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REVIEW

A Brief History of Lipid Oxidation

Earl G. Hammond · Pamela J. White

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Abstract The history of our understanding of fat oxidation is reviewed from the early observations that oxygen was involved to the discovery of the role of singlet oxygen. It includes the debate about relative importance of triglyceride hydrolysis and oxidation; the search for tests that correlated with oxidized flavor; the evidence that oxidation involved the formation of hydroperoxides; the development of tests for hydroperoxides; and the work on the chemistry, mechanism, and kinetics of oxidation by the British Rubber Producers Research Association. The review ends with the effort to isolate and determine the structure of the oxidation products of the common unsaturated fatty acids, their relative rate of oxidation, and the role of singlet oxygen and metals in initiation.

Keywords Autoxidation · Lipid chemistry · Lipid analysis

One dilemma in writing a history of lipid oxidation is deciding when to start. For example, Denisov and Afanas'ev [1] start their history of oxidation in organic chemistry with the discovery of oxygen by Scheele, Priestley and Lavoisier from 1768 to 1770; the synthesis of the first free radical by Gomberg in 1900; and the proposal of chain reactions by Hinselwood in 1929. Although our focus will be the oxidation of fats and oils, we should remember that advances in our field also depended on advances in general chemistry.

Nicolas Théodore de Saussure (1767–1845) published his work on the uptake of carbon dioxide and production of oxygen by plants [2]. He also used his manometer to follow the absorption of oxygen during storage of plant oils. He reported that during 4 months turpentine took up 20 times its volume of oxygen and produced five times its volume of carbon dioxide. Linseed oil was able to absorb more than 12 times its volume of oxygen during 4 months without producing a detectable amount of carbon dioxide. He speculated that the formation of a resin by the linseed oil might be caused by the oxygen uptake, but he believed more experiments were required to understand this change.

In an 1815 publication, Henri Braconnot (1780–1855) noted previous reports by most chemists had agreed that acids were formed during the rancidification of fats. However, Thenard and Parmentier had questioned the formation of acids during rancidification, and Parmentier suggested that it was the reaction of oxygen with the fat that caused rancidity. Braconnot did not further identify Thénard and Parmentier, but they were most likely Louis Jacques Thénard (1777–1857), a famous French chemist, and Antoine-Augustin Parmentier (1737–1813), a pharmacist known chiefly for advocating the growing and consumption of potatoes in France. Braconnot did not feel their hypotheses had been proven, and he reported that he had been able to remove the rancid-odor compounds from candles made of sheep's tallow by steam distillation and show that the distillate was acid to litmus paper. Of course, we now know it is quite possible to produce acids by oxidation of the aldehydes formed during fat oxidation. This was especially true of the highly oxidized fats favored by the early students of rancidity. So it seems both Parmentier's hypothesis and Braconnot's experimental results were correct [3].

E. G. Hammond (✉) · P. J. White
Department of Food Science and Human Nutrition,
Iowa State University, Ames, IA 50011, USA
e-mail: hammond@iastate.edu

During the 1800s and early 1900s, lipid chemists tended to be focused on the flavors of oxidized fats and oils, what factors accelerated or slowed flavor development and how to test for oxidation. Lipid chemists were able to titrate oxidized fat with a base and show that oxidation was often accompanied by increased acidity. This led to continual debate about the relative importance of fat hydrolysis and oxidation in the development of rancidity. As late as 1910, Leathes [4] wrote, “The changes undergone by fats and oils when they become rancid are probably initiated or favored by enzymes that hydrolyze the glycerides. The free fatty acids are then oxidized by the oxygen of the air in the presence of traces of moisture. But the part played by enzymes and also by the action of light is a subject of some dispute. The changes consist in (1) the appearance of hydroxy acids and (2) of lower volatile fatty acids, their esters or aldehydes; (3) the hydrolysis of the fat and (4) the disappearance of the liberated glycerol.”

