Rancidity and Stability in Shortening Products

Discussion of the Phenomena of Rancidity and Instability with a Review of Proposed Methods of Testing Fats for Rancidity*

By W. O. Pool†

RANCIDITY may be divided into three general types—ketonic, hydrolytic and oxidative. We are concerned principally with the oxidative and to a minor degree with the hydrolytic rancidity. Rancidity may be defined, in a restricted sense, as the condition produced in a fat by the formation of those substances which possess a characteristic, disagreeable odor and taste. In a broader sense, rancidity might be conceived as a condition of a fat resulting from a host of changes occurring in the fat under both abnormal and normal conditions. The original molecules are broken into simpler compounds, giving rise to at least twenty and probably many times that number of new compounds. It is very likely that the typical odor and taste of a rancid fat is due to only a few of these new bodies, but the actual condition which accompanies the rancid flavor is certainly the resultant of every change which has occurred in the process.

The ideal test for rancidity, broadly defined, would measure the average result of each weighted change that has taken place in the fat, while the ideal test for rancidity in a restricted sense would measure only those substances which cause the rancid taste and odor. But, with such a vast number of changes and with each change taking place at a varying speed, the ideal test must remain only an ideal.

The next best test would be one which would measure a single substance or group of substances which invariably accompanies rancidity, and whose amount is proportional to the degree of rancidity. Unfortunately, the percentage of the substances which are known to be present in all rancid fats seems to vary with many factors other than the state of rancidity. Nevertheless, it is tests of this sort on which we must rely for confirmation of taste and odor. It would be well to review these briefly, and to examine the basis on which each test stands.

Effects of Rancidity

OF THE many changes occurring in rancid fats, that of change in acidity is one of the most striking. Ritsert[1] in 1890 and Spaeth[2] in 1896, used the increase in the free fatty acid as a measure of the process of rancidity. In 1900, however, Reinmann[3] found that there was no direct relation between the amount of acid formed and the extent of rancidity. Since that time, it has been conceded that the acidity of a fat cannot be used to recognize rancidity. The behavior of the acid content of a fat is more dependent upon other factors than upon oxidation.[4,5,6,7] Moisture, in particular, will promote hydrolysis, and the increase in acid content will proceed at a much more rapid rate than oxidation. Holm and Greenbank,[8] in 1924, observed that in the absence of moisture oxidation of fats proceeds only to the aldehyde stage. Consequently, in the latter case, we should obtain a rancid fat which would be very low in acidity. Kerr and Sorber[9] state "that if a clear sweet fat is allowed to develop rancidity and the free acid is determined at regular intervals, it will be noted that during the first few weeks the percentage of free acid remains stationary or perhaps shows a slight increase; then a sudden drop is noted, the percentage of free acid falling off 0.2 to 0.4% or even more. Coincidently, the physical signs of rancidity appear. Following this reduction in the percentage of free fatty acid, there begins an increase in acidity." The same workers, however, concluded that acidity and rancidity do not, in general, bear any relation to each other and that the determination of the free fatty acid is worthless as a criterion of rancidity.

Oxidation of an unsaturated compound usually results in a rupture of the double bond, consequently the iodine value of a fat should undergo a decrease with the development of

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rancidity. This is actually the case, but the difference in the iodine value of the fresh and rancid samples is too small to be of any service in the recognition of rancidity.

When the long chain acids of a fat are broken down by oxidation, acids of lower molecular weight are formed. Saponification numbers of rancid fats are therefore greater than those of

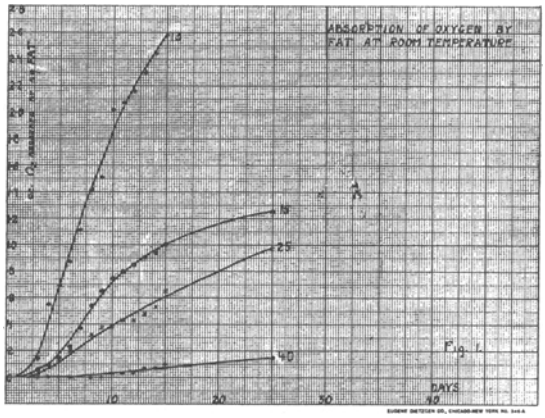

Fig. 1

fresh fats. The variation, however, is insufficient to be employed as a criterion of rancidity. In the process of going rancid, the relative amount of unsaponifiable matter increases, the heat of combustion decreases, due to slow oxidation, while the specific gravity and viscosity of a fat increase. None of these changes are simple enough or significant enough to enable us to use them as a means of detecting rancidity.

