt Grams	TREATMENT	Time Hrs.	Loss in Weight Gram	Per cent
5 (air dry)	Desiccator	115	0.0055	0.11
	Heated at 50° C.	24	0.0070	0.14
	Heated at 100–110° C.	12	0.2410	4.82
1.97 (air-dry)	Heated at 110° C.	12	0.0950	4.82
Moisture calculated for $\text{NaHC}_8\text{H}_4\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$				4.57

The salt is thus fairly stable up to 50°; at 100–110° the crystals lose $\frac{1}{2}\text{H}_2\text{O}$ and become opaque, but retain their prismatic form. This anhydrous salt may

¹ *Ann.*, **242**, 89.

² *Ber.*, **30**, 1496.

be used as a standard, but the potassium salt seems preferable.

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THE INFLUENCE OF HYDROXY ACIDS AND LACTONES UPON DETERMINATIONS OF THE CHEMICAL CONSTANTS OF FATTY ACIDS

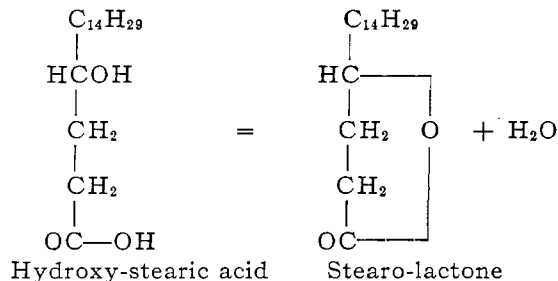
By C. A. BROWNE

Received October 6, 1914

The recent paper by Holland¹ upon "The Determination of the Acetyl Number of Oils, Fats, Etc.," recalls former discussions by Lewkowitsch, Benedikt and others regarding the value of the acetyl figure in the analysis of fatty acids. As the author has recently studied the determination of the acetyl number and other chemical constants in the insoluble acids of several decomposed butter fats, a few observations upon certain analytical data may possibly be of interest.

A serious difficulty, which often confronts the chemist in the analysis of fatty-acid mixtures, is the unstable character of the hydroxy-fatty acids. The latter, from their chemical behavior may be divided into two general classes: (1) the lactone-forming and (2) the non-lactone-forming hydroxy acids.

Lactone-forming hydroxy acids (more especially the γ acids) show a pronounced tendency, after being liberated, to form inner anhydrides. Thus γ -hydroxystearic acid, after separation from its salts or esters, passes immediately into stearo-lactone.



The non-lactone-forming hydroxy acids, on the other hand, do not possess the property of yielding inner anhydrides. The hydroxyl group of this class of fatty acids remains unchanged and, in distinction from the hydroxyl group of the lactone-forming acids, is free to react with acetic anhydride during acetylation.

This difference in properties of the two classes of hydroxy-fatty acids has frequently been disregarded by chemists in their treatment of the subject. It is evident, however, that this factor must play at times an important part in the analysis of complex fatty acid mixtures.

INFLUENCE OF HYDROXY-FATTY ACIDS AND LACTONES ON DETERMINATIONS OF THE ACID, SAPONIFICATION AND ETHER NUMBERS

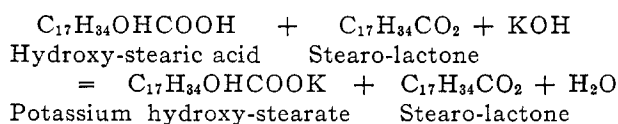
The insoluble acids prepared from the ordinary normal animal fats show usually but little difference between the acid and saponification numbers, the ether number in such cases being practically zero.

¹ *THIS JOURNAL*, **6** (1914), 482.

In the case, however, of oxidized and decomposed fats, which contain hydroxy compounds, the formation of lactones in the mixture of fatty acids causes a depression in the acid number and an increase in the saponification and ether numbers. This can best be understood by taking a specific example.

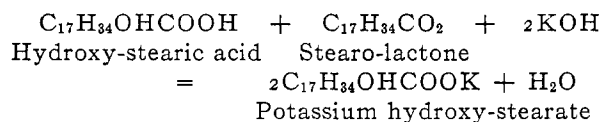
Hydroxy-stearic acid, $C_{17}H_{34}OHCOOH$, of molecular weight 300.288 requires for neutralization and saponification 56.108 molecular parts of KOH. The milligrams of KOH necessary to neutralize and saponify 1 g. of hydroxy-stearic acid are then $56108 \div 300.288 = 186.85$, the acid and saponification number.

