SUMMARY

The saturated fatty acids of alfalfa seed oil were investigated with the purpose of discovering whether or not the reported existence of a heptadecanoic acid here could be substantiated. By the application of phase rule principles to the analysis of a fraction which constituted approximately 6.3 per cent of the oil, it was found that this fraction was in reality not margaric acid but an equimolecular mixture of palmitic and stearic acids. The presence of these two acids in alfalfa seed oil has not been previously reported. Indications of the presence of myristic acid and higher homolog(s) of stearic acid have been found, although conclusive proof is wanting.

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1938 Report of the Glycerin Analysis Committee American Oil Chemists' Society

FOR approximately forty years the compound $(C_3H_5O_3Cu\ Na)_2.3H_2O$ has been known as the reaction product of cupric hydroxide, sodium hydroxide and glycerol in alcohol water solution[1]. Various attempts have been made to utilize the solubility of this compound in a method for glycerol estimation, but until the publication of Bertram and Rutgers[2] no claim of success for such methods has been advanced.

In brief, Bertram and Rutgers Method consists in treating not more than 800 mg. glycerol in aqueous solution not exceeding 10 ml. volume, in a stoppered 100 ml. measuring flask, with 10 ml. 30% (w/v) NaOH, followed by 60 ml. EtOH (methylated spirit of 96-97% by vol. containing 5% MeOH may be used). After mixing, enough 10% (w/v) $CuCl_2.2\ H_2O$ alcoholic solution is added gradually, in small portions with thorough shaking, to produce a clearly visible, permanently undissolved precipitate of cupric hydroxide, after which the flask is filled to the mark with alcohol.

All of these operations are conducted at room temperature (20° C.). The well-mixed contents of the flask is centrifuged at about 1300 r.p.m. for 10 minutes, 50 ml. of the clear solution are pipetted into a 300 ml. Erlenmeyer flask and then are added in succession 100 ml. distilled water, 4.5N H_2SO_4 until a slightly acid reaction is obtained and then about 10 gms. KI. The mixture is titrated with O.1 N thiosulfate until a perfectly white color is obtained. 1 ml. O.1 N thiosulfate = 0.0001 mol. glycerol. A blank determination is made and subtracted from the sample titration. The value of the blank titration is quite constant and is due to the slight solubility of cupric hydroxide in the medium.

Bertram and Rutgers claim that this method may be adapted to the estimation of certain other hydroxylated compounds which must contain at least two hydroxyl groups in adjacent and favorable positions and must be soluble in dilute aqueous or alcoholic NaOH. From these considerations, as well as by experimental evidence, it may be seen that trimethylene glycol will not react but that some interference may be expected from polyglycerol ethers. NH_4 salts and sulfites interfere but are easily eliminated.

With the full realization that this method offers more potential advantages than any suggested in recent years, your committee decided to subject it to careful investigation. Although Bertram and Rutgers advise against the use of pure glycerol as a standard for the reason that "in the course of the purification process decomposition, condensation and polymerization to a slight extent may occur," it was thought advisable to test the method in a preliminary way upon a laboratory redistilled glycerol which, by commonly accepted standards, might be regarded as pure. As in previous years, a C. P. glycerin made from choice salt crude, was fractionated through an efficient column, under about 5 mm. pressure, the first and last portions, of about one-third each, being rejected and the middle portion, of constant boiling point, being accepted as of sufficient purity for our purpose. Before distribution to the committee this fraction was diluted to about 90% concentration in order to minimize weighing errors due to the excessively hygroscopic nature of pure glycerol. Members of the committee were provided with photostatic copies of Bertram and Rutgers' paper and requested to test the method in their own way upon this C. P. redistilled glycerin and on any other samples or by any other methods of appraisal deemed suitable.

The results of our tests so far indicate that the proposed procedure is more of a principle than a method of analysis. The average glycerol content of the redistilled sample, determined by pyknometer specific gravity and the Bosart and Snoddy table, is 89.31%. The average of all reported results on this sample by the Bertram Method is 88.32% based upon 43 actual determinations, with extreme variations ranging from 80.03 to 92.50%. Analyses made upon other distilled glycerin and upon a number of samples of crude glycerin show a similar divergence from accepted glycerol content obtained by specific gravity on distilled samples and analyses by the acetin method on crudes. A few trials were made upon refined natural oils, which may be regarded as practically pure triglycerides and are recommended by Bertram and Rutgers as standards. The glycerin yield of these samples showed much better agreement with the accepted value calculated from ester value, or determined by bichromate or pyridine-acetin analysis[3], though in several cases the deviation was considerably outside usual tolerances.

Members of the committee noted conflicts with the claims of Bertram

and Rutgers that the amount of glycerol taken for analysis up to 0.8 gram is without effect upon apparent glycerol content. There appears to be a distinct increase in glycerol percentage with increase in the size of sample taken, up to the prescribed limit, so the effect of concentration cannot be neglected. Formula 30, 3A and absolute ethyl alcohols were tried with about equal success. Isopropanol appears to be unsuitable due to the insufficient solubility of NaOH in this solvent. The accuracy of glycerin analyses upon refined oils appears to be enhanced by an increase in the water content of the reaction mixture.

Since the Bertram Method was published in June of this year and was not available in this country until July, it is obvious that such tests as have been made are only preliminary and justify no final opinion of its value as an analytical method for glycerin. The consensus of opinion of your committee seems to favor further work with this method which has such advantages of speed and ease of operation as commend it to the consideration of every chemist engaged in glycerin analysis.

