A Monoglyceride-Rich Tung Oil Product

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A method for preparing tung monoglycerides (1) by the reaction of tung oil with an excess of glycerol in the presence of sodium methoxide as the catalyst has been adapted to the preparation of large batches of material. Laboratory scale studies have shown that a product analyzing as containing up to 50% of tung monoglycerides is produced when the reaction is carried out at 150°C. for one hour with an excess of 1 mole of glycerol and 1% of sodium methoxide (based on oil weight). The data were applied successfully to three batchwise pilot-plant preparations using from 30 to 47 pounds of tung oil to produce a product containing from 32% to 45% tung monoglycerides. Unreacted glycerol was successfully separated from the product by centrifugation, with no water or salt solution washing, to give a product containing 1.5% to 3.5% free glycerol.

Difficulties were encountered in analyzing the product for monoglyceride, and it was found that the triene conjugation contributed to high results, However, there also appear to be components other than simple monoglycerides in the product which analyze as monoglycerides to give a falsely high value, as evidenced by differences found by analyses of the products before and after essentially complete hydrogenation.

In 1957, McKinney and Goldblatt (1) reported on two laboratory methods for preparing tung oil monoglycerides from raw tung oil. The products prepared consisted of mixtures of the mono-, di-, and triglycerides of tung oil with from about 32% to 78% being made up of monoglycerides. These mixtures proved to be effective fugitive emulsifiers, a type of product which should have utility in a number of applications.

To explore more fully the possible agricultural and industrial uses of the tung monoglyceride material, larger quantities were needed. While satisfactory for preparing small quantities of the product, neither of the laboratory methods reported was suited to direct upscaling. The first method consisted of reacting dry, raw tung oil with anhydrous glycerol in the presence of sodium methoxide as the catalyst and gave a product containing about 32% monoglycerides. To recover the product free of unreacted glycerol required that the reacted mixture be dissolved in about four volumes of ethyl acetate, washed three times with water, dried with sodium sulfate, filtered, and finally desolventized under reduced pressure at 65°C. In the second method reported, a modification of that of Mattil and Sims (2), the reaction between the oil and glycerol was carried out in solution in pyridine, also with sodium methoxide catalyst, and gave a product containing 78% monoglyceride. This method required the use of five parts of pyridine (by weight) for each part of oil and glycerol. Freeing the product from pyridine and unreacted glycerol required washing the mixture of pyridine and product with 50% hydrochloric acid solution several times, followed by a hot salt water wash, followed by drying at 100°C. under reduced pressure.

The first of the methods reported, i.e., the reaction of tung oil directly with glycerol with sodium methoxide as the catalyst, was chosen for modification in scaling up to produce the larger quantities of tung monoglyceride product needed. This method was chosen largely to avoid the use of the large quantities of expensive pyridine with its accompanying recovery and rectification problems. In addition it was hoped that the yields reported might be improved and that unreacted glycerol could be separated from the tung oil monoglyceride product and the product sufficiently purified by methods other than those described. This paper reports the data obtained in investigations which were carried out to accomplish the above objectives, together with the results of the application of the data in batchwise pilot-plant preparations to produce sizable quantities of the product.

Experimental

Materials. American-grown tung oil, containing (by spectrophotometric analysis) 74.1% total eleostearate, 71.8% α-eleostearate, no β-eleostearate, 1.8% free fatty acids, and 0.08% moisture was used in the work. The glycerol used was of synthetic origin and contained 0.23% moisture. The sodium methylate employed as the catalyst was commercial dry powder of 95% purity. The nitrogen used for blanketing was freed of oxygen and moisture by passing it successively through alkaline pyrogallol and a column of anhydrous calcium sulfate.

Equipment. Laboratory reactions were carried out in a mantle-heated 3-neck flask equipped with a high-speed agitator, thermometer, and ports for admitting and venting nitrogen. The pilot-plant preparations were conducted in a conventional closed, steam jacketed, stainless-steel vessel of 15-gallon capacity. Two centrifuges were employed for separation of the product and unreacted glycerol: a No. 3 International fitted with a No. 258 (24-inch diameter) head holding six 500-ml. bottles, and a continuous DeLaval Gyro unit.