If we take a mixture consisting of one molecular part of hydroxy-stearic acid and one molecular part of stearo-lactone the reaction upon neutralization with KOH would be



In other words 582.560 molecular parts of the mixture would require for neutralization 56.108 molecular parts of KOH. The acid number of the mixture is then $56108 \div 582.560 = 96.31$.

If we saponify the same mixture with KOH, the formula for the reaction would be



That is, 582.560 molecular parts of mixture would require for saponification 112.216 molecular parts of KOH. The saponification number of the mixture is then $112216 \div 582.560 = 192.62$.

It is thus seen that if one-half of a sample of hydroxy-stearic acid should undergo lactonization the acid number would be depressed from 186.85 to 96.31 and the saponification number increased from 186.85 to 192.62. The original ether number of zero would become $192.62 - 96.31 = 96.31$.

The occurrence of fatty acids which show a higher saponification than neutralization value has been frequently reported. Tortelli and Pergami¹ give a long list of fatty acids from various sources which show striking differences of this kind, these differences being usually found to increase with the age of the sample. Obviously with these differences in the acid and saponification numbers similar differences will be produced in the calculations of the mean molecular weights of the fatty acids.

Lewkowitsch² has also determined the acid and saponification numbers of mixed fatty acids and his results in general confirm the figures of Tortelli and Pergami. The general explanation of the differences, according to Lewkowitsch, is the occurrence of hydroxylated fatty acids which subsequently undergo dehydration with formation of lactones.

A few of the results obtained by Tortelli and Pergami

¹ L'Orosi, 1901, 1; Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. 1, pp. 419-421.

² Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. 1, p. 421.

and by Lewkowitsch are given in Columns I to V of Table I. Two determinations made by the author upon the insoluble acids of decomposed butter fat are also included for comparison.

TABLE I

Source of insoluble fatty acids	I Acid No.	II Mol. wt. from I	III Sapon. No.	IV Mol. wt. from III	V Diff. II-IV	Mol. wt. original lactone-free acids
TORTELLI AND PERGAMI						
Linseed oil—3 yrs.	191.5	292.8	205.4	273.2	19.6	274.4
Cottonseed oil—2 1/2 yrs.	194.3	288.7	204.5	274.3	14.4	275.3
Cherry kernel oil	191.3	293.2	213.7	262.5	31.7	264.4
Olive oil—3 yrs.	194.5	288.4	200.9	279.1	9.3	279.9
LEWKOWITSCH						
Tung oil	181.3	309.5	198.7	282.3	27.2	284.0
Peach kernel oil	196.8	285.0	205.0	273.6	11.4	274.4
Olive oil	200.9	279.2	200.9	279.2	0.0	279.2
Lard	196.0	286.2	205.1	273.5	12.7	274.4
BROWNE						
Butter fat—17 yrs.	211.3	265.5	219.6	255.5	10.0	256.3
Butter fat—17 yrs.	209.4	267.9	218.0	257.3	10.6	258.1

CALCULATION OF THE MEAN MOLECULAR WEIGHT OF INSOLUBLE FATTY ACIDS

The customary method of calculating the mean molecular weight of insoluble fatty acids by dividing 56108 by the acid number has caused many erroneous reports of this constant to appear in the literature. In the case of fatty acids which contain lactones the calculation of the mean molecular weight from the saponification number of the insoluble acids is much more accurate but is still incorrect since the weight of fatty acids taken for analysis has not been corrected for the loss in water which has resulted from formation of lactones. The correction for this loss in weight can be made as follows:

The ratio between the weight of water lost by formation of lactones and the weight of KOH required to saponify lactones is represented by

$$\frac{H_2O}{KOH} = \frac{18.016}{56.108} = 0.3211.$$

Let a be the acid number and s the saponification of a mixture of fatty acids; then the grams of KOH required to saponify the lactones in 1 g. of fatty acids equal $0.001(s - a)$ and the weight of water lost by dehydration is $0.003211(s - a)$. The saponification number of the fatty acids before lactone formation

would then be $\frac{s}{1 + 0.003211(s - a)}$ which divided into 56108 would give the mean molecular weight (m) or

$$m = \frac{56108 + 18.016(s - a)}{s}$$

It was by this formula that the molecular weights of the original lactone-free acids in Table I were calculated. While the values thus found do not greatly differ from those calculated from the saponification numbers there might arise instances where the errors by the latter method would be of considerable importance.