Formation of Peroxides

IN 1915, Vintilesco and Popescu[10] observed that acidity is not a necessary accompaniment of rancidity. From this fact they deduced that fats could undergo an additive reaction with molecular oxygen without suffering hydrolysis with formation of free acids. They reasoned that the additive compound formed would probably be of a peroxide nature, and ought to be quickly displaced by easily oxidizable substances. Such was found to be the case. Rancid fats were reduced by a tincture of guaiac and a peroxidase. Fresh fats were unreactive, but after a comparatively short exposure to air, became reactive. Vintilesco and Popescu concluded from these experiments that the presence of a loosely combined form of oxygen was the chief characteristic of all rancid fats. This conclusion has been confirmed and extended by Kerr and Sorber[9]. Other workers[11,12,13] have used variations of such a procedure in order to measure the amount of peroxides in a fat. None of the methods, however, give quantitative checks in the hands of different analysts and all but the freshest fats give a positive test.

In 1920, Fahrion[14] devised a method for the determination of rancidity, founded upon the following facts:

Fresh fats have a negligible amount of hydroxy acids, but upon oxidation of the fats these acids are formed in considerable quantities, depending upon the extent of the oxidation. Once formed, the hydroxy acids are very stable and do not suffer a decrease due to volatilization. Based upon the insolubility of the oxidized acid in petroleum ether, Fahrion used the following procedure for their determination:

Three grams of the fat were saponified with alcoholic potash, and the alcohol was driven off by evaporation. The soap was dissolved in 50 to 70 cc. of hot water, and transferred to a separatory funnel. When cooled, 100 cc. of petroleum ether was added. The solution was acidified with hydrochloric acid, and shaken and allowed to stand overnight. The water solution was then drawn off and the petroleum ether filtered. The precipitate of oxidized acids was washed with petroleum ether several times and dissolved in the smallest possible amount of warm alcohol. The alcohol solution was transferred to a tared dish, the alcohol evaporated off and the oxidized acids weighed. The temperature was not allowed to exceed 95° C. The amount of oxidized acids varied

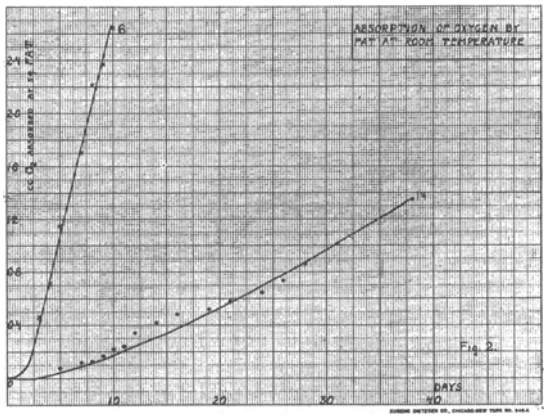

Fig. 2

from mere traces in fresh fats to about 28% in extremely rancid fats. All non-volatile acids of a thirty year old cottonseed oil were found to be hydroxy acids[15]. Results by this method are easy to duplicate but little work has been done toward determining the exact relationship between the amount of hydroxy acids in a fat and its condition with regard to rancidity.