The evaluation of butter particularly caused confusion about the nature of “rancidity”, because butter contains short chain fatty acids that reveal their strong flavors when milk fat is hydrolyzed. In the 1800s and early 1900s there was often ample time for bacteria to grown in cream in route to a creamery. Even when lipolytic bacteria were not growing in the cream, foaming could induce lipolysis via the natural lipases in milk. In addition, milk is susceptible to the formation of oxidized flavors especially when copper- and iron-containing equipment is used in milk’s transport or processing. Émile Duclaux (1840–1904) [5] was one of the first to begin distinguishing the various flavors of deteriorating butter and their causes. He believed that rancidity was caused by a spontaneous decomposition of triglycerides. Particularly he noticed the effect of sun light on butter flavor. Gradually, people learned to distinguish these flavors and their causes. Both dairy and lipid specialists claimed the term “rancidity” to describe the off-flavors in their products. So it became important to distinguish “hydrolytic rancidity” from “oxidative rancidity.” Currently the term rancidity is in less favor and other terms (lipolyzed flavor and oxidized flavor) are used frequently by both dairy and lipid specialists.

Tsujimoto [6] concluded from his work on polyunsaturated fish oil that the oxidation of the triglycerides, rather than free fatty acids, caused rancid flavors. The question of the importance of free fatty acids in rancidity had been almost resolved by 1939 [7] when C.H. Lea of Cambridge University in England wrote, “Much confusion existed in the earlier literature concerning the connection between free-acid content of a fat and rancidity… Early investigators used increase in free acidity as a general indication of the development of rancidity. Later it came to be recognized that atmospheric oxidation is considerably less important as a potential producer of free fatty acids than moisture and enzymatic or bacterial action.” Lea, citing one of his own experiments, pointed out that “in the earlier stages of light-accelerated oxidation at room temperature, very little change in free acidity occurs, with the result that a fat may be extremely rancid and yet possess a low acidity” [8].

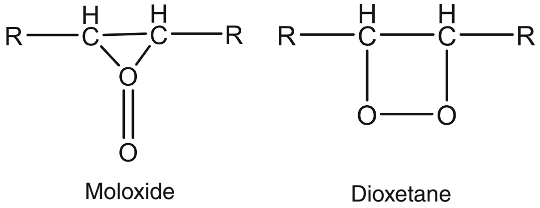

Fig. 1 Structures suggested for the addition of oxygen to fatty acids to account for the loss of unsaturation sometimes observed

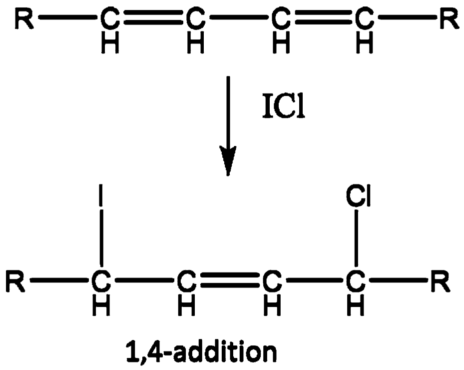

Fig. 2 Reaction of a conjugated double bonds with iodine chloride

Another problem for early students of fat oxidation was the iodine value. The Wijs method [9], using iodine chloride, replaced the earlier Hubl method of detecting double bonds in aliphatic chains. It was noted that for many oils, the iodine value decreased with oxidation. This gave rise to the belief that oxygen was adding to the double bond and forming moloxides or dioxetane rings (Fig. 1). Many of these observations were undoubtedly caused by conjugation of the double bonds of polyunsaturated fatty acid during oxidation. The Official Methods and Recommended Practices of the American Oil Chemists’ Society CD1–25 [10] carries the warning, in note one, that the Wijs method is not stoichiometric for conjugated fatty acids. The iodine chloride adds to the ends of a conjugated diene and leaves a new double bond in the middle of the four carbons making up the diene, and this new double bond adds iodine chloride very slowly (Fig. 2). Lea notes “a relatively advanced state of deterioration from the point of view of odor and flavor must be reached before an appreciable change in iodine-value is detectable. This is particularly true in the case of fats of the butter and beef fat type, in which oleic is the chief unsaturated acid.” [11].

