The Reaction of Nonconjugated Unsaturated Fatty Acid Esters With Maleic Anhydride[1]

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Introduction

The reaction of maleic anhydride with conjugated unsaturated fatty acids and their derivatives is so well known that a discussion of this application of the Diels-Alder reaction is unnecessary. It has become the basis of methods for quantitatively determining the degree of conjugation in unsaturated fats (1, 2, 3) expressed as diene or maleic anhydride values.

Subsequent investigations have shown that oxidation products of nonconjugated oils cause small but definite apparent diene values (4). However, it has been generally confirmed that the usual unsaturated fatty acids and esters do not react extensively with maleic anhydride under the conditions used in determining diene numbers.

It is not so generally known that maleic anhydride can react with the nonconjugated unsaturated fatty acids and their esters if the reaction temperature is raised to around 200° C. or higher. Müller-Lobeck (5) in 1936 patented a process for preparing a "stand oil of wood oil characteristics" by reacting up to 10 per cent of maleic anhydride with linseed or similar oil at 150° to 250° C., followed by condensation with glycerol. He considered that the maleic anhydride, or other similar unsaturated dibasic acid, catalyzed the conjugation and, hence, the polymerization of the nonconjugated oils. Clocker (6) recently patented the process and products of reaction of maleic anhydride or other similar compounds with nonconjugated unsaturated fatty acids and oils. In subsequent patents (7), he amplified the original and elaborated on many applications of the reaction products to paints, varnishes, lacquers, resins, driers, dispersing and wetting agents, etc.

In England, Bevan in 1939 obtained patents covering similar reaction products(8). He also described the reaction in the chapter on Maleic Acid Resins in a book entitled *Varnish Making* (9).

Excepting these references, mostly in patents, nothing appears in the literature concerning this interesting reaction. These references are very meager as to rate of reaction, maximum amount of maleic anhydride capable of reacting, or any data which might give a clue to the nature of the reaction products. It was thought that a study of the mechanism of this little known reaction would be of value in the utilization of the new products which it makes possible.

The present paper represents some experiments on this reaction which were started before the authors were aware of the references cited. The reaction of maleic anhydride with pure methyl esters of fatty acids was studied, with the thought that differences due to degree of unsaturation would be more definite than when working with an oil containing a mixture of acids.

Experimental

Unsaturated methyl esters were prepared as previously described (10) by one of us. Methyl stearate was prepared from Eastman's stearic acid, distilled in vacuo, and crystallized from methanol. Eastman's maleic anhydride was used. Iodine numbers were determined by the usual Wijs method (one-half hour with 150 per cent excess). Saponification equivalents were determined, using 0.5 N sodium hydroxide in ethanol (3 hours). The determination of free, unreacted maleic anhydride in the various reaction mixtures was by an adaptation of the Kaufman procedure (2) for diene numbers. The sample of reaction mixture, containing not over 0.10 gm. of free anhydride, was dissolved in 2 c.c. of acetone; 20 c.c. of toluene was added, followed by 20 c.c. of water, 15 c.c. of 15 per cent potassium iodide solution, 15 c.c. of 4 per cent potassium iodate solution, and 25 c.c. of 0.10 N thiosulfate. The flask was shaken frequently over a period of 2 hours. Addition of 25 c.c. of 0.10 N iodine solution was then followed by titration of excess iodine with standard thiosulfate solution. A blank with no anhydride was run at the same time. The difference between the blank and sample titrations represents the equivalent of maleic anhydride. One c.c. of 0.10 N thiosulfate is equivalent to 4.9 mg. of maleic anhydride. The maleic anhydride analyzed 98.5 to 99 per cent by this method.

The course of the reaction between fatty ester and maleic anhydride was followed by reacting weighed amounts of ester and maleic anhydride in sealed evacuated ampules made from test tubes. The tubes were cooled in solid carbon dioxide to prevent loss by vaporization during evacuation and then sealed to prevent oxidation during the reaction. They were then placed in an electrically-heated, thermostatically-controlled metal block for the desired time, when they were removed, cooled, and analyzed for unreacted maleic anhydride. The amount of maleic anhydride reacting with the known amount of ester could thus be calculated. Control samples with maleic anhydride alone were run in each series to confirm the fact that thermal decomposition of the maleic anhydride was not sufficient to seriously affect the results. Preliminary tests indicated that the reaction was rather complete in 1 hour at 250° C.