Analytical Methods. Analyses for monoglyceride (3), and free and total glycerol (4) were by the periodic acid methods as described in the Official and Tentative Methods of the American Oil Chemists' Society (3). Hydroxyl content was determined by a modification of the method of West, Hoagland, and Curtis (5). *Alpha, beta,* and total eleostearate were estimated by the spectrophotometric method of Hoffmann *et al.* (6) and moisture was determined by the American Oil Chemists' Society modification of the Karl Fischer Method (7). Hydrogenation was carried out in Parr hydrogenation apparatus at room temperature with absolute ethanol as the solvent and palladium on charcoal as the catalyst.

Difficulties similar to those reported by McKinney and Goldblatt (1) were encountered in analyzing the tung oil products for monoglyceride, i.e., values for monoglycerides of more than 100% were found for some of the first samples analyzed. Adjustment of the

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sample weight to assure an adequate excess of periodic acid, plus the exercise of care in maintaining the periodic acid solution fresh and at full strength, made it possible to obtain analyses for monoglycerides which were reproducible. However, when the monoglyceride contents of the samples were plotted against their content of hydroxyl and compared with theoretical random distribution data for mixtures of tung oil mono-, di-, and triglycerides similar to those of Feuge and Bailey (8) for cottonseed oil monoglyceride preparations, it was found that for about half of the samples analyzed the hydroxyl content was greater than was required by theory, while for the remainder of the samples it was too low. The excess of hydroxyl over that required by theory could logically be attributed to the hydroxyl contributed by β-monoglycerides, in which the hydroxyls are not adjacent to each other and, therefore, are not determined by analysis with periodic acid. However there was no tenable explanation to account for those instances in which not enough hydroxyl was found, unless it could be shown that some component in the material was reacting to consume periodic acid during titration to give a falsely high monoglyceride content. It was theorized that perhaps the periodic acid, or the iodine liberated during analysis, was reacting with the highly active triene conjugated unsaturation of the tung oil to give falsely high values for monoglycerides. To check this theory samples of the tung oil and representative samples of the tung oil product, analyzed as ranging from 10% to 58% in monoglycerides, were hydrogenated to essentially complete saturation and analyzed for monoglycerides after hydrogenation. The monoglyceride determined in the hydrogenated samples was plotted against that found in the samples before hydrogenation to give the smooth curve of Figue 1.

As shown by the data, the tung oil analyzed as containing 6.9% monoglycerides, whereas none was found after hydrogenation. The product samples showed differences in monoglyceride content before and after hydrogenation ranging from 8.8 to 17.5, with the difference being greatest when the apparent monoglyceride content of the unhydrogenated sample was about 35%. It appears from the tung oil data that the conjugated unsaturation of the tung oil does react with the analytical reagents in such a way as to indicate a higher content of monoglycerides than is actually present. The evidence however also indicates that there are other components of this tung oil monoglyceride product which have a similar effect. When the monoglyceride determinations were corrected for the apparent monoglyceride content of the raw tung oil by deducting 6.9 from the value found for monoglycerides, satisfactory agreement with hydroxyl content was obtained, i.e., hydroxyl content either closely approached or exceeded that required by theory.

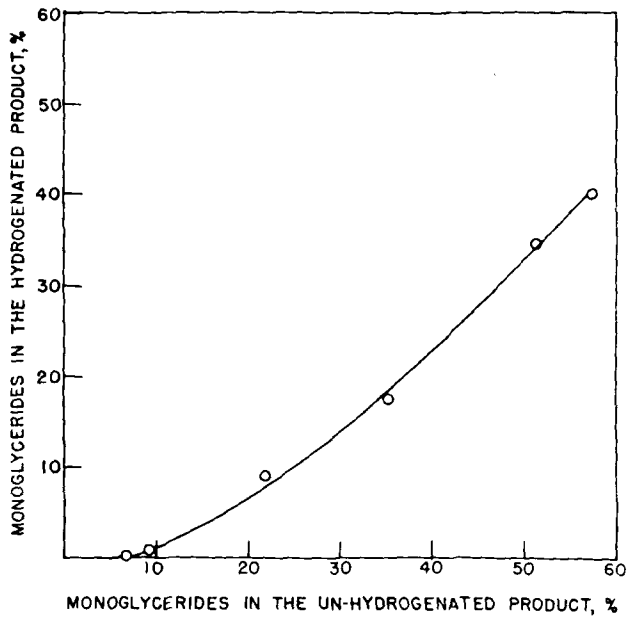

FIG. 1. The effect of hydrogenation on the apparent monoglyceride content of the product.