INFLUENCE OF HYDROXY ACIDS AND LACTONES ON DETERMINATION OF THE ACETYL NUMBER

It was one of the services of Lewkowitsch to call the attention of chemists to the necessity of determining the acetyl constant of fatty acids by a direct estimation of the acetic acid. He showed that the original method of Benedikt and Ulzer, by which the acetyl number was estimated by taking the difference

between the acid and saponification numbers of the acetylated fatty acids, usually gave too high results. This error was explained by Lewkowitsch as being due to the conversion of a part of the fatty acids during acetylation into anhydrides of the general formula $(\text{RCO})_2\text{O}$: the latter by not becoming completely hydrolyzed during the subsequent washing cause a depression in the acetyl-acid number with a consequent increase in the acetyl-ether number. As examples of the effects of anhydride formation Lewkowitsch¹ states that he obtained the following acetyl values: palmitic acid 82.6, stearic acid 82.29, capric acid 174.00, lauric acid 132.49. These high results, however, must have been due to some unusual condition of acetylation as no such values are obtained under the conditions described by Benedikt and Ulzer for their method.

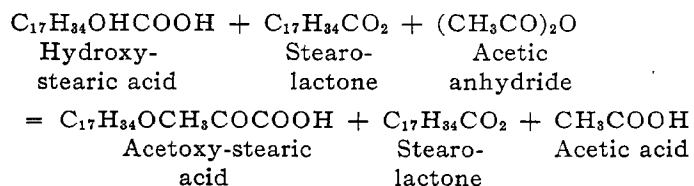
The errors of estimating the acetyl constant of fatty acids by taking the difference between the acid and saponification numbers of the acetylated acids were also recognized by Benedikt and Ulzer.² These authorities took the view, however, that, since fatty acids which contained no hydroxyl groups showed practically the same acid number before and after acetylation, the formation of fatty anhydrides of the formula $(\text{RCO})_2\text{O}$ was not the real cause of the error. Benedikt and Ulzer attributed the discrepancies rather to the formation during acetylation of inner anhydrides

or lactones of the general formula $\text{R} \begin{array}{l} \diagup \text{O} \\ | \\ \diagdown \text{CO} \end{array}$, which

would cause a decrease in the acetyl-acid number and an increase in the acetyl-ether number. Since, however, this increase in the acetyl-ether number is due primarily to hydroxy acids which have undergone lactonization, the acetyl-ether number would still remain a fairly accurate measure of the hydroxy acids which were originally present.

As for the lactones which might occur in the mixed fatty acids and would also cause an increase in the acetyl-ether number, Benedikt and Ulzer³ subtract the ether number due to such lactones from the acetyl-ether number and call the remainder the true acetyl number (Reine Acetylzahl).

A clearer idea of the various questions involved may be secured if we take again the previous example of an equimolecular mixture of hydroxy-stearic acid and stearo-lactone. The action of acetic anhydride upon such a mixture would be

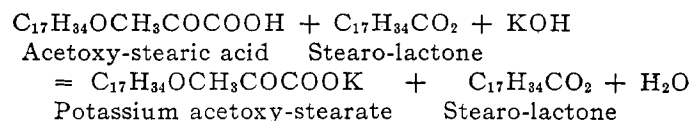


When the acetylated acids are neutralized with KOH, as in the determination of the acetyl acid number, the reaction proceeds as follows:

¹ Lewkowitsch, *J. Soc. Chem. Ind.* (1890), p. 660.

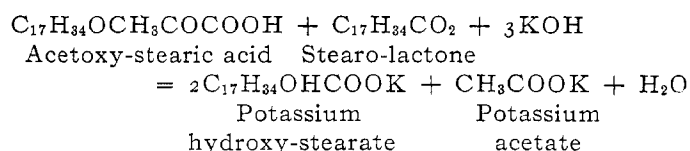
² Benedikt-Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 179.

³ Benedikt and Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 650. In the sentence "Davon ist die constante Verseifungszahl in Abzug zu bringen" Verseifungszahl is obviously a misprint for Aetherzahl.



624.576 molecular parts of acetylated mixture require for neutralization 56.108 parts of KOH. The acetyl-acid number of the mixture would then be $56.108 \div 624.576 = 89.83$.