Issoglio, Kreis and Kerr

IN 1916, Issoglio[16] devised a test for rancidity, depending upon the presence of easily oxidizable and volatile substances in rancid fats. As a means of separating these bodies from the sample being tested, he employed steam distillation, using a standard solution of potassium permanganate to receive the oxidizable compounds from the fat. Back titration with standard oxalic acid solution enabled him to calculate the amount of permanganate which had been used in oxidizing the substances distilled from the fat. He expressed his oxidizability value as the number of milligrams of oxygen required to oxidize the organic compounds distilled from a standard amount of fat. The results checked fairly well and an oxi-

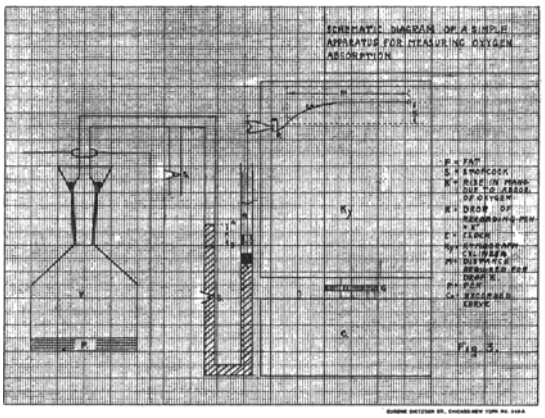

Fig. 3

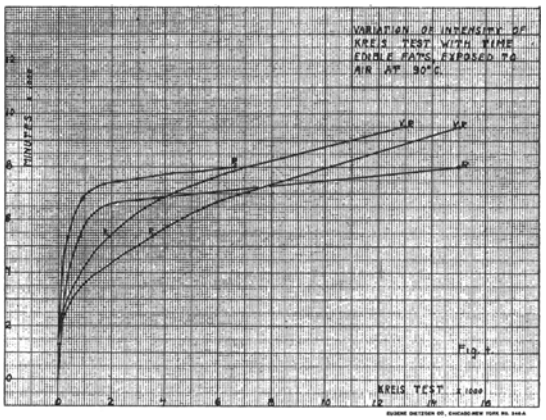

Fig. 4

dizability value, greater than 15, is confirmatory evidence of rancidity.

Kerr[17] modified the Issoglio procedure and used extraction with boiling water in order to separate the oxidizable substances from the fat being tested. The latter method has several advantages over the former and gives results which are just as consistent. However, the oxidizability value seems to behave very erratically in an aging sample of fat. Kerr found that on exposing a sample of fat to the air that the Kreis test became more intense at an increasing rate, but that the oxidizability number of the same sample had an initial value of 7, and later fluctuated between 7 and 13, and upon final analysis was approximately equal to 9. More work is necessary upon this test before its usefulness as a criterion on rancidity can be definitely determined.

The most widely used method for the detection of rancidity in fats is that devised by Kreis[18] in 1903, and later improved by Kerr. The Kerr procedure[17] is as follows:

10 cc. of the suspected fat are placed in a test tube or bottle and 10 cc. of concentrated hydrochloric acid are added. The tube is stoppered and shaken vigorously for approximately thirty seconds. 10 cc. of a 0.1% solution of phloroglucinol in ether are then added and the tube is closed, shaken, and allowed to stand for a few minutes. A red or pink color in the acid layer indicates a positive reaction. The Kreis test is expressed as a number which is a measure of the amount a fat must be diluted with a non-reacting solvent in order to give a negative result under the above conditions. The accuracy of the Kreis test, as a measure of rancidity, is very doubtful. In 1918, Kerr stated that a Kreis test greater than 20 represented fats which had definitely become rancid, and that the intensity of the test was roughly proportional to the rancidity. However, he added that the Kreis test was too delicate to be used alone as a criterion of rancidity, and that it was not specific for rancid fat.