Comparison of the percentages of combined glycerol found in the products by analysis with the percentages calculated on the basis of random distribution showed none of the products analyzed as containing as much combined glycerol as was required by theory. Correction of the monoglyceride values by deducting 6.9 brought their combined glycerol content more nearly into agreement with theory; however values for combined glycerol continued to be somewhat low.

Because of the foregoing the authors have concluded that the materials determined in the tung oil products as monoglycerides by the periodic acid method are not simple monoglycerides alone. For this reason subsequent use of the term "tung monoglycerides" in this paper (including tables and figures) refers to the materials determined as monoglycerides by the periodate method of analysis, and all values given have been corrected by deducting 6.9 from the percentages found by analysis.

Procedures. For both laboratory and pilot-plant experiments the same general procedure in conducting the reaction was followed. Oil was weighed into the reaction vessel which had previously been dried, flushed, and filled with dry, oxygen-free nitrogen. The dry powdered sodium methylate catalyst was suspended in about two parts by weight of commercial hexane, and then added to and thoroughly mixed with the oil. Suspension of the sodium methylate in hexane was found necessary to prevent its agglomeration on addition to the oil. Glycerol was then added slowly to the mixture of oil and catalyst while continuing agitation. The mixture was immediately heated rapidly to temperature and maintained there for the desired length of time. At the end of the heating period the mixture was cooled rapidly to about 120°C. (when necessary) and the catalyst neutralized by the addition of a 100% excess (with respect to sodium methoxide) of glacial acetic acid. The mixture was agitated and maintained under a blanket of nitrogen throughout the operation.

Two methods of separating the oil product containing the monoglycerides and the unreacted glycerol were investigated. The first was by extraction of the reacted mixture with hexane, and the second was by centrifugation.

For the first method the reacted mixture was diluted with an equal volume of hexane, mixed well, and permitted to settle. The supernatant hexane miscella containing the fatty product was decanted and

desolventized by stripping it under reduced pressure with nitrogen. For the centrifugation studies centrifugation time and force were varied, and the free glycerol content of the fractions determined.

Results and Discussion

Conditions Affecting the Reaction. The effects of the four variables: temperature of reaction, time of reaction, the excess of glycerol over the theoretical requirement of two moles per mole of tung oil, and the amount of sodium methoxide catalyst, were investigated in the laboratory.

In the series of experiments to determine the most favorable reaction temperature the temperature was varied while reaction time, glycerol excess, and amount of catalyst were held constant at 120 minutes, 1 mole, and 1% of the oil weight, respectively. The data given in Figure 2 show that the percentage of tung monoglyceride found in the product was a function

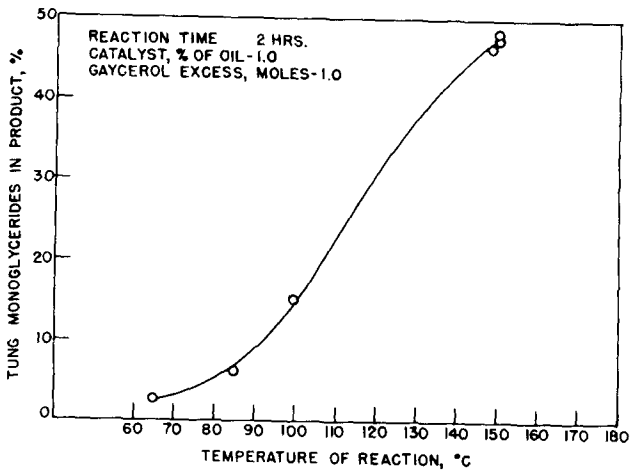

FIG. 2. The effect of the temperature at which the reaction was carried out on the monoglyceride content of the product.

of the temperature at which the reaction was carried out. This is no doubt attributable to the fact that the solubility of glycerol in oil increases with temperature and indicates that use of temperatures higher than 150°C. would enhance the yields. However it was found that as the temperature was increased there was a loss of eleostearate (probably owing to polymerization) with increasing processing temperature which was essentially a straight line function of the temperature. For instance, the original eleostearate content of the tung oil was 74.1%; after processing for two hours at 100°C. it had dropped to 64%. As it was desired to retain as much of the characteristic eleostearate in the product as possible, no temperature higher than 150°C. was used.