Without an understanding of the nature of the oxidation reaction and its products, lipid chemists turned to various reactions to try to find a test that seemed to correlate well with rancidity. Rancidity itself was hard to measure, because sensory evaluation was not well developed at the time. People with extensive experience might be regarded as expert tasters, but statistical treatment of sensory data was seldom applied, and it was difficult to compare work from one laboratory with the next.

Fahrion [12] observed that in highly oxidized fats, some of the material was no longer soluble in petroleum ether, and he suggested this as a method for quantifying oxidation. This method was not very sensitive and was soon abandoned. Issoglio [13] developed a test based on the volatile materials that could be isolated by steam distillation. Kerr [14] suggested a variation in which the volatile material was isolated by extraction with boiling water. The amount of material extracted was determined by the amount of potassium permanganate needed to oxidize it. Lea [15] reports that the results of these methods were "somewhat erratic."

Kreis [16] developed a test for rancidity based on reacting melted fat or oil with hydrochloric acid and phloroglucinol (1,3,5-trihydroxybenzene) in diethyl ether solution. A red color in the aqueous layer is indicative of rancidity, and the darkness of the layer was a rough measure of the extent of rancidity. Many variations of this method have been proposed, and colorimeters and spectrophotometers have been used for quantification. Powick [17] found that acrolein treated with hydrogen peroxide to form 2,3-epoxypropanal gave a strong Kreis test. 2,3-Epoxypropanal could easily be transform into malonaldehyde, which also gives a positive Kreis test. The Kreis test has generally been abandoned for the more sensitive thiobarbituric acid or TBA test that also gives a reddish color with malonaldehyde.

Kohn and Liversedge [18] noted a red color on incubating animal tissues with thiobarbituric acid. Bernheim et al. [19] showed that the color depended on fat oxidation. Patton and Kurtz [20] introduced the test as a measure of oxidation in milk fat. Many variations of this test have followed. The test is particularly sensitive to the oxidation of linolenic acid, and TBA is known to react with other aldehydes. The TBA test is used today mostly by meat scientists who value the ease with which malonaldehyde can be extracted from complex animal tissues. On the other hand, some purists in the measurement of fat oxidation feel so strongly about the inappropriateness of the TBA test that they have been reported to ban thiobarbituric acid from their laboratories.

Stamm [21] developed a colorimetric test for rancidity based on the reaction of fats with diphenylcarbazide. He believed this test was a test for carbonyl compounds. Actually the diphenylcarbazide is known to be oxidized to red-purple diphenylcarbazone. Hamm et al. [22] showed that this test is both a pH indicator and a test for peroxides. If used in a solution acidified with acetic acid, the Stamm test can become a sensitive colorimetric measure of peroxides. Like many colorimetric peroxide tests the test gives high values by reacting with oxygen dissolved in the solvents, but this can be corrected by a suitable constant.

There was evidence that rancid fat contained carbonyl compounds, so various tests were developed to determine them. Forming derivatives with hydroxylamine, hydrazine or semicarbazide directly in the fat were proposed but did not work very well because of the solubility of the derivatives in the fat. So tests for the actual flavor compounds of oxidized fats and oils were not available until the development of thin-layer and gas chromatography.

One notable development in lipid oxidation of the 1930s that had enduring value was the development of methods to measure peroxides. By this time it was generally agreed that oxidized fats always had peroxides. Lea developed a method based on the release of iodine from potassium iodide by fat dissolved in acetic acid and chloroform. Lea believed it was important to exclude dissolved oxygen in the reaction mixture by boiling the solvents during the reaction. Water was added and the iodine released was determined by titration with thiosulfate [23]. This method has generally been replaced by the Wheeler method [24], which is endorsed by the AOCS Official Methods and Recommended Practices Cd 8–53 [25]. This method has a 1-min reaction time and does not require removal of oxygen. Wheeler also used a starch indicator in the titration. The method determines hydroperoxides but not the more stable dialkyl peroxides.[1] Mair and Hall [26] have reviewed the issues involved in obtaining accurate peroxide values.