The Glycerin Analysis Committee has had under consideration for several years the Methods of Crude Glycerin Analysis recommended by the International Committee. Our efforts to improve the absolute accuracy of the acetin method have been unsuccessful. Since these methods are in universal use commercially and have stood the test of over a quarter century, your committee has no hesitation in recommending their adoption as tentative methods of the American Oil Chemists' Society. These methods are to be found in the Journal of Industrial and Engineering Chemistry, Vol. 3, pp. 682-86 (Sept. 1911).

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A. O. C. S. GLYCERIN ANALYSIS COMMITTEE
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M. L. Sheely,
B. S. Van Zile,
C. C. Zeigler,
J. T. R. Andrews
(Chairman)

ABSTRACTS

Oils and Fats

Edited by
M. M. PISKUR and RUTH LINDAHL

PROCESSING OF PARAFFIN CARBONIC ACIDS IN THE SOAP INDUSTRY. Cl. Bauschinger. *Fette u. Seifen 45,* 629-30 (1938).

THE COMPOSITION OF A FAT ACID MIXTURE OBTAINED BY THE OXIDATION OF SYNTHETIC PARAFFIN. E. Jantzen, W. Rheinheimer and W. Asche. *Fette u. Seifen 45,* 613-5 (1938). The fatty acids were prepd. from Fischer-Tropsch paraffin. The characteristics were: solidification point 26.2°C, color yellow, sapon. no. 247.25, acid no. 244.2, I no. 4.86, OH no. 3.7, oxy acid non-detectable, unsapon. .29%. The compn. calcd. from Me-ester fraction technic was: $C_8H_{16}O_2$ — 0.2, $C_9H_{18}O_2$ — 1.6, $C_{10}H_{20}O_2$ — 4.1, $C_{11}H_{22}O_2$ — 8.0, $C_{12}H_{24}O_2$ — 11.9, $C_{13}H_{26}O_2$ — 13.50, $C_{14}H_{28}O_2$ — 14.30, $C_{15}H_{30}O_2$ — 14.8, $C_{16}H_{32}O_2$ — 10.9, $C_{17}H_{34}O_2$ — 7.50 and over C_{17} — 13.20%.

THE CARBONYL NUMBER IN FAT ANALYSES. W. Leithe. *Fette u. Siefen 45* 615-6 (1938). Carbonyl groups occur in oiticica oil and synthetic fat acids that are prepd. by oxidation of paraffins. Method for light colored samples: A 0.5-2 g. sample is heated for 2-3 mins. with 20 cc. hydroxylamine soln. (4 g. hydroxylamin-HCl, 80 cc. water, 800 cc. 95% alc. are dissolved and 600 cc. N/2 alc-KOH are added and the soln. filtered). Methyl orange is added and the soln. is titrated with N/2 HCl. A blank detn. is made on 20 cc. of hydroxylamine soln. CO-No. =

$$\frac{\text{(cc N/2 HCl for blank-cc. N/2 HCl for sample) } 28.1}{\text{wt. of sample}}$$

With highly colored samples the coloring matter is extd. with ether after the heat treatment; the ether ext. is washed with water; the water returned to the flask and titration and calcns. are made as described above. With pure compds. the results were close to the calcd. value. Oiticica oils gave CO-nos. between 105-115.

DETERMINATION OF THE CARBONYL NUMBER WITH SPECIAL CONSIDERATIONS TO ITS APPLICATION IN THE FAT FIELD. H. P. Kaufmann, S. Funke, and F. Y. Lin. *Fette u. Seifen 45,* 616-20 (1938). CO-no. can aid in the detn. of addns. of oiticica oils to other drying oils, detn. of ketonic constituents of essential oils, and detn. of licanic acid in oiticica oil. Together with other characteristics one can detn. the percentage compn. of a mixt. contg. licanic, eleostearic, linolenic, linoleic, oleic and satd. acids.

DETECTION OF HORSE FAT IN MIXTURES OF PORK, BEEF AND MUTTON FAT. Bruno Paschke. *Z. Untersuch. Lebensm. 76,* 476-8 (1938). Adulteration of fats with horse fat cannot be detected by the official methods. The author proposes a new method which depends on the amt. of linolenic acid present. The hexabromides found in fats were horse fat 41.2, pork fat 2.8, beef fat 3.0 and mutton fat 3.3 mg./g. The figures for the last three contg. 30% horse fat are 8 to 11. The addn. of 30% horse fat to pork, beef or mutton fat can be detected by detg. hexabromide no.

THE DETERMINATION OF THE UNSAPONIFIABLES. J. Grossfeld and K. Höll. *Z. Untersuch. Lebensm. 76,* 478-82 (1938). Methods for detn. of unsapond. matter in oils were investigated. By the usual methods 100% of added paraffins and about 27% of added cholesterol were separated. In order to increase the efficiency of cholesterol separation a new method is proposed. Briefly, after the sapon. with alcoholic-KOH the mixt. is dissolved in a fixed amt. of petroleum ether and the soap is removed by extn. with water. An aliquoted portion of the petroleum ether is evapd. in a tared container, dried and weighed. In tests, this method yielded detn. of 78% of the cholesterins and 100% of the paraffins.

THE OXIDATION PRODUCTS OF THE UNSATURATED ACIDS OF LINSEED OIL. L. C. A. Nunn and I. Smedley-