

Rancidity.

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I. DEVELOPMENT OF RANCIDITY.

BOTH on account of its commercial and its scientific importance, rancidity is a subject which arouses perennial interest. Animal and vegetable fats and oils become rancid under certain conditions. The change is primarily autoxidative in character and is very often accompanied by secondary reactions such as molecular condensation, the development of colouration and undesirable odours. Raw vegetable oils have generally better keeping qualities than animal fats, primarily because of certain antioxidative principles present in them.¹ The natural antioxidants present in olive and linseed oils can be removed almost completely by repeated boiling with water.² Refined oils are less stable than natural oils, chiefly because of the removal of antioxidants in the process of refining. It is significant that vegetable oils are rich in aliphatic acids.

When exposed to oxygen, natural fats exhibit the typical characteristics of an autocatalytic oxidation. There is a latent or induction period during which the amount of oxygen absorbed is very small. After this the rate of oxygen absorption increases and the onset of rancidity generally coincides with the end of the induction period.

Among the many factors that have been mentioned as accelerators in the production of rancidity may be mentioned heat,³ light,⁴ acidity,⁵ moisture,⁶ enzymes,⁷ metals⁸ and speaking very broadly, any physical factor capable of adding energy to the system.

Conflicting views have been held regarding the role of moisture as a catalyst in the oxidation of fats. It is now generally believed that the presence of moisture has a retarding action upon the development of rancidity.⁹ Moisture prevents the formation of aldehydes and ketones which are stable products and which produce the tallowy odours and flavours. In a humid atmosphere the end products are acids without tallowy odours. Since acids act as catalysts in oxidation processes, it should be expected that after a preliminary stage, the rate of oxidation would increase. It is also probable that the action of moisture varies greatly with the nature of the fat in question.

Several theories have been propounded from time to time with a view to elucidating the mechanism of autoxidation. All of them agree in one point, viz., that the first change in the reaction consists in the addition of molecular oxygen to the double bond of the unsaturated acids with the production of highly reactive peroxides. These peroxides then isomerise, decompose into, or react with water to form a complex series of products like aldehydes, ketones and acids of lower molecular weight. A thorough knowledge of the chemical changes taking place during rancidity will be of scientific interest while a clear understanding of the bearing of the initial stages would be of great practical value.

Animal fats are abundant in carotinoid pigments. Most of the workers are agreed that they function as procatalysts.¹⁰ Again, neutral substances like sterols become prooxidants after irradiation.¹¹

Light has an accelerating action on the autoxidation of fats.¹² There is no doubt that oxidation takes place continually in oils and fats, but this action proceeds more rapidly in the presence of light than in the dark. Experimental evidences show that green light delays the development of rancidity almost to the same extent as does the exclusion of all light.¹³ Disappearance of ability to absorb blue light is apparently accompanied by development of rancidity. Invisible ultra-violet light has also the same accelerating effect as blue light. The process is autocatalytic, i.e., once oxidation has set in, removal of the source of light does not reduce the rate to that of the unexposed fat.¹⁴ The reaction continues to proceed in the dark at a rate depending upon the amount of oxygen already present. From this it may readily be seen that the potential storage life of many fatty products is seriously impaired by the methods employed in their manufacture.

There is now ample evidence to show that the organoleptic rancidity is not developed when the oil is protected from light.¹⁵ In fact, it has been claimed that light alone is sufficient for the production of rancidity,¹⁶ as fats will produce the odour and taste typical of rancidity, in the absence of air when exposed to light.

Temperature is another factor that accelerates rancidity. Heating at 100° C. has more marked effect on production of rancidity than exposure to air.¹⁷ Exposure to temperatures upto 50° C. has no marked effect, which shows that at 100° C. some intramolecular change is probably taking place. The best temperature for preservation is 0° C. or lower. It has been shown by several

¹ Matill and Crawford, *Ind. and Eng. Chem.*, 1930, **22**, 341.

² Banks and Hilditch, *J. Soc. Chem. Ind.*, 1932, **51**, 411T.

³ Bevis, *J. Soc. Chem. Ind.*, 1923, **42**, 417T.

⁴ Greenbank and Holm, *Ind. and Eng. Chem., Anal. Edn.*, 1930, **2**, 9.

⁵ Holm and Greenbank, *Ind. and Eng. Chem.*, 1924, **16**, 518.

⁶ Davies, *J. Soc. Chem. Ind.*, 1928, **47**, 185T.

⁷ Pennington and Hepburn, *J. Am. Chem. Soc.*, 1912, **34**, 210.

⁸ King, *et al.*, *Oil and Soap*, 1933, **10**, 204.

⁹ Greenbank and Holm, *Ind. and Eng. Chem.*, 1924, **16**, 598; French, Olcott and Matill, *Ind. and Eng. Chem.*, 1935, **27**, 724; Holmes, Carbet and Hartxler, *Ind. and Eng. Chem.*, 1936, **28**, 133.

