STUDIES ON RANCIDITY—A RESUME

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Notwithstanding the interest of oil chemists in the subject of rancidity, the chemistry of this condition is still imperfectly known. It has been demonstrated, to be sure, that rancidity is caused by oxidation, presumably by oxidation of the oleic acid radical and of such other unsaturated acids as may be present. It is commonly known that rancid fats respond to general tests for aldehydes and for peroxides, as well as to the Kreis test which is given by some, but not all, aldehydes. Also a few of the constituents of rancid fats have been identified, *viz.*, azelaic acid, and most of the saturated fatty acids and aldehydes up to the C_9 compounds, while heptylic aldehyde has been prominently mentioned as the probable cause of the rancid odor.

Yet very little is known of the chemical mechanism by which rancidity is produced, or of the various factors which might serve to catalyze the process. The exact significance of the Kreis test has been a matter of conjecture and its reliability as an index of rancidity has been questioned because of the positive response that is sometimes obtained when the test is applied to nonrancid cottonseed oils. Even Scala's work, attributing the rancid odor to heptylic aldehyde, naturally involved the personal equation and would seem to be in need of corroboration.

Some of these questions have been discussed and a study of certain aspects of rancidity has been reported in a paper recently published in the Journal of Agricultural Research.* In these studies it was ascertained first of all that oleic acid, even when highly purified, will develop rancidity on exposure to air, responding to the various tests usually associated with the rancid condition; so that the compounds responsible for the odor and reactions of the rancid condition must be among the possible oxidation products of oleic acid. Between twenty and thirty compounds so listed by previous workers, or reported as having been found in rancid fats, were therefore prepared or purchased and submitted to a rapid sorting test. Not one of these compounds responded to the Kreis test for rancidity, while all but nonylic and heptylic aldehydes could be eliminated as sources of the rancid odor. Of these two aldehydes the latter especially resembled rancid fat in odor, although both compounds lacked a certain sharpness of odor which is generally present in rancid fats. Evidently rancid fats contain other constituents—hitherto unrecognized oxidation products of oleic acid—which singly or collectively contribute to the odor of rancidity and are responsible for the reaction of rancid fats in the Kreis test.

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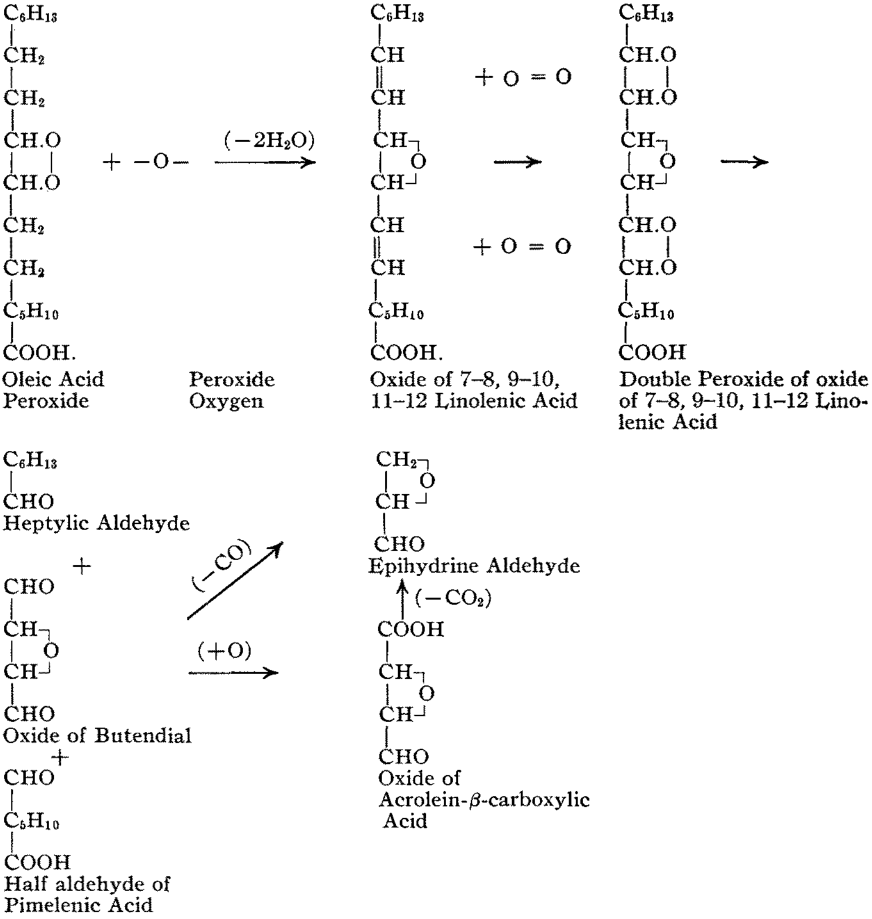
* "Compounds Developed in Rancid Fats, with Observations on the Mechanism of their Formation." W. C. Powick, *Journ. Agrl. Res.*, **26**, 323 (1923).