Holm and Greenbank[19] in 1923 found that the intensity of the Kreis test of oxidized butter fat and lard was proportional to the amount of oxygen absorbed. These workers concluded, however, that although intensity of the Kreis test is a measure of oxidation, it has no direct quantitative relation to the degree of rancidity as measured by the olfactory sense. The reaction producing the colored compound on which the Kreis test is based has been ascribed to the condensation of phloroglucinol with various substances occurring in the rancid fat. It remained, however, for Powick[13] to definitely prove that the pink or red color indicating a positive Kreis test was due to a compound formed from the phenol and epihydrin aldehyde. This aldehyde, which is very unstable, does not exist as such in the fat. It is probable that in a rancid fat there is a parent substance in the form of an acetal which, upon treatment with an acid, decomposes to give the short-lived epihydrin aldehyde. A diethyl acetal of epi-

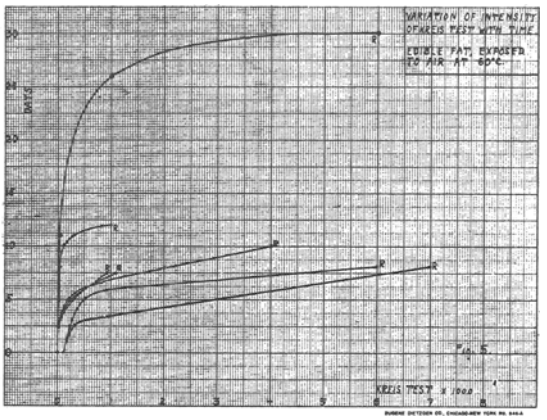

Fig. 5

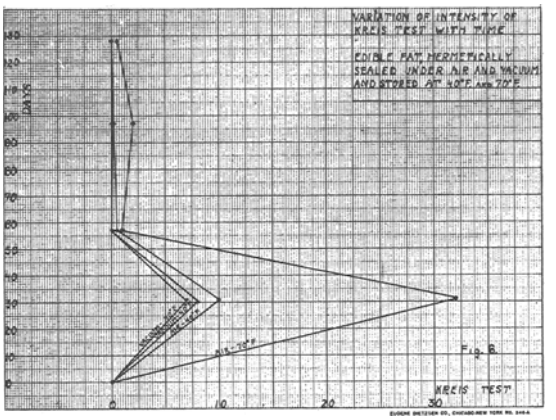

Fig. 6

hydrin aldehyde synthesized by Powick gave a Kreis test which was spectrographically identical with the positive test given by a rancid fat. The basis of the Kreis test is seen, therefore, to rest upon the unproved assumption that an acetal of epihydrin aldehyde occurs in all rancid fats in an amount which is proportional to the degree of rancidity. The status of the Kreis test is at present uncertain. Although it has been rejected by many scientific investigators as a means of detecting rancidity, it is still finding wide use commercially. The final report of the Kreis Test Committee will, no doubt, settle the very puzzling question as to the validity of the test in the determination of rancidity.

Stability

THE stability of a fat might be said to be the resistance which a fat offers to oxidation or to those changes which promote rancidity. It is a variable property whose origin is thought to be due to the comparatively low reactivity of glycerides with oxygen and to minute amounts of substances in the fat which act as negative catalysts to oxidation. All of the tests for stability depend in their final analysis upon the determination of the rate of oxidation. This is sometimes measured directly as in the oxygen absorption tests,[19] but usually the determination is of a very indirect nature as in the Bailey[20] test. The ordinary holding test for the determination of the keeping quality of fat, in which a sample is placed in a container and allowed to become rancid under ordinary conditions, has the disadvantage of requiring too great a length of time for completion. In some cases months might be required for information needed within days. Consequently, the process must be hastened without greatly changing those reactions which cause rancidity. This could easily be accomplished by elevating the temperature, by increasing the concentration of the oxygen or by increasing the surface at which the oxidation occurs.

Schaal of the Technical Bureau of the Biscuit and Cracker Manufacturers' Association devised such an accelerated test for stability which gives excellent results. 100 grams of a sample of fat are placed in a beaker and kept at an elevated temperature until it possesses a definitely rancid odor. The temperature usually used is 60° C. and the time required for the fat to become rancid at this temperature varies from four to more than forty days. By the use of this test, four unknown samples were classified with regard to their stability by five different laboratories with almost perfect agreement. Checks on the same samples are rather close, and the variation is very great between a fat of high stability and one of low stability. The two most serious disadvantages of this method are the large personal error, and the questionable effect of minute amounts of the volatile products from one sample upon an adjacent sample. A minor objection is the length of time required by fats of high stability to become rancid. Nevertheless, the test is finding widespread use at the present and is to be recommended as one of the best stability tests we now have.

