An Investigation of Oven Methods for Determining the Moisture Content of Shelled Peanuts

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Air-oven methods, using ground, sliced, and whole shelled peanuts, were investigated. The use of ground samples was found to be unsatisfactory. Slightly more accurate results were obtained with whole nuts than with sliced nuts. The method of heating 50-g. samples of whole shelled peanuts for 3 hrs. at 130°C. in a forced-draft oven gave results agreeing closely with those obtained by the Karl Fischer method for samples of low moisture content.

THE ACCURATE ANALYSIS of peanuts is important, not only for purposes of grading but also in estimating the value of the products obtained when the peanuts are processed. Correct moisture determinations are essential to the analysis. If electronic moisture meters are used, the accuracy of these devices is limited by the accuracy of the oven or chemical method against which they are calibrated.

A variety of oven methods are used, or have been proposed, for the determination of the moisture content of shelled peanuts. Fifty g. of whole kernels are heated for 3 hrs. at 130°C. (7) or for 5 hrs. at 130°C. (4) in a forced-draft oven. Samples are ground in a food chopper, and 5-g. portions are heated for 5 hrs. at 130°C. in a forced-draft oven (4); or 5 to 10 g. of the ground material are heated for 5 hrs. at 101°C. in the forced-draft oven (1). In another method the kernels are ground to a paste, and 2 g. of the paste are heated to constant weight (5 hrs.) in a vacuum oven at 95–100°C. (6). Sliced nuts are heated for 3 hrs. at 130°C. or for 16 hrs. at 105°C. in a forced-draft oven (9). It would be remarkable if these diverse methods gave comparable or equally satisfactory results.

Oven methods are empirical. The establishment of a method requires that a decision be made as to the time and temperature of heating. Drying is usually considered complete when the samples reach constant weight. Time and temperature for some procedures are selected by comparing results with another method, which may itself be empirical.

The purpose of this investigation is to find which of the methods, using a forced-draft oven, gives results in best agreement with those of a standard method. Oven methods were studied for whole, sliced, and ground peanuts. Some of the factors which tend to produce errors were also investigated.

The Karl Fischer method, as it has been applied by Hart and Neustadt (2,3) to the determination of moisture in seeds, is used as the standard. This method has been found satisfactory in determining the moisture content of such oil-bearing seeds as soybeans, flaxseed, sunflower seed, and safflower seed. The water is extracted from the seed without the use of high temperatures. It has been shown that the extraction is complete and that the Karl Fischer reagent determines the water in the extract accurately. All determinations by the Karl Fischer method were made in quintuplicate.

Experimental

Samples. Forty-seven samples of peanuts, divided about equally among the three types, Virginia, Spanish, and runner, and ranging from 4.75 to 14.44% moisture content were held in sealed mason jars at 40°F. A wad of cotton, to which a few drops of formaldehyde had been added, was placed in the top of each jar to prevent mold in high-moisture samples. Before being tested, each sample was put through a Boerner divider three times.

Choice of Oven Method for Whole Kernels

Time and Temperature of Drying. The Brabender oven was used to find the correct drying-time for a given temperature. In this oven it is possible to weigh the samples without removing them from the oven. Thus a graph may be made of time *vs.* weight loss. Ten of the 47 samples were used and three temperatures, 120°, 125°, and 130°C. were tried. In Figure 1
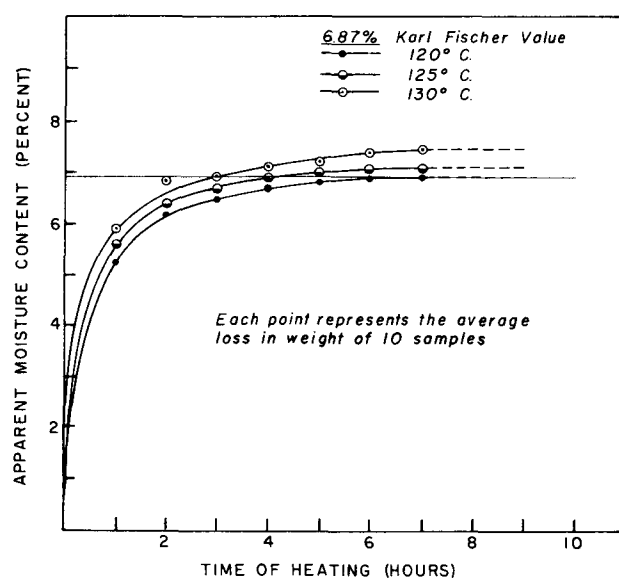

FIG. 1. Relationship between loss in weight and time of heating at specified temperatures for shelled peanuts.

the heating time is plotted against the average apparent moisture content for the 10 samples at the three temperatures. The graphs indicate that, at 120°C., 8 hrs. would be required to cause a weight loss equal to the average moisture content obtained by the Karl Fischer method. At 125°C. 4½ hrs. would be required, and at 130°C., 3 hrs. Three hrs. at 130°C. were chosen to avoid an excessively long heating-period.