In case the acetylated mixture be saponified with an excess of KOH the reaction would be



The acetyl-saponification number of the acetylated mixture would then be $168324 \div 624.576 = 269.50$.

The acetyl-ether number (acetyl number of Benedikt and Ulzer) is then $269.50 - 89.83 = 179.67$.

The acetyl number of Lewkowitsch, *i. e.*, the mg. of KOH necessary to saponify the combined acetyl would be $56.108 \div 624.576 = 89.83$.

The relationship of the theoretical constants for the non-acetylated and acetylated mixture of hydroxy-stearic acid and stearo-lactone is shown in Table II:

Hydroxy-stearic acid and stearo-lactone	Acid No.	Sapon. No.	Ether No.	Acetyl No.	Lactone No.
Non-acetylated.....	96.31	192.62	96.31	...	96.31
Acetylated.....	89.83	269.50	179.67	89.83	89.83

The acid number of the acetylated mixture is lower and the ether and saponification numbers are higher than the similar constants of the non-acetylated product.

The lactone number, *i. e.*, the mg. of KOH necessary to saponify the lactones in 1 g. of acids is lower in the acetylated mixture.

If we subtract the ether number of the non-acetylated from the ether number of the acetylated mixture we obtain 83.36—the so-called "Reine Acetylzahl" of Benedikt and Ulzer; this value, owing to the non-correction for increase in weight of the fatty acids during acetylation, is less than 89.83—the true acetyl number of Lewkowitsch.

Theoretically, the increase in weight of fatty acids during acetylation is expressed by the ratio of the acid number of the non-acetylated divided by the acid number of the acetylated acids.

Let a be the acid no. of the non-acetylated acid.

Let α be the acid no. of the acetylated acid.

Let s be the saponification no. of the non-acetylated acid.

Let σ be the saponification no. of the acetylated acid.

Let e be the ether no. of the non-acetylated acid.

Let ϵ be the ether no. of the acetylated acid.

Let x be the acetyl no. on basis of non-acetylated acid.

Let ξ be the acetyl no. of the acetylated acid.

The ratio of KOH used in saponifying acetyl to the increase in weight of fatty acids during acetylation is expressed by:

$$\frac{\text{C}_2\text{H}_2\text{O}}{\text{KOH}} = \frac{42.016}{56.108} = 0.7488$$

If x be the true acetyl number on the basis of the non-acetylated acids, the g. of KOH necessary to saponify the acetyl after acetylating 1 g. of mixed acids would be $0.001x$. The weight of the 1 g. of acids after acetylating would then be $1 + 0.0007488x$.

Then

$$\frac{x}{1 + 0.0007488x} = \xi$$

$$\text{and } x = \frac{\xi}{1 - 0.0007488\xi} \quad \text{I}$$

$$\frac{a}{1 + 0.0007488x} = \alpha \quad \text{II}$$

Substituting I in II we obtain

$$\xi = \frac{a - \alpha}{0.0007488a} \quad \text{III}$$

The small denominator in Formula III causes a very great multiplication of any experimental errors. The following methods of calculation are less objectionable.

Theoretically, the lactone number of the acetylated acids equals $\frac{e\alpha}{a}$, then the acetyl number of the acetylated acids is found by the equation

$$\xi = \epsilon \frac{e\alpha}{a} \quad \text{IV}$$

Since $e = s - a$ and $\epsilon = \sigma - \alpha$, we obtain by substituting these values for e and ϵ in Equation IV

$$\xi = \sigma - \frac{s\alpha}{a} \quad \text{V}$$

The determination of the acetyl number in the insoluble acids of two decomposed butter fats was carried out by the author both according to the original Benedikt-Ulzer method and the improved method of Lewkowitsch. The determinations were all made upon the same weighed sample of acetylated acids.

After determining the acetyl acid and acetyl-saponification numbers, the calculated amount of standard acid was added to unite with all the alkali combined as potassium soaps. The insoluble acids were filtered off and the free acetic acid in the filtrate determined by titration.

The insoluble acids from the determination of the acetyl numbers were washed with boiling water, dried, and the acid and saponification numbers of the de-acetylated product determined. A summary of the results is given in Table III.