Variations of such temperature accelerated tests for stability are many. Richardson increases the acceleration by using Petri dishes instead of beakers, thus offering a greater surface at which the oxidation could occur. Wesson achieved the same result by distributing the sample under investigation upon absorbent cotton. Bailey[20] went one step further by passing a current of air over the heated fat. His method, however, differed fundamentally from the previous tests in that organoleptic tests were not used for determining the completion of the reaction. His procedure is as follows:

Air is drawn at a definite rate over 3 grams of fat, evenly distributed upon a standard size filter paper, maintained at a constant temperature of about 90° C. The air is then passed into a modified solution of Schiff's agent which possesses the property of turning pink in the presence of aldehydes. The time required for the first appearance of this color is taken as an indication of the susceptibility of the fat to rancidity.

Bailey found the test useful in determining which of two fats would remain sweet the longer. In its present state of development it is merely comparative, and every batch of samples must be run with a control of proven quality. Wesson[21] has done some work with the Bailey test and states that tests made in the oven closely confirm the results of the Bailey stability test.

The oxygen absorption test measures the time required for a definite quantity of fat to absorb a specified volume of molecular oxygen. This is accomplished by placing the sample in a closed system, at some constant temperature, and measuring the absorption of the gas by the decrease in pressure within the system. The method was originated by Holm and Greenbank in the Bureau of Animal Industry, and in their hands, gave very consistent results. Since that time many workers have confirmed the reliability of the results obtained by this procedure as a measure of stability of edible fats. The working temperature is generally about 90° C., and the time required by the fat to absorb 30% by volume of oxygen is generally taken as the oxygen absorption value. This time will vary from three hours for a fat of very low stability to over sixty hours for a fat of extraordinary stability. If the fat is agitated or if the working temperature is increased, the oxygen absorption values become correspondingly lower. Oxidation is also greatly accelerated if pure oxygen or ozone be used instead of air as the oxidizing medium. This test is excellent as a means of measuring the keeping quality of edible fats, but due to the initial cost of the apparatus it is doubtful if it will ever find very widespread use except in research work.

Explanation of Figs. 1 - 8

FIG. 1 shows the rate of oxygen absorption at room temperature by four edible fats. The figures terminating the curves are the number of days required by the fat to become rancid under the conditions of the Schaal Test.

Fig. 2 represents the same sort of experiments shown by Fig. 1. Each curve is an average of four separate experiments on the same fat. As before the terminating figures of the curves are results of the Schaal Tests on the corresponding fats.

Fig. 3 is a schematic diagram of an apparatus for the rough determination of the oxygen absorption value of a fat.

Figs. 4 and 5 show the increase of the value of the Kreis test with time. Samples in these experiments were exposed to air. Points at which rancidity occurred are denoted by "R" on each curve.

Figs. 6 and 7 represent the increase of the intensity of the Kreis test when the samples are exposed to a limited amount of oxygen. The curves in Fig. 6 are averages of six individual experiments all of which gave very similar results. Each curve in Fig. 7 is an average of four experiments.

Fig. 8 consists of two generalized curves, one based on data from Figs. 4 and 5 and the other derived from inspection of Figs. 6 and 7. The two curves in Fig. 8 are not drawn to scale with respect to one another.