Great progress was made from 1929 to 1940 in understanding the mechanism of the oxidation of alkenes. Progress was brought about by selection of a suitable, readily available and representative model compound. Although fatty acids might have filled this need, their isolation in a pure form was laborious and their high boiling point complicated separations of the heat-sensitive oxidation products by distillation. Also, the lipid chemists who were interested in oxidation were focused on flavor for which methodology was still lacking.

The first step in understanding the mechanism was taken by Stephens [27] at the University of Minnesota. He

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[1] Colin Henry Lea did undergraduate work at Liverpool and was admitted to Cambridge in 1928. He completed his Ph.D. in 1932 on the topic of Rancidity. He worked for many years at the Low Temperature Research Station at Cambridge. In 1953 he was recognized with a D.Sc..

Donald H. Wheeler worked for General Mills in St. Paul, Minnesota for many years and was a regularly attender of the meetings of the American Oil Chemists' Society.

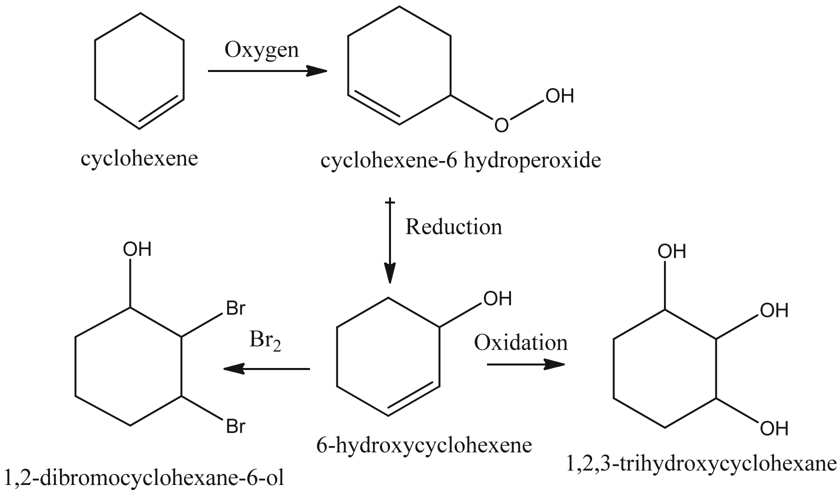

Fig. 3 Oxidation of cyclohexene to cyclohexene hydroperoxide, its reduction to cyclohexenol, and its further oxidation reduction and bromine addition

oxidized 800 g of cyclohexene for 4 months by slowly bubbling oxygen though it. He was able to isolate 6 g of material boiling at 50–56 °C at 0.5 Torr. This substance was pungent, corrosive to the skin, and showed reactions typical of a peroxide. The molecular weight suggested it was monomolecular, although a bimolecular compound also was isolated from the distillation residue. Stephens had chosen an ideal compound with which to study the oxidation mechanism.[2]

Criegee et al. [28] produced the same product reported by Stephens by shaking cyclohexene in a vessel under an oxygen atmosphere at 35 °C while it was exposed to an ultraviolet lamp. The product, although not pure, had carbon–hydrogen contents comparable to that of cyclohexene hydroperixide. Criegee et al. provided several lines of evidence that the peroxide was a hydroperoxide (Fig. 3). (1) It could be reduced to cyclohexanol. (2) It could be oxidized to cyclohexatrienol. (3) Treatment with acid gave 2-cyclohexenol. (4) It added two atoms of bromine. (5) It contained an active hydrogen that could be recovered with methyl magnesium bromide. (6) It gave off oxygen with lead tetra-acetate, a reaction characteristic of hydroperoxides. The reactions of the hydroperoxide were consistent with the attack of the oxygen being alpha to the double bond rather than on the double bond itself.[3]