Determination of Sample. Duplicate moisture determinations were made on 22 samples (3 hrs. at 130°C.), using 10-, 25-, 50-, 75-, and 100-g. samples.

The 10-g. portions were placed in grain moisture boxes 2 in. in diameter and ½ in. deep. All other weights were dried in grain-can lids, 5½ in. in diameter and ⅝ in. deep. In all cases the kernels were spread in a single layer. Each 100-g. portion required two can lids. Figure 2 shows the weight of the samples plot-
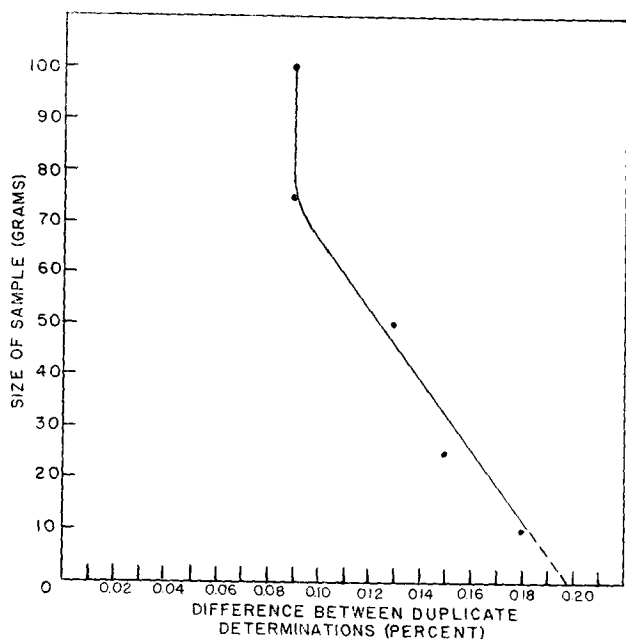

FIG. 2. Relationship between weight samples of peanuts and agreement between duplicate determinations.

ted against the average difference between duplicate determinations. The minimum difference between duplicate determinations is attained with portions weighing 75 g. or above. No great loss of accuracy occurs in using 50-g. portions.

Oven Method for Sliced Peanuts

The advantage of slicing or grinding, from the standpoint of accuracy, is that a large sample of sliced material may be thoroughly mixed and a small uniform portion taken for analysis. A Henry nut slicer was used. In this mill rotating fins push the nuts against a razor blade projecting through a slit in the cylindrical wall. The thickness of the slices is determined by adjusting the distance the blade extends into the cylinder. There is however no scale or other means of precise adjustment that would assure uniform thickness when the mill is reassembled after cleaning.

Ten samples of sliced nuts were heated in the Brabender oven at 130°C. The weight loss at the end of 3 hrs. coincided with the average of the values obtained by the Karl Fischer method for these samples (Figure 3).

There was very little loss in weight in the period between 1 hr. and 7 hrs. The sliced nuts became continuously browner during the heating-period. This suggested that some factor was causing gain in weight and compensating for the normal loss in weight due to browning. One cause for gain in weight in a substance with a high oil content is oxidation of the oil. This was investigated. Oil was pressed from two portions of a sample of sliced peanuts. One portion

had not been heated, and the other had been heated in the forced-draft oven for 3 hrs. at 130°C. The peroxide value of each oil was determined by the A.O.C.S. method. The oil from the unheated peanuts had a peroxide value of 0.4, and that from the heated peanuts was 82.4. In five other samples in which the slices were thicker, the values for the unheated peanuts were 0.2, 0.2, 0.6, 0.8, and 0.4, and those of corresponding heated portions were 14.4, 22.6, 19.2, 11.6, and 17.8.