For determination of the effect of reaction time, the time at temperature was varied with the temperature being held constant at 150°C. Glycerol excess and amount of catalyst were the same as in the preceding series. The results of these tests, given in Figure 3, show that at the conditions employed the tung monoglyceride content of the product reached a maximum at a reaction time of 60 minutes. From the data it appears that there is but little improvement in yield gained by extending the reaction time beyond about 30 or 40 minutes. It was also found

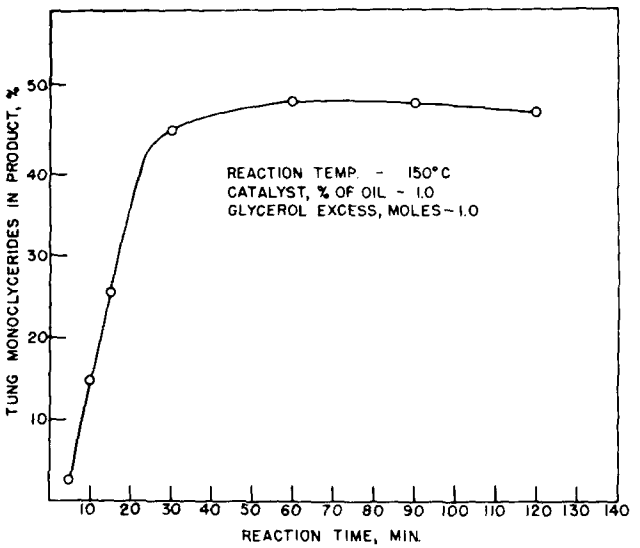

FIG. 3. The effect of reaction time on the monoglyceride content of the product.

that there was a decrease in the total eleostearate content of the product with increasing reaction time, i.e., from about 63% at a reaction time of 15 minutes to about 55% at 120 minutes.

The effect of varying excesses of glycerol over the stoichiometric quantity of two moles per mole of oil is shown by Figure 4. For these tests the temperature was 150°C., reaction time 120 minutes, and amount of catalyst 1% of the oil weight. As shown by the data, increasing the excess of glycerol over theory resulted in improved wields until the excess reached six moles, after which there was no significant improvement.

Experiments to determine the minimum quantity of sodium methoxide catalyst necessary were also carried out. In these tests the reaction temperature, reaction time, and glycerol excess, were held constant while the amount of catalyst was varied between 0.25% and 2.0% of the oil weight. It was found that 0.75% and 1.0% of sodium methoxide was adequate to promote the reaction. With less than 0.75% catalyst, yields of monoglycerides decreased sharply, while with more than 1% there was no significant improvement. Calculations based on the assumption that a portion of the sodium methoxide reacts with, and is inactivated by, the moisture present in the mixture (0.08% in the oil and 0.28% in the glycerol) show that if the oil and glycerol were absolutely dry only about 0.25% of sodium methoxide would be required to catalyze the reaction.

Separation of Product and Unreacted Glycerol. On standing, the reacted mixtures tended to separate into three layers: a relatively clear top phase of fatty material, a middle phase which appeared to consist of an emulsion of fatty material and glycerol, and a cloudy bottom phase which was predominantly glycerol. The mixtures which were low in material analyzing as tung monoglycerides separated most poorly, i.e., at 10% to 15% tung monoglyceride content (in the purified fatty product) and as much as 75% of the total volume of the mixture was in the emulsion phase, while for mixtures in which the purified product analyzed as containing about 50% monoglycerides, the emulsion phase constituted about 10% of the total volume.

Attempts to separate the fatty product from unreacted glycerol by water washing were notably unsuccessful. Addition of water in any form, even as strong solutions of acids or salts, invariably resulted in the formation of emulsions which were extremely difficult or impossible to break. As separation of the two components by water washing was obviously impractical other methods were investigated.