It has long been suspected that the first stage in the atmospheric oxidation of oleic acid consists in the direct addition of molecular oxygen at the double bond with the formation of oleic acid peroxide. This supposition is in harmony with chemical theory and with the presence in rancid fats of peroxide oxygen and of nonylic aldehyde which is presumably formed by cleavage of oleic acid peroxide. A direct study of oleic acid peroxide and its decomposition products would undoubtedly be desirable; but as there is no known method for isolating this compound, the closely related oleic acid ozonide was prepared and examined instead. The latter compound was found to have a sharp, penetrating odor suggestive of that quality in the odor of rancid fats which is not accounted for by the presence of heptylic and nonylic aldehydes; and after partial hydrolysis with formation of nonylic aldehyde, it yielded an odor closely resembling that of rancid fats. Presumably, oleic acid peroxide resembles the ozonide in odor, and is responsible for the sharp quality in the odor of rancid fats. Neither the ozonide itself, however, nor the products obtained by hydrolyzing it with water *i. e.*, the C_9 aldehydes and acids, gave a characteristic response in the Kreis test; but when the ozonide was warmed gently with concentrated hydrochloric acid, evidently experiencing thereby a different kind of decomposition, a definite, though somewhat delayed response, was obtained. Presumably, similar results would have been obtained with the peroxide.

The compound responsible for the Kreis test, however, defied separation and the experiments with oleic acid ozonide offered no clue as to its identity. Attention was therefore directed to the color reactions of phloroglucine. Apparently, most, though not all, of the compounds that yield red condensation products with phloroglucine are aldehydes that contain a double bond—a fact which suggested the examination of acrolein and crotonic aldehyde. In case of acrolein in dilute aqueous solution, no response to the Kreis test could be observed. In case of crotonic aldehyde, on the other hand, an intense red color was immediately obtained; yet this color, unlike that obtained with rancid fats, was fugitive and disappeared within a few minutes when the solution was agitated. The conduct of these aldehydes, when mixed with hydrogen peroxide, however, was entirely different, the acrolein-hydrogen peroxide solution giving an intense and comparatively stable red color in the Kreis test, while the crotonic aldehyde-hydrogen peroxide solution gave no response whatever.

A rigid spectroscopic and spectrophotometric examination identified the Kreis color body obtained from acrolein and hydrogen peroxide with that obtained from rancid fats, and differentiated them both from the similar colors obtained from a variety of other compounds and from certain specimens of nonrancid cottonseed oils. The former colors showed a distinct absorption band in the yellow-green region at wave length 5500 Å, while the latter colors showed continuous absorption at the violet end of the spectrum. This distinction is probably not without its utility to cotton-oil chemists.

On further investigation of the reaction between acrolein and hydrogen peroxide it was found that the reaction product which gives the characteristic response to the Kreis test is formed only in strongly acid solution, that it reacts with phloroglucine in weakly acid solution, and that it does not contain peroxide oxygen. After examination of a number of the C_3 aldehydes with negative results, epihydrine aldehyde diethyl acetal was synthesized and in the Kreis test was found to yield a red color spectroscopically identical with that obtained from rancid fats and from acrolein hydrogen peroxide mixtures; while elementary analysis of a dried and somewhat altered sample of the Kreis color body prepared from the latter source showed it to correspond in composition to an anhydride of the phlo-



roglucide of epihydrine aldehyde. It thus appears that the color obtained in the Kreis test on rancid fats is due to the formation of a phloroglucide of epihydrine aldehyde.

No direct evidence of the presence of acrolein or of free epihydrine aldehyde in rancid fats could be obtained, although some of the experiments would seem to indicate that the epihydrine aldehyde radical is present in the form of one of its simple compounds, possibly as an acetal, and that its formation is not dependent upon the action of the concentrated hydrochloric acid employed in the Kreis test.

However, that may be, it is certain that the Kreis test depends on the ultimate formation of the epihydrine aldehyde radical, and that the formation of oleic acid perioxide is the first of a series of reactions that may culminate in the production of this radical. The formation of C_9 aldehydes and acids in the development of rancidity is comprehensible enough, but the formation of C_7 (heptylic) and C_3 (epihydrine) aldehydes is somewhat puzzling. Only by the introduction of new double bonds into the oleic acid chain or into that of its C_9 cleavage products, does the further fragmentation of the molecule seem possible. Solway has suggested a plausible mechanism for the formation of heptylic aldehyde and acrolein in the oxidation of linolenic acid; and the accompanying adaptation of his scheme is suggested as a possible explanation of the processes at play in the development of rancidity.

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THE SULFURIC INDEX OF COTTONSEED OIL AND IN ADMIXTURES WITH OLIVE OIL

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Mazzaroni,[1] in determining the thermal index of oils by the Tortelli method, observed that the reaction of the oil and sulfuric acid was always accompanied by the formation of a gas, chiefly sulfurous anhydride, and that the quantity of gas given off varied with the nature of the oil under examination. This led to an attempt to measure the quantity of the gas liberated by passing it into an appropriate iodine solution and noting the quantity of iodine consumed. Mazzaroni termed this factor the "sulfuric index," a heretofore unrecorded constant of an oil.

The purpose of the work here reported was to utilize the principle advanced by Mazzaroni and to show to what extent the sulfuric index can be utilized as a means of identification of simple oils or of the constituent oils in mixtures.

It was necessary to devise an arbitrary procedure and apparatus in order to control every factor that enters into this determination.

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[1] *Staz. Sperim. Agrar. Ital.*, **48**, 583–594 (1915).