Moisture determinations were made on sliced nuts from 22 samples. About 100 g. of peanuts from each sample were sliced, then thoroughly mixed by stirring with a spatula. Portions of this material (about 3 g.) were weighed, placed in grain moisture boxes, and heated 3 hrs. at 130°C. in the forced-draft oven. The average loss in weight for the 22 samples was 6.36%. The average moisture content for the same samples, as determined by the Karl Fischer method, was 6.28%. The average differences between oven-determined moisture contents and Karl Fischer determinations was 0.072%; the standard deviation of these differences was 0.521%. When determinations were made on the same samples by the method of heating 50 g. of whole kernels at 130°C. for 3 hrs., the average difference between the moisture content and the corresponding Karl Fischer value was 0.14%, and the standard deviation of these differences was 0.16%.

That variations in the setting of the blade in the mill may be the cause of error is illustrated by the results obtained in the following experiment.

Peanuts from the same sample were sliced at four different settings of the mill, which gave progressively thinner slices. Moisture determinations were made on the portions obtained from each setting. The results for the respective settings were 9.04, 8.92, 8.84, and 8.79%. The greatest difference between duplicate determinations was 0.07%.

There is another source of error which tends to make this method unsatisfactory. Oil and gummy materials exude from the peanuts when heated and harden on the moisture boxes so that they cannot be removed except by thorough washing with detergent. Consequently, unless the boxes are tared after each use, error is introduced. It was found that after one use the average increase in tare weight for 26 moisture boxes was 0.0015 g. If the original tare weight had been used in the next determination, the error would have amounted to 0.05%.
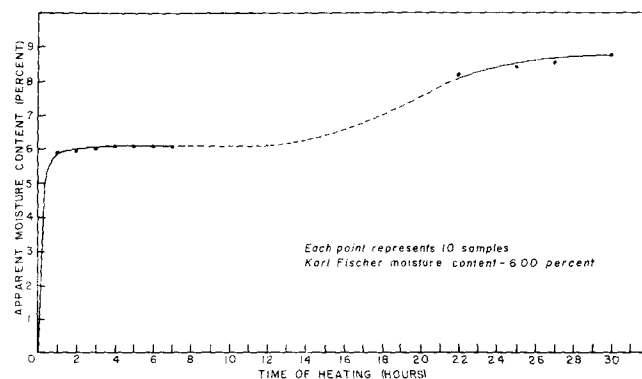

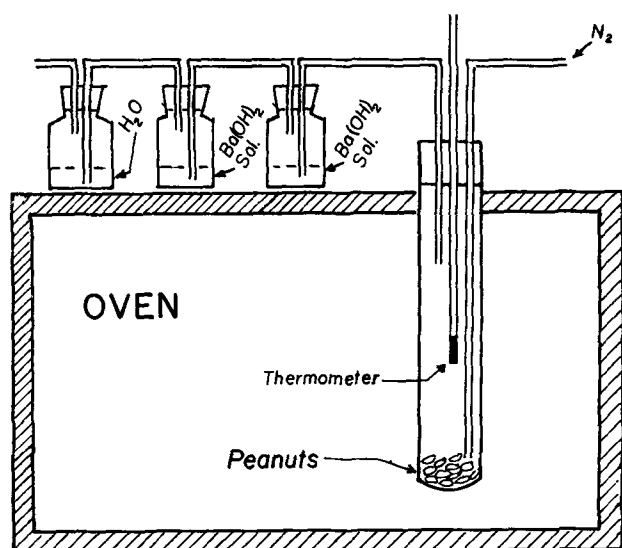FIG. 3. Change in apparent moisture content of sliced peanuts at 130°C. with increase in time of heating.

FIG. 4. Diagram of equipment used for determination of non-aqueous volatile material.

Oven Methods for Ground Peanuts

An attempt was made to use the Universal food chopper in preparing samples for the oven. All blade sizes were used. In the case of some low-moisture samples it was found possible to obtain a fairly satisfactory grind with the coarse blade; however, in most cases, when 50 or 75 g. had passed through the mill, oil was pressed out to the extent that it dripped from the grinder. Heat developed, and the mill became clogged. In every case the ground material was oily and difficult to mix. It was impossible to grind samples with a moisture content of 9% or higher. If this method was used, a pre-drying stage would certainly be necessary.

Possible Sources of Error in Oven Methods

Loss of Nonaqueous Volatiles. Pickett and Holley (8) found that, when peanuts were roasted at 150°C., 98% of the nonaqueous volatile matter given off was carbon dioxide and that it was produced by the browning reaction. Since browning had been observed in the peanuts heated to 130°C., the amount of carbon dioxide given off during oven drying was determined.