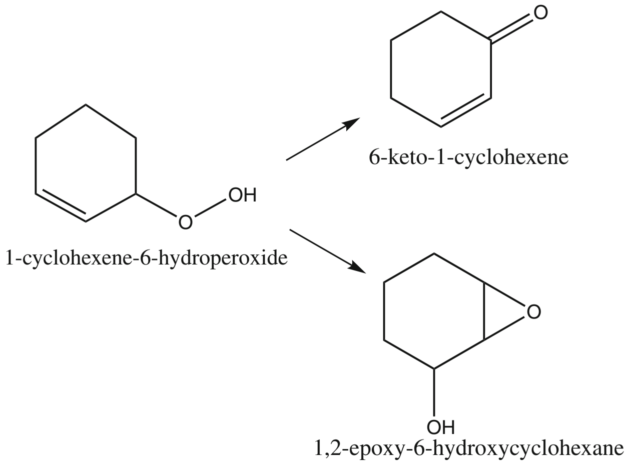

Fig. 4 Modes of decomposition of cyclohexene hydroperoxide

In 1932, Ernest Harold Farmer, a teacher at the Royal College of Science became interested in the chemistry of rubber, and in 1938, he joined the British Rubber Producers as senior chemist and collected a small staff to work on theoretical hydrocarbon oxidation as well as the oxidation of rubber [29]. Farmer and Sundralingam [30] confirmed the work of Stephens by making cyclohexene hydroperoxide. The work of Criegee et al. was not available in England at this time because of World War II, and they rediscovered many of the findings of Criegee. They agreed with Criegee et al. [28] that the oxygen added alpha to the double bond to form hydroperoxides. They also pointed out

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[2] When Hammond was a graduate student at the University of Minnesota 1950–1953, he met Stephens and was a frequent guest in his house on White Bear Lake because he attended a church youth groups with Stephens' daughter, Betty, to whom we are indebted for information about Stephens. Betty Stephens Gallagher notes that her father was an unusually silent man. Hammond says if he had been aware that Stephens had done this early experiment on cyclohexene peroxide and that he would write this paper ~60 years later, he would have made more effort to overcome Stephens' taciturnity.

According to Betty Stephens Gallagher, Henry Stephens was born 1897 in Glencaim, Ontario. About 1906 his family moved to Alberta where later the town of Vermillion sprang up. He attended the University of Toronto (1921) and Magill University (1923). He taught at the University of Minnesota from 1923 to 1937. He also worked summers for 3 M Corporation and in 1937 started 3 M's research department and became a Vice President of the company. He retired in 1954 and died in 1975.

[3] Criegee (1902–1975) studied at Tűbingen, Greifswald and Wűrzberg, receiving his doctorate in 1925. In addition to his work on cyclohexene peroxide, he discovered several important organic reactions.

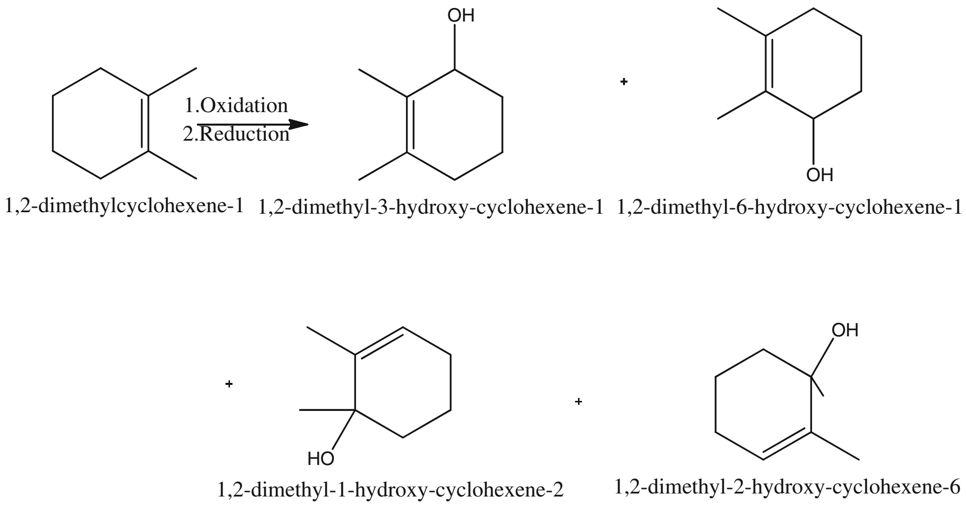

Fig. 5 Possible products by alpha attack and the shift of the double bond position during oxidation of 1,2-cyclohexene-1. The double bonds are consistently number 1 and 2 to make clear the shifts in double bond position that have occurred. The tertiary alcohols formed when the double bond shifts were the proof the shift had occurred