¹⁰ Greenbank and Holm, *Ind. and Eng. Chem.*, 1934, **26**, 243.

¹¹ Matill and Crawford, *loc. cit.*

¹² Greenbank and Holm, *Ind. and Eng. Chem., Anal. Edn.*, 1930, **2**, 9.

¹³ Coe and Le Clerc, *Ind. and Eng. Chem.*, 1934, **26**, 245.

¹⁴ Lea, *Proc. Roy. Soc., London*, 1931, **1088**, 175.

¹⁵ Coe and Le Clerc, *loc. cit.*

¹⁶ Wagner, *Z. Nahr. u. Genussm.*, 1913, **25**, 704.

¹⁷ Bevis, *loc. cit.*

workers that each increase in temperature by 10° C. approximately doubles the rate of increase of rancidity.¹⁸

Certain metals in oil-soluble form are known to have a marked effect on the stability of fats. Copper is a powerful prooxidant for autoxidative reactions. The use of copper equipment in the handling of milk and its products is thus a potential source of danger. Manganese in somewhat higher concentrations, likewise, has a strong prooxidation effect; but ferrous iron, tin and nickel at low concentrations have no effect. Zinc has a stabilising action. Generally, the materials used for wrapping fatty products also contain some of these metals in soluble form and may thus act as promoters of rancidity.

As has been pointed out before, the oxidative rancidity involves the oxidation of the unsaturated bonds. Absorption of small amounts of oxygen produce tallowy odours and flavours and, as such, deterioration through oxidation can be prevented by preventing the initial changes. With this object in view, several substances which retard the uptake of oxygen (antioxidants) are used as preservatives. Their use first originated with the classical researches of Mouren and Dufraisse.¹⁹ The efficiency of autoxidative catalysts rests entirely upon the relationship between their susceptibility to oxidation and their catalytic properties. Theoretically, any oxidisable substance should be capable of acting as an autoxidative catalyst under proper conditions. Hydroxy-derivatives of aromatic compounds (poly-phenols) are the most effective inhibitors of oxidation. Activity is associated in some manner with the ortho- or para-configuration.²⁰

Rancid products can be materially improved by removing the products of decomposition such as acids, aldehydes, etc. With this object in view, numerous processes have been patented. However, all these treatments can only be regarded as temporary improvements, since fat so purified will again become rapidly rancid.

In view of what is known concerning the factors responsible for producing rancidity, it may be said that to insure good keeping quality great stress should be laid on the freshness of the fat in the product.

II. METHODS FOR DETERMINING RANCIDITY.

While it is true that the recognition of rancidity by taste and odour is so easy that there is no need for the use of chemical tests, there are nevertheless many cases in which reliable tests may prove of great value. For instance, rancid fat may be mixed with fresh fat in order to disguise its condition and thus be sold as a fresh product. A large number of methods have therefore been proposed from time to time for estimating rancidity, e.g., acid value,²¹ iodine value,²² organic peroxides,²³ colour estimation

for aldehydes or other products of oxidation,²⁴ permanganate titration of water-soluble volatile constituents,²⁵ and the fading of methylene blue colour.²⁶ None of the above methods is, however, quite reliable, since the chosen component may be the product of a secondary process and before a final conclusion can be drawn about the state of a fat, it should be examined by at least three or four different methods.

III. RANCIDITY CHANGES IN 'GHEE'.

Ghee is prepared exclusively from butter fat, from which the water is expelled by heat. The butter is allowed to become somewhat acidic and is then clarified by melting and decantation.

In India, ghee is regarded as a very valuable product and is consumed in large quantities. A similar product is used in Egypt and is known as 'samna'. Besides being an important item of food, it is the chief source of vitamin A. Ghee is more important than milk for the reason that it is more concentrated and affords an easy method for disposal of extra amounts of milk. But, on account of its high content of lower fatty acids, especially butyric acid, upon slight hydrolysis, ghee produces a strong characteristic odour of these acids. Most of the other fats are rich in higher acids, like stearic, palmitic, etc., which are odourless. On hydrolysis these fats give comparatively little of the 'off' odours. Again, oxidation of unsaturated acids like oleic and linoleic is responsible for the tallowy odours. It will thus be seen that milk fat presents a combination of fatty acids which due to hydrolysis may cause intense rancidity or tallowiness due to oxidation.

Though much work has been done on various aspects of rancidity little is known about its effect on the vitamin A content of the milk fat. Since rancidity is primarily an oxidation reaction this might naturally affect its vitamin A content.²⁷ It would be interesting to study the various factors which favour the development of rancidity in ghee and their effect on vitamin A and to ascertain whether a higher vitamin A content is an index of increased stability of the product.