It was thought that a determination of the maximum amount of maleic anhydride capable of reacting with the various esters might be of considerable help in interpreting the reaction. The following tests were made to determine this maximum: The first series was made by varying the ratio of maleic anhydride to ester, and determining the amount of maleic anhydride which had reacted after 1 hour at 250° C. Figure 1 shows the curves for the four esters, linolenate, linoleate, oleate, and stearate, and for soybean oil. The theoretical curve for complete reaction of

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[3] A cooperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

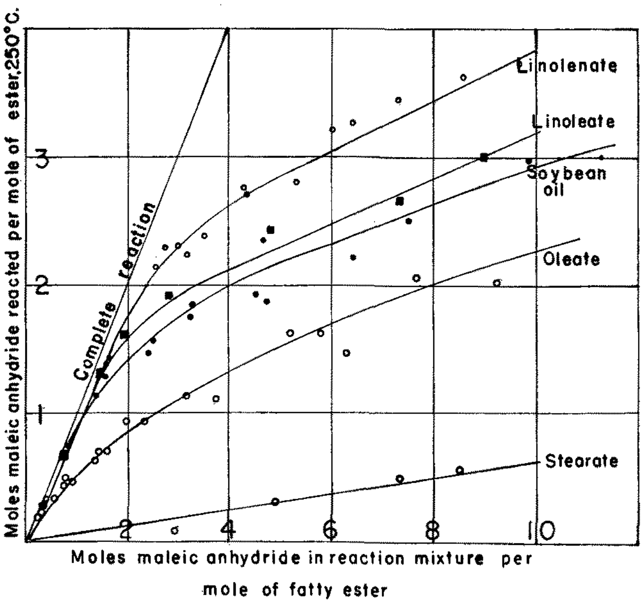


FIG. 1. Reaction of varying proportions of maleic anhydride with fatty esters for one hour at 250° C.

maleic anhydride is also shown. It will be seen that methyl stearate reacts very little compared to the others. This slight degree of apparent reaction may be due in part to ester-anhydride interchange and in part to thermal decomposition of the unreacted maleic anhydride. Methyl oleate reacts more slowly than the linoleate or linolenate, and shows only an indefinite break at around 1 mole. Methyl linoleate reacts rather completely up to nearly 2 moles, and thereafter it apparently reacts much less. Methyl linolenate shows a rather similar curve, with the break occurring between 2 and 3 moles of maleic anhydride. Soybean oil behaves as would be expected from its composition. The slope of these curves beyond the breaks is greater than can be accounted for by decomposition or other reactions not associated with unsaturation (compare with the slope of the methyl stearate curve). This would indicate that some slower secondary reaction follows the main one at 250° C. It was thought that the secondary reactions might be greatly minimized at a lower temperature, while the main reaction might still be rapid enough to give significant results. A second series was therefore run at 200° C., as shown in figure 2. At this lower temperature, the methyl stearate reacts still less, methyl oleate approaches 1 mole, methyl linoleate 2 moles, and methyl linolenate somewhat over 2 moles. Again, soybean oil behaves in an expected manner.

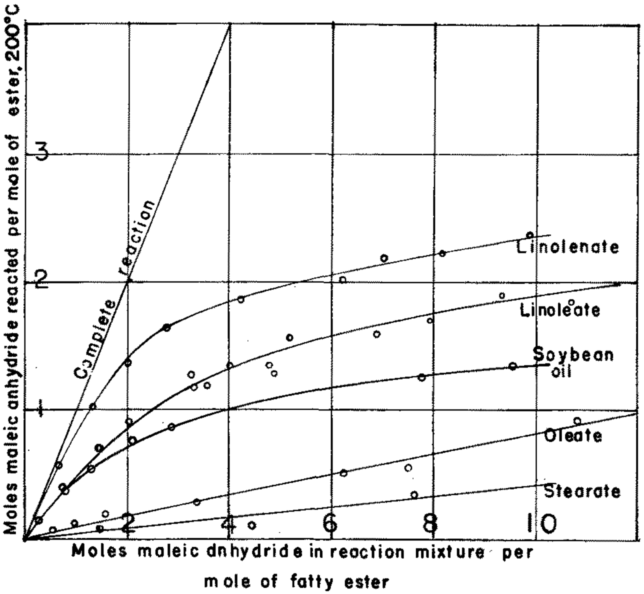


FIG. 2. Reaction of varying proportions of maleic anhydride with fatty esters for one hour at 200° C.