other instances of alpha attack. They studied the stability of the cyclohexene hydroperoxide and showed that one cause of the decrease of iodine value often observed during oxidation could be attributed to secondary reactions of the hydroperoxides, such as the formation of epoxides by attack of the hydroperoxide on double bonds (Fig. 3). They also showed that ketones can be formed by decomposition of cyclohexene hydroperoxide with the generation of water. They synthesized 1-methylcyclohexene-1 and 1,2-dimethylcyclohexene-1 and showed the formation of hydroperoxides in a manner similar to cyclohexene (Fig. 4).

Farmer and Sutton [31] continued these discoveries with an examination of the oxidation products of methyl oleate. They showed again that peroxides were an early product and that the double bond was intact. The peroxide could be hydrogenated to methyl hydroxystearate or reduced to methyl hydroxyoleate. In the same year, Farmer and Sutton [32] examined a concentrate of methyl docosahexaenoate from fish oil and found that it rapidly absorbed oxygen at room temperature, which often was followed by chain scission. Moreover, the rancid flavor of oxidized fish oil was entirely in the volatile fraction. They confirmed the report of Edisbury, Morton and Lovern [33] that the absorption spectrum of fish oil increased at short wavelengths by oxidation. In 1946, Farmer and Sutton [34] reported that this change in the absorption spectrum is caused by double-bond conjugation, which can occur when a methylene group between two double bonds loses a hydrogen atom. They suggested such double bond migration can also occur in the oxidation of single double bond compounds such as cyclohexene, demonstrating this with the peroxidation of 1,2-dimethylcyclohex-1-ene, which yielded the 3-and 6-hydroperoxy-1,2,dimethyl cyclohexene-1, and the 5- and 2-hydroperoxy-1,2-dimethyl-cyclohexene-1,6. The 2-hydroperoxy form had a tertiary carbon, and they showed that some of the hydroperoxide was on a tertiary carbon, proving that the double bond had migrated (Fig. 5). Farmer and Moore [35] reported a reaction of *tert*-butyl peroxide with olefins, including cyclohexene, which under nitrogen atmosphere resulted in dimerization of the cyclohexene.[4]

Other members the Rubber Producers Research Association, Bolland and Gee, also made important contributions to the kinetics of fat oxidation. Bolland [36] and Bolland and Gee [37] worked out the basic equations for the rate of chain oxidation of ethyl linoleate, and its autocatalytic nature. They also showed that the rate varied with oxygen pressure and temperature, the rate of initiation was a function of the square of the peroxide concentration, and the molar heat of activation of the oxidation reaction was 17.5 kcal. They also demonstrated energetic favoritism for conjugation of the double bonds in linoleate during oxidation. Bolland and ten Have [38] showed that hydroquinone worked as an antioxidant by removing the peroxy free radical and stopping the reaction chain. They also demonstrated conversion of hydroquinone to benzoquinone during its behavior as an antioxidant. Bolland [39] measured the energy required to extract an alpha-hydrogen from 23 unsaturated hydrocarbons. In Bolland's last paper [40] he and his coworkers attempted to determine the rate constant for the

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[4] Farmer was born in 1890 at Longford in Derbyshire. He served in World War I and was seriously wounded in 1914. By 1919 he was attending the Royal College of Science from which he graduated with a D.Sc. in 1924. By 1951 Farmer's health had began to fail, and he died in 1952 (24).

Sundralingam went to Ceylon and worked there in the rubber industry. Sutton went to South Africa and continued to study oxidation, and Moore continued to work on the chemistry of rubber.

termination reaction at low oxygen pressure but failed because of experimental difficulties.[5]

The work of Farmer and the Rubber Producers Research Association group was summarized in the Journal of the American Oil Chemists' Society [41] and two books edited by Lundberg [42] on autoxidation and antioxidants.