TABLE III—INSOLUBLE FATTY ACIDS FROM BUTTER FATS

No.		Acid No.	Sapon. No.	Ether No.	Acetyl No.	Lactone No.
1	Non-acetylated.....	211.32	219.59	8.27	...	8.27
1	Acetylated.....	194.71	238.88	44.17	37.04	7.13
1	De-acetylated.....	201.52	209.13	7.61	...	7.61
2	Non-acetylated.....	209.45	218.02	8.57	...	8.57
2	Acetylated.....	196.21	238.65	42.44	35.72	6.72
2	De-acetylated.....	205.00	212.35	7.35	...	7.35

The same relationship is noted between the constants of the non-acetylated and acetylated acids as between the theoretical constants of Table II.

It will be instructive to compare the acetyl numbers actually determined with the numbers calculated by Formulas III and IV.

The calculation from the acid numbers of the non-acetylated and acetylated acids, using Formula III, gives for Sample 1 an acetyl number of 105.00 and for Sample 2 an acetyl number of 84.40. These calculated values, which are several times those actually found, show a depression in the acid number of the acetylated acids greater than that, due to the increase in weight from acetylation, a depression of 1 in the acid number making a difference of about 7 in the acetyl number as thus calculated.

This excessive depression of the acid number of the acetylated acids, as already stated, was explained by Lewkowitsch as being due to the formation of fatty anhydrides, and by Benedikt and Ulzer as being due to the formation of lactones. There is, however, one other possibility, and that is the decomposition of some of the fatty acids during acetylation. Table III shows that the constants of the de-acetylated acids are uniformly lower than those of the acids before acetylating and this would indicate the formation of small amounts of decomposition products by the boiling acetic anhydride. The much darker color of the de-acetylated acids is an additional indication of such decomposition. If the formation of fatty anhydrides or lactones were the sole cause of the depression in the acetyl-acid number, the constants of the de-acetylated and non-acetylated acids should agree.

If the calculation of the acetyl number be based upon the acid numbers of the de-acetylated and acetylated acids we obtain, using Formula III, for Sample 1 an acetyl number of 45.06 and for Sample 2 an acetyl number of 57.26. The values thus calculated approach much nearer those actually found; there still remains, however, a marked discrepancy which may be due to the dehydration of a small amount of fatty acids during acetylation with formation of anhydrides or lactones.

If the calculation of the acetyl number be based upon the ether or saponification numbers, using Formulas IV or V, experimental errors are less magnified than by use of Formula III and a much closer agreement in the results is obtained.

	Lactone No.		Acetyl No.	
	1	2	1	2
From ether no. of non-acetylated acids.....	7.62	8.03	36.55	34.41
From ether no. of de-acetylated acids.....	7.36	7.03	36.81	35.41
Direct determination.....	7.13	6.72	37.04	35.72

As was the case with Formula III, the calculations from the constants of the de-acetylated acids agree more closely with the actual determinations than the calculations from the constants of the non-acetylated acids.

A comparison of the lactone numbers shows the determined values to be lower than those calculated, whereas if lactones or anhydrides were formed during acetylation the determined lactone values might be expected to be higher. The contradiction may perhaps be due to the fact that some of the lactones in the fatty acids exist in an unstable δ or other form, and by the action of the acetic anhydride become acetylated with the hydroxy acids; these decomposed lactones during the drying of the de-acetylated acids

might again be reformed in whole or in part. In confirmation of this view it might be mentioned that Lewkowitsch¹ obtained pronounced acetyl values with certain substances of a lactonic nature. The discrepancies, however, in view of the limitations which attend an indirect method of calculation, are not great enough to warrant making any sweeping conclusions. Further investigations upon the fatty acids from other sources are needed before this and other doubtful points can be decided. Changes during acetylation through the partial destruction of fatty acids, through the formation of small amounts of fatty anhydrides or lactones, and through the slight acetylation of preexisting lactones, may, however, be considered as among the possible causes of disturbances in the normal process of acetylation.

Finally, it must be admitted that there is much truth in the argument that, since the lactones in a mixture of fatty acids are derived from preexisting hydroxy acids, the acetyl number of Benedikt-Ulzer is a truer measure of the original hydroxyl content of fatty acids than the acetyl number of Lewkowitsch. Thus γ -hydroxy-stearic acid in the glyceride molecule can be acetylated and would show an acetyl number by the method of Lewkowitsch, whereas, the separated fatty acids would show no acetyl number on account of the formation of stearo-lactone.