The molecular ratios for the combination of maleic anhydride with the esters were shown more clearly by a third series, in which the time reaction curve was followed at 200° C., using 100 per cent excess of maleic anhydride. That is, for methyl oleate—2 moles, for linoleate—4 moles, and for linolenate—6 moles of maleic anhydride were added for each mole of ester. The mixtures were then heated for various lengths of time and the combined maleic anhydride was determined as before. The results are shown in figure 3. The slowness of the reaction of methyl oleate is made very clear. Methyl linoleate levels off at very close to 2 moles, while the linolenate levels off at about 2.5 moles. The fact that the unsaturated esters react with approximately 1 mole of maleic anhydride for each double bond would suggest that the reaction might be a direct addition onto the double bond. Subsequent work showed this to be true only in a limited sense.

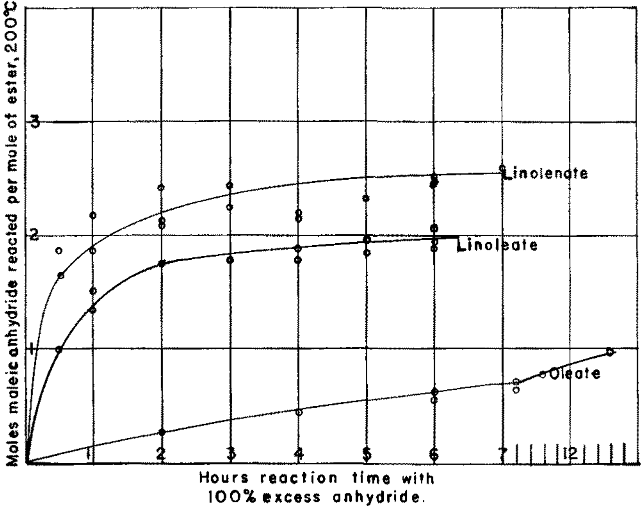


FIG. 3. Reaction of 100 per cent excess of maleic anhydride with fatty esters at 200° C. at various reaction intervals.

The linoleic ester reaction seemed to be the most definite in its nature, since the curve rose rapidly and leveled off quite flat at very close to 2 moles of maleic anhydride at 200° C. For this reason, and also because linoleic acid is the most abundant acid in soybean oil, it was decided to prepare a quantity of the reaction product for further examination. Thirty grams, 0.102 mole of methyl linoleate was heated with 40 gm., 0.408 mole of maleic anhydride for 3 hours at 200° C. in a flask heated in an oil bath. The apparatus was flushed with nitrogen before closing and provision was made to collect any evolved gas. The amount of gas collected was about 1 mole per cent of the maleic anhydride used, indicating negligible decomposition. Analysis of the reaction mixture showed that 1.93 moles of maleic anhydride had reacted per mole of linoleate. Most of the excess anhydride was distilled off under reduced pressure at 90-95° C., with the aid of a small stream of nitrogen introduced through a capillary. The loss in weight and weight of condensed anhydride confirmed the previously found molar quantity of combined anhydride.

The residual reaction product still contained 3.6 per cent of unreacted maleic anhydride. Its neutralization equivalent, determined by dissolving in pyridine, adding an equal volume of water, and titrating to phenolphthalein end-point, was 142.0. If this is corrected for the 3.6 per cent free maleic anhydride, the value becomes 153. The theoretical value for a product from 2 moles of maleic anhydride plus 1 mole of methyl linoleate is 122.5. This means that less acidity is found than would be expected if the combined maleic anhydride retained its anhydride grouping and if all of such grouping were titrated. Saponification equivalent was found to be 107, or 112 if corrected for free anhydride. The theoretical value is 98, which again shows less carboxylic acid grouping than expected, even when saponified. Decarboxylation during the reaction would not account for these discrepancies, since very little gas was evolved. The phenomena may indicate that part of the maleic anhydride is combined through the carboxyl group. The iodine number of the product was 48.6. If corrected for free maleic anhydride, which was found to have a zero iodine number, the value is 50.4. A compound of 2 moles of maleic anhydride with one of methyl linoleate would have an iodine number of 51.8 if it contained one double bond. This would indicate that only one of the double bonds disappears when 2 moles of maleic anhydride react with 1 mole of linoleate and means that the mechanisms of the reactions of the two molecules of anhydride must differ from one another. The molecular weight (benzene, f. p.) was found to be 705, whereas the theoretical value is 500, indicating some association of polymerization.