A number of people undertook studies of the primary products of the oxidation of linoleic, linolenic and oleic esters to verify the structures predicted by the theories of the Rubber Producer's Association. They used adsorption chromatography, partition chromatography, solvent partition, and urea fractionation to isolate the oxidation products of the methyl esters of oleate, linoleate and linolenate. Generally, those who used the last three methods were the most successful. Various techniques also were used to determine the positions and *cis–trans* orientations of the double bonds and the position of the hydroperoxide groups. Several groups worked on these projects: Colgate-Palmolive-Peet, the Eastern and Northern USDA Regional Research Laboratories, The Hormel Institute, The National Chemical Research Laboratory of South Africa, and Tory Research Station Aberdeen. This work established the current understanding of the structure of hydroperoxides and verified the theories advanced by the Rubber Producers' Research Association. These aspects of fat oxidation were reviewed by Frankel [43].

Further work showed the frequent presence of cyclic peroxides in oxidized fats. Lundberg et al. [44] first proposed the existence of these compounds. Begemann et al. [45] and Ross and Franke [46] gave evidence of the presence of four hydroperoxides with oxygen-containing rings. Neff et al. [47] isolated two hydroperoxides that also contained epidioxy six-membered rings from singlet oxygen attack of methyl linoleate. The mechanisms of possible structures and likely routes to their formation were reviewed by Chan [48] and Frankel [49].

Gunstone and Hilditch [50] isolated pure methyl oleate and linoleate by crystallization and methyl linolenate by bromination and found their individual rates of oxidation to be 1:12:∼25. These values have been approximately confirmed by subsequent studies on ester mixtures [51–56], verifying that control of the rate of oxidation, is not by the initiation of free radicals, but by the rate of extraction of hydrogen from a position alpha to a double bond.

The possibility of the existence of singlet oxygen was suggested as early as 1916 [57], but its role in the initiation reaction of fat oxidation was not appreciated until after the discovery of singlet oxygen by Khan and Kasha [58], and the discovery that singlet oxygen could be generated readily by the reaction of hydrogen peroxide and perchlorate ion [59]. Singlet oxygen can also be generated by the transfer of energy from pigments that have absorbed light energy to form ordinary oxygen. The singlet oxygen adds readily to double bonds directly and results in peroxides with different structures than those generated by the chain reaction. Carotenes can remove the energy from singlet oxygen and reduce its effect [48, 49]. This history would be greatly expanded if we were to report all the advances since 1950. This era also witnessed the identification of many flavor compounds generated in the oxidation of lipids and the introduction and regulation of commercial antioxidants, but a new review of their history must wait for another time.

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[5] John Lawson Bolland attended Edinburgh University and received a B.Sc. in pure science in 1935 and a Ph.D. in 1937. From Edinburgh he went to Cambridge and worked with E.K. Rideal, J.H. Plumber and H.W. Melville. He left Cambridge in 1939 and went to work for the British Rubber Research Association where he continued to work until about 1950. He seems to have moved earlier to Manchester, where he published his last papers on rubber (1950), cellulose (1953), and the light-catalyzed oxidation of alcohols (1953). He was honored with a D.Sc. by Edinburgh in 1953.

Geoffrey Gee was born June 6 1910 in Disley, Cheshire into a devout Methodist working-class family. Encouraged by his family, Gee secured a scholarship to Manchester University. In 1933 and in the depression he was not able to obtain support to finish his Ph.D. program at Manchester, but he did obtain support to work under Eric Rideal at Cambridge where Gee developed an interest in polymerization. Eventually he received a permanent position at the British Rubber Producers Research Association in 1938 and continued there until 1953, eventually becoming director. In 1953 he went back to Manchester University where he led the physical and inorganic departments.

In 1963 he became Dean and Pro-Vice Chancellor of Manchester University and continued in this post until 1977. He died in 1996.

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