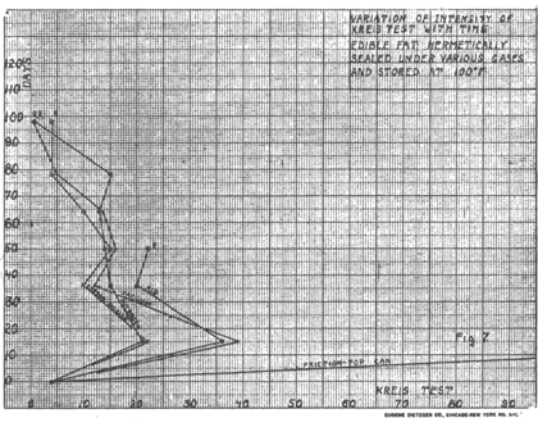

Fig. 7

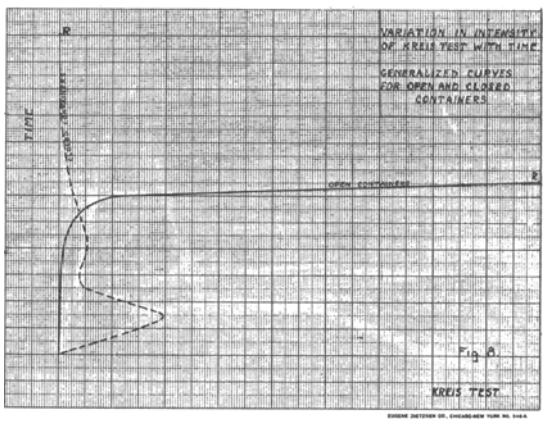

Fig. 8

Discussion of Data Contained in Figs. 1 - 8

IT IS evident from Figs. 1 and 2 that the results given by the Schaal Test are approximately inversely proportional to the speed with which a fat absorbs oxygen.

In Figs. 4 and 5 it is seen that the value of the Kreis test increases at an increasing rate if the sample is exposed to an unlimited supply of oxygen. Kerr in 1918 and Holm and Greenbank in 1923 have noted the same phenomenon.

Figs. 6 and 7 indicate that the change in the Kreis test takes an entirely different course in samples of fat exposed to only a limited amount of oxygen. In samples of fat having restricted access to oxygen, the Kreis test reaches a maximum and then begins a decrease which often results in the fat exhibiting a lower value than that it originally possessed. It is possible that this difference in type of change in the Kreis test of exposed and unexposed samples of fat might furnish an explanation of anomalous and contradictory results obtained by different workers in using the Kreis test as a means of detecting rancidity. A fat may have a negative Kreis test and be definitely rancid if it has been hermetically sealed, while the same fat may possess a comparatively high Kreis test and be non-rancid if exposed to an unlimited amount of oxygen. As many manufacturers of edible fat are placing their products on the market in hermetically sealed containers, increasing caution must be exercised in using the Kreis test in the detection of rancidity.

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Governing Committee, A. O. C. S.

The Governing Committee met May 13th, 1931, at 7:30 P. M. in Room G, Hotel Roosevelt, New Orleans, La. The Secy.-Treas. read the minutes of the last meeting, which were accepted unanimously.

Mr. Irwin submitted the following amendments to the By-Laws of the Society:

Article 5. Section A., to read as follows:

"The Society shall meet twice annually;—Spring and Fall. The Spring Meeting shall be known as the Annual Meeting of the Society; and shall be held at the same place selected by the National Cottonseed Products Association, within one week of the meeting of the National Cottonseed Products Association.

"The Fall Meeting shall be held at a place and time decided upon by the Governing Committee; and shall have equal powers as to making of rules and adoption of methods, as at the Spring or Annual Meeting.

"Due notice, of the time and place of each meeting, shall be sent to the membership by the Secretary of the Society."

Add as Article 9; Section A.:

Adoption of Methods

"Methods of Analysis offered, if adopted, shall be 'Tentative Methods', for a period of one year; after which they may be adopted as 'Official Methods', at any subsequent meeting of the Society."

On motion of R. H. Fash, seconded by M. M. Durkee, the proposed amendments were unanimously approved, to be submitted to the Annual Meeting, May 14th, 1931, for adoption by the Society. The Secy.-Treas. was was authorized to get a new supply of Moisture Dishes, and Binders for Methods of Analysis. The Secy.-Treas. was authorized to request Mr. C. B. Cluff to prepare a new supply of Official Fullers Earth; also to convey to Mr. Cluff the thanks of the Society, through the Governing Committee, for his cooperation in the past, in preparing the Official Fullers Earth.