Washing with hexane proved to be practical and gave very good results. When an equal volume of hexane was thoroughly shaken with the reacted mixtures and permitted to settle by gravity, a relatively

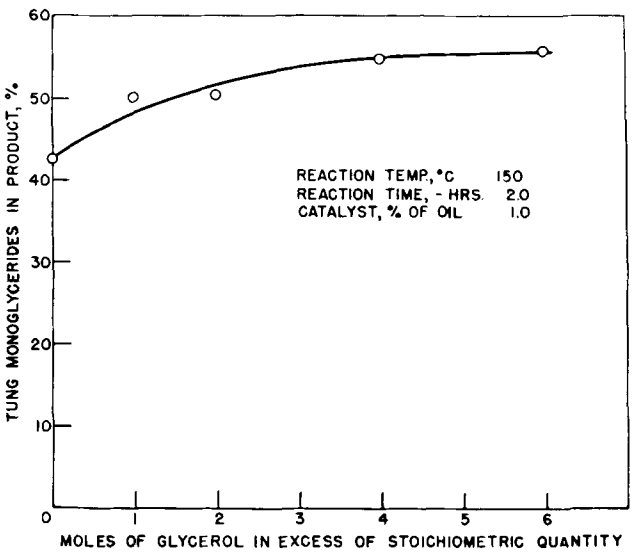

FIG. 4. The effect of excess glycerol on the monoglyceride content of the product.

sharp separation between the hexane soluble fatty phase and the hexane insoluble glycerol phase was obtained. With a settling time of one hour the desolventized supernatant fatty portion was found to contain about 2.4% of unreacted free glycerol; after settling overnight the free glycerol content had been reduced to about 0.6–0.8%. Centrifugation of the mixture of hexane, product, and glycerol greatly accelerated the separation but did not yield products any lower in free glycerol.

Direct centrifugation of the reacted mixture, using the No. 3 International centrifuge, was next investigated. Tests were conducted on both small batches prepared in the laboratory and on the larger batches prepared in the pilot plant. As would be expected, the data showed that the degree of separation of product and free glycerol, as measured by the free glycerol content of the top phase centrifuged product, was a function of centrifugation time and force. Centrifugation for 10 min. at 410 G (in bottles) gave a product containing 2.10% free glycerol. Increasing the force to 2000 G gave a product having 1.23% free glycerol, while increasing the time at 2000 G to 15 minutes decreased the free glycerol in the product to 1.1%. Free glycerol in the bottoms of these tests ranged from as low as 60% to as high as 97%, with the bottoms from the mixtures yielding purified products high in tung monoglycerides tending to be highest in free glycerol.

Continuous centrifugation of the reacted mixtures, using the DeLaval Gyro-Test centrifuge, was used in processing the material from two pilot-plant runs. Separation of the fatty product and the unreacted glycerol was efficient and rapid at a feed rate of about 10 gallons per hour with a centrifuge speed of 12,000 r.p.m. (6.63-in. diam. bowl, Ca. 13,500 G). For the first of the runs using continuous centrifugation the product, amounting to 84.4% of the batch, was found to contain 1.54% free glycerol while the bottoms contained 92.8%. For the second run the corresponding values were product: 68.5% with 3.45% free glycerol; bottoms: 31.5% with 97% free glycerol.

A total of four pilot-plant runs were made. The data for the four runs are given in Table I.

TABLE I

Pilot Plant Runs

Run No.	1	2	3	4
Reaction temp., °C	148	126	140	150
Reaction time, min.	120	70	60	72
Glycerol excess, moles	1.06	3.97	4.07	1.03
Catalyst, % oil	0.98	0.75	1.00	1.10
Input—				
Tung oil, lbs.	46.8	40.2	30.1	40.8
Glycerol, lbs.	15.1	25.3	19.3	13.0
Catalyst, lbs.	0.46	0.30	0.30	0.45
Acetic acid, lbs.	0.55	0.20	0.31	0.60
Output—				
Product, lbs. (fatty phase)	53.1	33.81	33.9	45.2
Bottoms, lbs. (glycerol phase)	8.7	30.11	15.6	8.3

For Runs 1 and 2 centrifugation was done batchwise using 500 ml. bottles and centrifuging at 2500 and 2800 r.p.m., respectively, in the No. 3 International centrifuge. For Run 1 fair separation of the product and unreacted glycerol was obtained, the product containing 45% of tung monoglycerides and 2.71% free glycerol by analysis. Run 2, in which a lower reaction temperature, a greater excess of glycerol, and and less catalyst were used than for Run 1, was unsatisfactory with respect to both tung monoglyceride content and amenability to centrifugal separation. The clarified product which was produced analyzed 8.5% monoglycerides and 1.07% free glycerol, while the yield of clarified product was less than the quantity of input oil. Separation was extremely poor, the emulsion present being only partially broken by centrifuging at the maximum force obtainable with the centrifuge used. The bottoms from this run analyzed only 80.17% free glycerol, showing that a high percentage of the product was emulsified with the unreacted glycerol. The poor reaction obtained and the difficulty of separation with Run 2 was attributed chiefly to pickup of moisture by the large proportion of glycerol used and the high humidity prevailing at the time of the run.