An attempt to vacuum-distill a portion of the product showed that it could not be distilled without decomposition. No ebullition occurred until a bath temperature of 235° C. was reached. Decomposition started and became worse as the temperature was raised to 305-325° C., at which bath-temperature range the material passed over with a vapor-temperature range of 250-285° C. Decomposition products increased the measured pressure to 1-2 mm. and caused mechanical carry-over. A residue of about 15 per cent was left. The distillate showed an increased saponification equivalent of 146, indicating decarboxylation during the heating. The iodine number was increased slightly, to 58.

Another similar preparation was subjected to molecular distillation in a simple pot still. The main fractions distilled with a bath temperature of 200° C., at a rate of about 0.4 gm. per hour under a pressure of 2-10 microns. The iodine number was 48-51, saponification equivalent 130, and molecular weight 650. The residue represented about 10 per cent of the material. The increased saponification equivalent again indicates decarboxylation during the prolonged heating, but not as much as previously, since the temperature was lower.

Since the iodine number indicated that one double bond remained in the product when methyl linoleate combined with 2 moles of maleic anhydride, it is evident that, on the average, for each molecule of maleic anhydride reacting in such a way as to saturate one double bond another molecule reacted in some way which did not affect the unsaturation.

It would be interesting to know whether the two types of reaction occurred with equal ease or whether one preceded or was more rapid than the other. This was tested by reacting the esters with less than the maximum amount of anhydride, and determining the iodine number of the product as well as the amount of anhydride reacted. It will be recalled that maleic anhydride has zero iodine number by the Wijs method. Figure 4 shows the average number of double bonds saturated per mole of maleic anhydride reacted, as varying amounts of maleic anhydride were reacted with the respective esters. It will be seen that methyl oleate reacts without appreciably affecting the double bond. In the case of the linoleate, if both types of reaction occurred simultaneously and with equal speed, the curve would be horizontal at a value of 0.5 double bond per mole of anhydride reacted. Actually, for linoleate, the value approaches unity as less anhydride is reacted. This indicates that the reaction which saturates the double bond occurs much more readily than the other reaction. Apparently when an excess of anhydride is used, this second reaction occurs mostly as a consecutive reaction, but rapidly enough so that no very sharp break is observed in the previous figures for one mole of anhydride. In the case of linolenate, if three molecules of anhydride reacted simultaneously and with equal speed, so that two of them reacted to saturate one double bond each, and the third did not affect unsaturation, the curve would be horizontal at a value of 0.67 double bond per molecule of anhydride reacted. The curve for methyl linolenate actually is close to one double bond per mole of anhydride reacted up to somewhat over 1.5 moles of reacted anhydride and then drops off to about 0.66. This indicates that the first molecule of anhydride reacts very rapidly to saturate a double bond, and that the reaction of the second molecule is principally of the same nature, rather than addition without saturation. The incomplete addition of the third molecule of anhydride apparently occurs without affecting unsaturation, similar to the second molecule adding to linoleate, or the slow incomplete addition to methyl oleate.

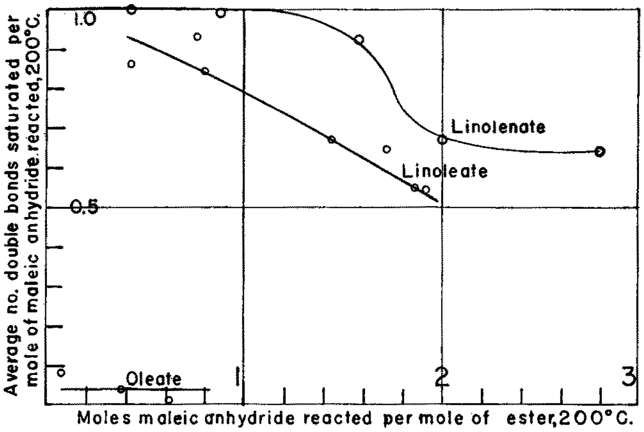
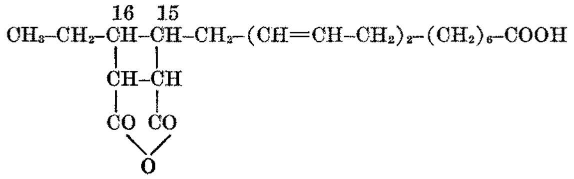


Fig. 4. Average number of double bonds saturated per mole of maleic anhydride reacted with fatty esters as varying proportions of anhydride are reacted.