The acetyl value of a mixture of fatty acids may be calculated back to the condition preceding lactone formation in the following way:

The ratio between KOH used to saponify lactones and the increase in weight which the acids would undergo from acetylation of lactones is represented by

$$\frac{C_2H_4O_2}{KOH} = \frac{60.032}{56.108} = 1.07$$

Let ϵ and ξ be respectively the acetyl-ether and true acetyl numbers, then $\epsilon - \xi$ = the lactone number and $0.001(\epsilon - \xi)$ = the g. of KOH required to saponify the lactones in 1 g. of acetylated acids. $1.07 \times 0.001(\epsilon - \xi) = 0.00107(\epsilon - \xi)$ = the increase in weight of 1 g. of acetylated acids if the lactones present were also acetylated.

The original acetyl number, calculated to the acetylated hydroxy acids before lactone formation, then

$$= \frac{\epsilon}{1 + 0.00107(\epsilon - \xi)}$$

In the author's experience a combination of the Benedikt-Ulzer and Lewkowitsch methods for determining the acetyl number has been found to throw most light upon the chemical changes which have taken place in insoluble fatty acids as a result of oxidation. The determinations of acid, saponification, ether, acetyl and lactone numbers can all be performed upon one weighed sample of acetylated acids and the results enable the chemist to estimate the relative distribution of the free and lactonized hydroxy acids.

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¹ Lewkowitsch, *Analyst* (1899), 339.

A NEW METHOD FOR THE DETERMINATION OF UNSAPONIFIABLE MATTER APPLICABLE TO ETHER EXTRACTS, FATS, OILS AND WAXES¹

By J. B. RATHER²

Received October 27, 1914

Methods for the removal of unsaponifiable matter from fats and oils fall into two divisions:³ (1) Extraction of the soap solution with solvents, and (2) the extraction of the dried soap with solvents. The method here proposed differs from both of these general processes in that the fatty acids are removed from the unsaponified material by precipitation from ethereal solution.

Stellwaag⁴ in his work on the unsaponifiable matter in concentrated feeding stuffs and Fraps and Rather⁵ in their investigation on the unsaponifiable matter in hays have shown the need of a rapid and reasonably accurate method for the systematic removal of unsaponified matter in the determination of fats.

PRECIPITATION METHOD

The method used for the determination of unsaponifiable matter in ether extracts was adopted after considerable experimental work. The data on which it is based will be published in another place.⁶ The process, designated as the Precipitation Method, is as follows: Add 20 cc. of approximately 2 *N* alcoholic sodium hydroxide to a known amount of the sample (about 0.4 g.), and boil under a reflux condenser for one hour. Evaporate nearly to dryness and add 3.5 cc. glacial acetic acid, or its equivalent in weaker acetic acid. Add 50 cc. of redistilled ether and warm to dissolve the extract. Add 25 cc. water and warm a minute more. Transfer to a 500 cc. pear-shaped separatory funnel with a short neck and wash out the flask with 5 successive 20 cc. portions of ether, pouring the washings in the funnel. Turn the funnel on its side and shake gently. The two layers should now be clear and the aqueous layer nearly colorless. Draw off the lower layer into a 500 cc. Erlenmeyer flask. Add to the ethereal solution 10 cc. of warm 1 : 2 aqueous sodium hydroxide solution, turn the funnel on its side and shake gently. Allow the precipitate to settle, add 25 cc. warm water, hold funnel in vertical position and give rotary motion. Allow the two layers to separate, and draw off the clear aqueous solution into the Erlenmeyer flask, leaving any emulsion in the funnel. Repeat and then shake gently as above with 5 successive 30 cc. portions of cold water, allowing a short time for the two solutions to separate, and add the washings to the soap solution in the Erlenmeyer flask. Transfer the ethereal solution to a tared 200 cc. flask, evaporate or distil off the ether, and dry to constant weight in a steam oven at 100° C.

The following correction for fatty acids in unsaponified should be used for material high in fatty acids and low in unsaponified. Add 20 cc. of 0.2 *N* hydrochloric

¹ Abstracted by the author from Texas Experiment Station, *Bull.* 169.

² Under the general direction of G. S. Fraps, Chemist.

³ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Vol. I, p. 456-60.

⁴ *Landw. Versuch. Stat.*, 37, 148.

⁵ Texas Exp. Sta., *Bull.* 150.

⁶ *Loc. cit.*