The peanuts to be tested were placed in a long test tube, which was closed with a stopper bearing an inlet tube extending to the bottom of the test tube, a thermometer and an outlet tube leading through two wash bottles, containing barium hydroxide solution, and finally through a bottle containing water (Figure 4). The test tube was inserted into an oven and heated 3 hrs. at 130°C. while a stream of carbon dioxide-free nitrogen was passed through the train. The weight of CO_2 evolved was calculated from the weight of barium carbonate precipitated. In one determination where the sample contained no moldy or blackened nuts, the weight of the CO_2 was equal to 0.08% of the weight of the sample. In a sample consisting entirely of moldy peanuts the weight of CO_2 evolved was equal to 0.22% of the weight of the sample. The CO_2 evolved from a sample with a moisture content of 13.56% was equal to 0.26% of the sample weight. The water produced in these reactions is also a source of error.

By replacing the barium hydroxide solution in the wash bottles with standard acid solution, it was possible to test for ammonia in the same type of experiment. That no ammonia was evolved from peanuts heated to 130°C. was indicated by the fact that there was no change in the acid concentration.

It was possible to determine the amount of oily material evolved by using the same apparatus and placing petroleum ether in the wash bottles, which were surrounded with ice water. The peanuts were heated for 3 hrs. in a stream of nitrogen. At the end of the run all tubing was washed with petroleum ether. The petroleum ether was separated and evaporated to dryness on a steam bath. The oily material was left as a residue. In a sample containing no moldy peanuts the weight of oil was equal to 0.04% of the weight of the sample. In another sample containing moldy peanuts the weight of the oil was equal to 0.18% of the weight of the sample.

Presence of Moldy Peanuts. All moldy and blackened peanuts were removed from three samples. Oven-moisture determinations (3 hrs. at 130°C., using 10-g. portions) were made on the good peanuts and on the moldy peanuts taken from each sample. The moisture content of the moldy peanuts averaged 0.39% higher than that of the good peanuts.

Variations in Peanut Kernel Size. The kernels in a sample of peanuts were divided into size groups according to weight as follows: 0 to 0.19 g., 0.20 to 0.39 g., 0.40 to 0.59 g., etc. Oven-moisture determinations were made on each size group, using 10-g. portions. In another experiment the size groupings were 0.10 to 0.29 g., 0.30 to 0.49 g., etc. In Figure 5 the medium weight per kernel for each size group is plotted against the moisture content for that size. The
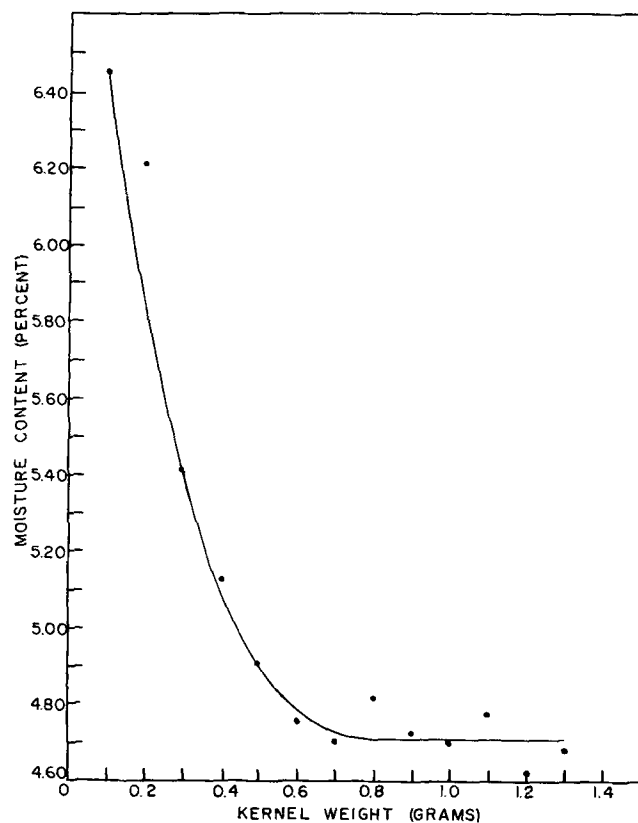

FIG. 5. Relationship between oven moisture content and kernel size of peanuts.

graph indicates that any variation in relative amounts of the different kernel sizes in replicates will produce differences in moisture content.

Losses in Weight Due to "Bleeding." It was found that some kernels exuded a small amount of oil when heated. When such a kernel was heated on paper, a translucent grease spot was left. Also a gummy fluid which hardened on cooling was sometimes given out. It had a caramel odor and gave a positive osazone test for reducing sugars. When 50-g. or 75-g. samples were used, it was not practicable to use tared moisture boxes. Consequently an error was introduced since some oil was left in the box when the dried sample was weighed.