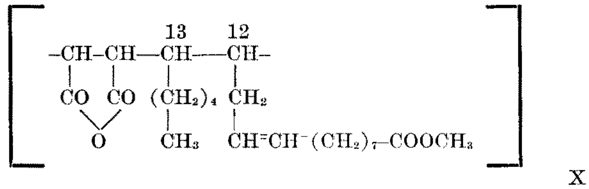
Discussion of Results

The data presented are not sufficient to allow much more than speculation as to the structure of the addition products. Several mechanisms may be considered for the addition which saturates a double bond. These would apply only to the first molecule of anhydride reacting with linoleate, and the first two which react with linolenate; oleate reacts without affecting unsaturation. Clocker (6) postulated the direct addition of a molecule of maleic anhydride to the △15 double bond of linolenic acid, with formation of a four-membered ring:



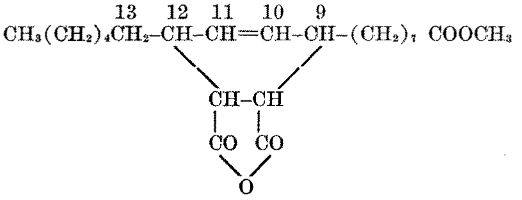
(after Clocker)

and a similar addition on the △9 double bond of oleic acid as one of two possible structures of this reaction product. Another mechanism which would saturate the double bond is co-polymerization, such as occurs between maleic anhydride and styrene or stilbene. Such a polymer with the linoleate might have as a structural unit:



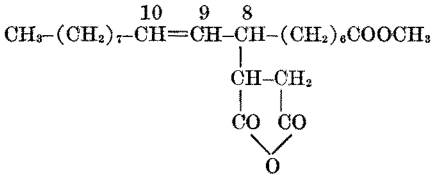
Morrell and Davis (11) proposed this type of structure for a product which they considered to be the combination of three molecules of maleic anhydride with a nonconjugated pentaethylenic C_{20} ester. Such a mechanism would lead to products of very high molecular weight. It might account for the 10 or 15 per cent of residue on molecular distillation and in part for the somewhat high molecular weight found for the linoleate product, but it obviously is not the principal reaction.

In the authors' opinion, the most acceptable mechanism for this addition which saturates a double bond is that the polyethenoid ester shifts to a conjugated configuration and then adds maleic anhydride by the usual Diels-Alder mechanism. With methyl linoleate, such a mechanism would give:



or a similar structure with the maleic anhydride attached to carbons 10 and 13 and with the remaining double bond between carbons 11 and 12. Conjugation of nonconjugated unsaturated fatty acids has been definitely proved to occur with alkaline catalysts by Kass and Burr (12), and the idea that conjugation precedes thermal polymerization has recently been emphasized by Bradley and Johnston (13). This theory also is supported by the fact that only the linoleate and linolenate, which are capable of conjugation, add maleic anhydride in this manner. The fact that the second molecule of anhydride reacts with methyl linolenate in this way is also in accord with this theory, since the product with one molecule of anhydride added on still has two double bonds which could conjugate.

The most reasonable mechanism for the addition of maleic anhydride without affecting unsaturation appears to be the formation of a substituted succinic anhydride by transfer of a hydrogen atom from the fatty acid chain to the maleic anhydride and addition of the succinic anhydride radical to the fatty acid chain. Clocker (6) preferred such a mechanism for the addition product with oleic acid, since he isolated a product which had an iodine number indicating a double bond in the product. The present work confirms the fact that oleic ester reacts without affecting the double bond and further indicates that the second molecule of anhydride reacting with linoleate and the third molecule reacting with linolenate adds on in a similar manner. Precedence for the formation of a substituted succinic anhydride is found in the fact that it has been stated that toluene reacts at 300° C. with maleic anhydride to form benzyl succinic anhydride (14). The point of attachment might be on a carbon involved in the remaining double bond or more probably an adjacent carbon. Thus the oleate product might be:



or a similar compound with the succinyl group attached on carbon 9, 10, or 11. The postulated mechanisms are based on the data presented. If the determination of unsaturation in the reaction products (Wijs method, one-half hour with 150 per cent excess) were incomplete, it would mean that more substitution occurred without affecting the double bond than the data indicate. Much more work would be necessary to definitely prove the accuracy of structural formulas for the various products.