For Runs 3 and 4 centrifugation was done in the continuous centrifuge. Run 3 gave a product containing 42.2% tung monoglycerides and 3.45% free glycerol. The bottoms contained 97% free glycerol. The product from Run 4 contained 32.2% tung monoglycerides and 1.54% free glycerol while the bottoms contained 92.8% free glycerol.

It is to be noted that the tung monoglyceride content of the material produced in the pilot-plant runs was lower than would be anticipated on the basis of data for laboratory preparations. This was attributed in part to the fact that the pilot-plant runs were made at more humid atmospheric conditions than prevailed

in the laboratory, with a resultant pickup of moisture by the glycerol which had the effect of inactivating a portion of the catalyst. In addition, the pilot-plant batches required a much longer heat-up time than the laboratory preparations and agitation of the pilot-plant batches was not as efficient.

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A Method for the Determination of the Water-Insoluble Combined Lactic Acid Content of Shortenings Containing Lactylated Emulsifiers

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Shortenings containing glycerol lactopalmitates and glycerol lactostearates are analyzed for water-insoluble combined lactic acid content using a procedure adapted from that of Barker and Summerson (1). Water-soluble constituents are extracted from a chloroform solution of the shortening. The water-washed shortening is saponified and then acidified to release the lactic acid, which is degraded to acetaldehyde by heating with concentrated sulfuric acid. The acetaldehyde is reacted with p-phenyl phenol in concentrated acid solution to produce a purple colored reaction product. The intensity of the color is proportional to the concentration of the acetaldehyde. Absorption is read at 570 mμ using a lithium lactate solution as a standard.

The method has been applied to the analysis of shortenings containing from 0.70 to 1.10% water-insoluble combined lactic acid.

UNTIL RECENTLY, monoglycerides of long chain fatty acids were the chief emulsifiers in shortenings. Within the past few years they have been supplemented with, and partially replaced by, glycerol lactopalmitates (GLP) and glycerol lactostearates (GLS), which are mixed glycerol esters containing varying amounts of lactic and fatty acids. The effectiveness of these emulsifiers in a shortening depends on the concentration of GLP or GLS in the shortening and on the chemical composition of the emulsifier itself. Those esters which contain 1 molecule of fatty acid and 1 or more molecules of lactic acid per molecule of glycerol are the most effective emulsifiers.

Current shortening analysis methods, including monoglyceride determinations and saponification values, are not adequate to evaluate a lactylated shortening. Although the saponification value is influenced by the lactic acid content, the small amount of lactic acid esters present in a shortening, compared to the fatty acid esters, is insufficient to raise the overall saponification value of the shortening by more than 2 or 3 units. Since esterified lactic acid is the critical component in these shortenings, a determination of combined lactic acid content would serve as a basis for shortening evaluation.

In the manufacture of GLP and GLS, varying amounts of mono-, di-, and trilactin, as well as small amounts of free lactic acid, are present in the final product. These do not contribute to the emulsification properties of the GLP or GLS and must therefore be removed before determining combined lactic acid on the shortening. Upon removal of these products by washing, the lactic acid can be released from its esters by saponification and measured in its free state.

The literature contains various methods for lactic acid determination in biological fluids, dried milk, dried eggs, and wine. In the Hillig (5) method, lactic acid is extracted from aqueous solution with ethyl ether by a continuous liquid-liquid extraction. The extract is taken up in water solution and lactic acid determined colorimetrically with ferric chloride. There are several methods of lactic acid determination based on its degradation to acetaldehyde, which may then be determined colorimetrically with veratrol (6), p-phenyl phenol (1), or hydroquinone (2), or may alternatively be absorbed in bisulfite solution and the addition product determined titrimetrically (3). Lactic acid may also be determined colorimetrically after oxidation to pyruvic acid (4).

An adaptation of the Barker and Summerson procedure for determining lactic acid in biological materials (1), in which the lactic acid is degraded to