Oxidation of Oil. Oil was expressed from some whole unheated peanuts and from peanuts of the same sample which had been heated for 3 hrs. at 130°C., using a Carver press. The peroxide value was determined on each oil. The value for the heated peanuts was exactly the same as that for the unheated: 0.12. Oxidation does not appear to be a source of error.

Moisture Contents of Whole Kernels by Oven and Karl Fischer Methods

Moisture determinations were made on all of the 47 samples used in this investigation. There was good agreement between the two methods for peanuts with low moisture content; but there was a gradual increase in the positive direction of the deviation of the oven results from the Karl Fischer method results as the moisture content of the samples increased. The browning reaction and "bleeding" were noticeably greater in the high-moisture peanuts, and agreement between duplicates was not as good. In Figure 6 the
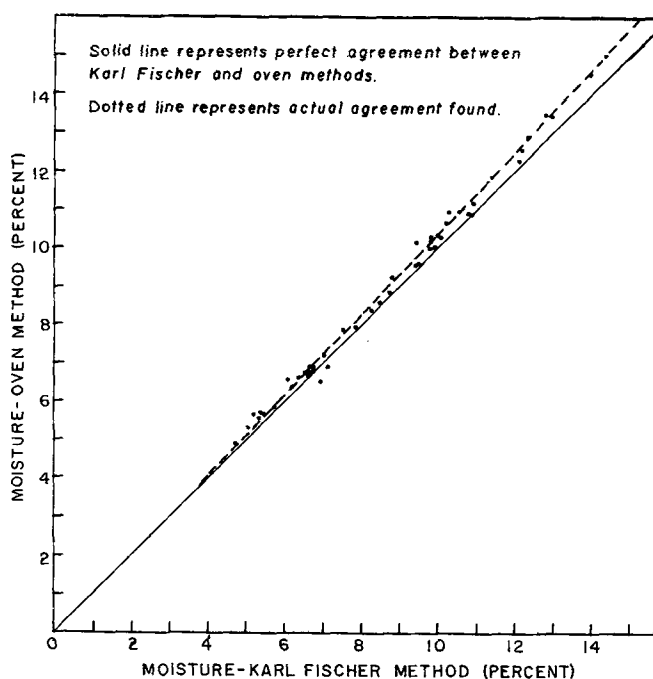

FIG. 6. Moisture contents of peanuts determined by oven and Karl Fischer methods.

results obtained by the Karl Fischer method were plotted against those obtained by the oven method. Considering the Karl Fischer determinations as standard and expressing oven determinations as a function

of that standard, results in the regression equation

$$Y = -0.0747 + 1.0346\,X \qquad (1)$$

as the best-fitting linear function by the method of least squares. An analysis of variance of the data indicates that the standard deviation of the observations from this fitted function is 0.178%. Assuming that oven determinations are equal to Karl Fischer determinations, then the differences can be considered as deviations from the regression function

$$Y = X \qquad (2)$$

and the standard deviation of the observations from this function would then be 0.947%. By using equation 1, it was possible to prepare a chart of corrections which, when subtracted from the oven results, would bring about somewhat better agreement with the Karl Fischer method results.

Discussion

Moisture methods involving the use of sliced peanuts offered no advantages which would compensate for the extra time and work involved. Determinations by using sliced nuts were found to be less accurate than results obtained by using whole kernels.

Grinding samples as a preliminary to oven drying is not practical unless kernels are predried to a low-moisture value. Such a procedure involves more time and work and introduces additional chances for error.

The method of heating 50 g. of whole kernels for 3 hrs. at 130°C. is recommended. This method gave the most satisfactory results obtainable within practical limits as to size of sample, temperature, and time of heating; and there is also good agreement with the Karl Fischer method. Its accuracy is affected adversely by chemical reactions in which nonaqueous volatile matter is evolved, the most important of which appears to be the browning reaction in which carbon dioxide is lost. Losses from chemical reactions are more extensive in moldy peanuts and in those with higher moisture contents. Small kernels have a higher moisture content when in equilibrium with a given relative humidity than do large ones. Consequently an uneven distribution of kernel sizes could produce errors. At higher moisture levels there is greater disagreement between duplicate determinations. The work of Karon and Hillery (5) has shown that peanuts with a moisture content of 10% or higher would be in equilibrium at 25°C. with a relative humidity of 80% or higher. They found also that, above about 10% moisture content, relatively large differences in moisture content produced little change in equilibrium relative humidity. Consequently, if a sample of such peanuts in a sealed container had originally an uneven distribution of moisture, this unevenness would persist for a long time. There would be a strong probability that different portions taken from this sample would be unequal in moisture content.