On motion of R. H. Fash, seconded by M. M. Durkee, J. C. P. Helm was unanimously nominated as Secy.-Treas. of the Society for year 1931-1932. The Secy.-Treas. was instructed to write all members of the Society, with the aim of starting and maintaining a permanent mailing list for distributing revisions of methods each year, at a cost to each subscriber not to exceed 50c per year. On motion of R. H. Fash, seconded by M. M. Durkee—a unanimous vote of thanks and approval of all acts as President, was given Mr. W. H. Irwin; and the Local Committee of the Annual

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Cost Accounting

(*From page* 344)

give the feeling of accomplishment. Satisfactory employment must do both. The field of cost accounting should be broad enough to satisfy the demands of the most ambitious, since its function is to analyze all the elements of cost entering into a business, distribute them equitably to all its different departments and activities and finally equate them against the product. If properly carried out, the cost accounts become the chart, compass and sextant of modern business, the determining factor in fixing its course and policy. To use another figure, the cost accounts should be the fluoroscope which lays bare all the intimate inner workings of a business, and the cost accountant is in the position of the observing physician —ready to note and act upon any pathological signs which may appear.

With this intimate knowledge of the complete details of a business, it is hardly necessary to enlarge upon the opportunities for service offered.

Few chemists enter the commercial field with chemical work as the ultimate objective. Most have their ambitions directed toward executive positions and regard the laboratory as a good mounting block. In most manufacturing businesses there are three main avenues of advancement open—sales, office and operation. Most workers have but one choice, but for the technically trained cost accountant two avenues are always open, and the distance he can go along either or both is limited only by his capabilities and his willingness to accept responsibility.

With cost accounting, so to speak, just at the transition from an art to a science, it would seem to be an opportune time to urge that the chemical profession recognize cost accounting for the process industries as coming within the scope of its activities, and that educators take what steps are necessary to offer special preparation for this line of chemical work. This is done not from a selfish point of view as preempting a line of employment for chemists, but with a firm conviction that a properly trained chemist is the logical candidate for such a position, and that his employment in this capacity will be for the best interests of all concerned.

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The acreage devoted to coconuts in the Philippines during 1930 was 1,359,297 acres reports Trade Commissioner Rohrer at Manila. This compares with 1,312,200 acres devoted to the crop in the previous year, 1929.

Governing Committee

(*From page* 336)

Meeting, May 14 and 15, 1931, was authorized to draw on the finances of the Society to the sum of $150.00, to defray expenses of Meeting, Banquet and Entertainments of the Meeting; if the fees collected at Registration Desk were not sufficient. There being no further business, the meeting was adjourned.
J. C. P. HELM, *Secy.* W. H. IRWIN, *Chairman.*

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Marseilles Olive Oil Market

Conditions in the Marseilles olive oil market were fairly satisfactory during the June quarter. Prices were lower than at the time of the last crushing season, but this is due mainly to the fall in the value of the peseta, as the huge Spanish production necessarily has an effect on all markets. However, prices which were regularly declining up until the end of May showed an upward tendency in June, and the present situation is favorable. The small yield of the past season is expected to remedy the condition caused by the abundant world production of 1929-30, and to clear stocks which were being held. The lower prices have apparently created a new demand for olive oil replacing to a certain extent that for other vegetable oil.

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Mexican Oil Seeds 1931

In the quarterly Review of Commerce and Industries of the March quarter of 1931, the coquito crop was estimated at 2,700 tons. The final figures obtained show the production at 2,800 tons. The season ended the present year in the month of May with the great majority of the crop being sent to Guadalajara.

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The cod fishing season has come to an end, reports Commercial Attache Lund at Oslo, Norway, under date of July 16, 1931. Production of cod liver oil declined from 78,338 bbls. last season to 58,950 bbls. during the current season.

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It was reported in a recent dispatch from Minister Eberhardt at San Jose, Costa Rica, that the leading crusher of oil seeds in Cuba had been instituting inquiries in Costa Rica concerning available supplies of oil seeds and nuts, presumably for export to Cuba.

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Howard Kellogg, president of Spencer Kellogg and Sons, Inc., and of its grain elevator subsidiary, has purchased a seat on the Chicago Board of Trade.