Summary

1. The non-conjugated unsaturated fatty acid esters react with maleic anhydride at 200° C. or above.
2. At 200° C., methyl oleate reacts with almost 1 mole, methyl linoleate with 2 moles, and methyl linolenate with 2.5 moles of maleic anhydride, when an excess of anhydride is present. Methyl stearate reacts negligibly.
3. Methyl oleate reacts without affecting unsaturation.
4. The first molecule of anhydride reacting with methyl linoleate reacts mostly to saturate one double bond, while the second one adds on without affecting unsaturation.
5. The first two molecules of anhydride reacting with methyl linolenate react mostly to saturate one double bond each, while the third molecule adds on without affecting unsaturation.

6. The possible structures of the reaction products have been discussed.

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A Modified Procedure for Obtaining "Total Residue at 160°C." in Crude Glycerine

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Introduction: The procedure for obtaining "Total Residue at 160° C." as outlined in the Journal of Industrial and Engineering Chemistry, 3,682 (1911), has undergone no essential changes. In the light of newer theoretical knowledge and with the aid of more highly-developed chemical tools, the author has made a critical investigation into this determination. The result was a much shortened and simplified procedure.

Apparatus: A specially designed oven was assembled which made use of the radiant, penetrating heat of the commercial infrared drying lamps. The parts of this oven, which are all inexpensive and easily obtained, are listed as follows:

(A) Enamelware dish of approximately ten inches diameter and four inches depth. A small hole is bored through the side, flush with the bottom of the dish, to admit a laboratory thermometer.

(B) Infrared drying lamp, 250-watt, with built-in reflector. (General Electric, Model R-40, 250-watt.)

(C) Reflector of thin gauge aluminum, about nine inches across, which screws on a standard electric light socket. This is used primarily to shield the oven from drafts.

(D) A burette stand and clamp for holding and adjusting the height of the lamp above the samples.

Procedure: The preparation of the samples follows the official method. The total percentage of Na_2O to methyl orange indicator is found by titration of a 10 per cent solution of crude glycerin in water. A ten-gm. sample of crude glycerin is weighed into a 100 c.c. volumetric flask, sufficient standard hydrochloric acid or sodium hydroxide is added to adjust the percentage of Na_2O to 0.2 per cent, and the volume is made up to 100 c.c. with distilled water.

Aliquot portions of 10 c.c. each are pipetted into tared evaporating dishes, 70 m.m. in diameter and 15 m.m. in depth. These are placed in pairs adjacent to the center of the bottom of the enamelware dish. The lamp with aluminum reflector attached is adjusted four inches above the evaporating dishes and with its axis in line with the center of the enamelware dish. The thermometer is inserted through the hole in the side of the latter until the bulb rests in the middle of the dish.

The lamp is switched on. Temperature is disregarded until fumes are no longer observed. This usually takes about one hour. The temperature is then regulated to 160° C. by adjusting the height of the lamp. The samples are baked at this temperature for one-half hour and then are placed in a dessicator preparatory to weighing. The acetylizable on the residue is subsequently obtained in the regular manner.

Experimental: These results were obtained on the standard sample of crude glycerin issued by the A.O.C.S., February 1, 1929.

Per cent total residue at 160° C. (modified procedure)

10.35
10.20
10.29
10.27
10.25% average (10.28% A.O.C.S. analysis)

Per cent acetin in residue as glycerol

0.46
0.36
0.54
0.56
0.48% average (0.48% A.O.C.S. analysis)

Ten grams of C. P. glycerol were dissolved in distilled water and made up to a volume of 100 c.c.; 10 c.c. portions were run by the modified procedure as outlined above.

Sample	Added material	Increase in weight after drying
1.	none	less than 0.0001 gm.
2.	none	less than 0.0001 gm.
3.	0.0792 gm. NaCl	0.0792 gm.
4.	0.0624 gm. NaCl	0.0624 gm.

Summary: Evidence has been presented that by means of the infrared drying lamp "Total Residue at 160° C." may be obtained in one drying. Analytical results on a standard A.O.C.S. sample of crude glycerin agree well with the established analysis for both "Total Residue" and "Acetin on Residue." Pure glycerol even in the presence of sodium chloride is completely evolved without a trace under the infrared lamp at 160° C. The equipment and technic are much simplified. Work time on the determination is reduced by two hours and elapsed time by eight hours.

With these points in mind the author respectfully recommends to the Glycerin Analysis Committee that further work be done on this procedure with a view toward substituting it for the present one.