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Glycidyl Esters. II. Synthesis of Esters of Commercial and Pure Fatty Acids

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The reaction of salts of carboxylic acids with epichlorohydrin in the presence of quaternary ammonium halides to form glycidyl esters has been demonstrated to be applicable to a variety of acids derived from fats, including commercial mixtures.

The glycidyl esters of pelargonic, lauric, oleic, dimerized linoleic, ricinoleic, behenic, and sebacic acids as well as those of the fatty acids derived from tallow, wool wax, and soya oil have been prepared in 80–95% yields and purities.

THE INCLUSION of oxirane groups in materials derived from animal and vegetable fats has been studied widely, and several of the products of these studies are in commercial use. A common property of such epoxidized fatty materials is that the oxirane function is located internally along the hydrocarbon chain as, for instance, in 9,10-epoxystearic acid. On the other hand, the investigation of fat-derived materials with terminal epoxide groups has been neglected almost entirely. A program of preparation of glycidyl esters was undertaken for the purpose of partially filling this need.

A review of the literature revealed that several methods of preparation of glycidyl esters were available, but none appeared entirely suitable to the problem at hand. The direct esterification of glycidol with acid chlorides of carboxylic acids (4,5,16) requires not only several reaction steps to arrive at the desired product but also involves the use of relatively expensive chemicals. The reaction of monocarboxylic acids with epichlorohydrin (15), especially when catalyzed by compounds of the Friedel-Crafts type (7,13) or by basic organic nitrogen compounds (11,14), results in the formation of α-carboxylic esters of γ-chloropropylene glycol. These are then dehydrohalogenated in the presence of alkali to give the desired glycidyl ester (Equation A, Figure 1). Over-all yields are low.

Glycidyl esters can also be obtained directly from fatty acids and epichlorohydrin by the use of quaternary ammonium halide catalysts and a large excess of epichlorohydrin (10) (Equation B, Figure 1). The latter, besides acting as solvent, absorbs the hydrogen chloride evolved. Disadvantages of this method are that for each mole of ester formed two moles of epichlorohydrin are used up and that in many cases the products obtained are difficult to purify.

The uncatalyzed reaction of epichlorohydrin with salts of carboxylic acids, rather than with the free acids, has also been reported. Epichlorohydrin consumption is decreased to the stoichiometrically re-

quired amount, but the presence of even small amounts of moisture decreases the yields of glycidyl esters (1,8).

A number of glycidyl esters of fatty acids were prepared in high yields by Kester and co-workers (5,6) by the reaction of soaps of fatty acids and excess epichlorohydrin in the complete absence of moisture. Carried out at normal pressure, the reaction time was 5–11 hrs., but considerably less time was required at superatmospheric pressures. High pressures or traces of moisture caused the formation of considerable amounts of high-boiling and polymeric by-products. This method was described as inapplicable to the preparation of diglycidyl sebacate.

Recently the authors reported (9) the preparation of glycidyl stearate and diglycidyl azelate by reaction of sodium stearate and disodium azelate, respectively, with epichlorohydrin in the presence of benzyltrimethylammonium chloride (Equation C, Figure 1). This procedure, which may be carried out in moist or even partly aqueous media, requires only brief reaction periods, gives high conversions to glycidyl esters, yields easily purifiable reaction products, and may be adapted readily to bench-scale preparations. It is the purpose of the present paper to show the applicability of the new procedure to a variety of carboxylic acids of fatty origin.

Discussion

As reported earlier (9), both the carboxylic acids and their soaps react readily with epichlorohydrin in the presence of certain quaternary ammonium halides to give glycidyl esters. The soaps however give higher yields and purer products and were used exclusively in the present studies.

The required soaps were either prepared separately and isolated (nonaqueous method), or an aqueous solution of the neutralized acids was used directly (aqueous method). Experiments involving the isolation of soaps made from fatty acid stocks are illustrated in the experimental section and summarized in Table I. The procedure, which involved neutralization of an acetone solution of the acids, followed by filtration of the precipitated salts, was chosen for its convenience and ease of handling in the laboratory. In all cases somewhat less than the stoichiometrically required amount of base was used to avoid, as much as possible, the presence of free alkali in the soaps. As a result, some loss of fatty material was incurred