Again it is necessary to find some cheap, and efficient method of stopping this spoilage. In the case of an edible fat like ghee, only non-toxic and harmless antioxidants can be used as preservatives. Antioxidants like lecithin, 'jagari', hydroquinone, etc., can be tried for ghee. The effect of these antioxidants on the stability of vitamin A should also be studied. It has been quite recently shown that a combination of two antioxidants affords a remarkably strong protective action which is greater than what could be expected from the mere additive effect.²⁸

It is well known that while ghee prepared under good conditions can be preserved with care for

¹⁸ Morgan, *Ind. and Eng. Chem.*, 1935, 27, 1287.

¹⁹ Mouren and Dufraisse, *Chemical Reviews*, 1927, 3, 113.

²⁰ Matill, *J. Biol. Chem.*, 1931, 90, 141.

²¹ "Animal and Vegetable Oils, Fats and Waxes" by G. Martin, p. 152.

²² DeGroote, *et al.*, *Ind. and Eng. Chem.*, Anal. Edn., 1931, 3, 243.

²³ Davies, *loc. cit.*; Taffel and Bevis, *J. Soc. Chem. Ind.*, 1931, 50, 87T; Lea, *loc. cit.*; Wheeler, *Oil and Soap*, 1932, 9, 89.

²⁴ Kerr, *J. Ind. and Eng. Chem.*, 1918, 10, 471; Schibsted, *Ind. and Eng. Chem.*, Anal. Edn., 1932, 4, 204; Lea, *Ind. and Eng. Chem.*, Anal. Edn., 1934, 6, 241.

²⁵ Kerr and Sorber, *Ind. and Eng. Chem.*, 1923, 15, 383.

²⁶ Greenbank and Holm, *Ind. and Eng. Chem.*, Anal. Edn., 1930, 2, 9.

Royce, *Ind. and Eng. Chem.*, Anal. Edn., 1933, 5, 244.

²⁷ Powick, *J. Agric. Res.*, 1925, 31, 1017.

²⁸ Holmes, *et al.*, *Ind. and Eng. Chem.*, 1936, 28, 133.

about six months, the bazaar ghee is usually seldom stable for more than a fortnight. Apart from the question of vitamin A, rancid ghee has no market value and therefore in an agricultural country like India preservation of ghee for sufficiently long periods of time is economically important.

Milk fat, like all other fats, does not absorb oxygen as soon as it comes in contact with it but passes through an induction period. At lower temperatures this period is considerably longer. Presence of moisture is detrimental as it hydrolyses lecithin to trimethylamine, which, in turn, produces a fishy odour. A measure of the length of the induction period will furnish a valuable index of the keeping quality and freshness of a ghee sample.

Acidity is another important factor determining rancidity. Sweet cream butter may be stored for long periods with very little change in flavours.²⁹ Cold storage of milk fat is advantageous in that it prevents the development of acidity, but it also prevents the destruction of lipase due to low acid concentration. Lipase liberates the lower and volatile fatty acids which are responsible for 'off' flavours. Thus, butter preserved in the cold gets rancid in a comparatively short time when raised to room temperature.

Inert gases have been extensively adopted for the purpose of preserving fats. Carbon dioxide

(15 per cent.) retards the onset of rancidity in beef fat stored at 0°C.³⁰ However, according to some authors,³¹ carbon dioxide cannot be considered as an inert gas for dairy products containing milk fat since the increased acidity hydrolyses the glycerides into fatty acids.

In connection with the development of rancidity in ghee it may be mentioned that enzymic action plays very little part as these are destroyed during its preparation. Some workers do not attach much importance to bacterial action as well. Jensen and Grettie³² have reviewed the general question of the action of micro-organisms on fats. It is not unlikely, that micro-organisms play an important role since it has been mentioned by several investigators that the development of moulds has an adverse effect on the stability of milk fat.³³ Rancidity can be caused by 'Ps. fluorescens'.³⁴ This conclusion is further supported by the fact that the storage of ghee in unclean vessels leads to its spoilage. The beneficial action of zinc is noteworthy in this connection.

Milk fat contains higher alcohols like sterols and lipoids like lecithin. A study of the effect of these constituents on the stability of ghee and vitamin A may lead to very interesting results.

³⁰ Lea, *J. Soc. Chem. Ind.*, 1933, 52, 9T.

³¹ Holm, Wright and Greenbank, *J. Dairy Sci.*, 1927, 10, 33.

³² Jensen and Grettie, *Oil and Soap*, 1933, 10, 23.

³³ Bevis, *J. Soc. Chem. Ind.*, 1933, 42, 417T.

³⁴ Derby and Hammer, *Iowa Agr. Expt. Station Research Bull.*, 1931, No. 145.

RESEARCH NOTES.

MATHEMATICAL AND PHYSICAL.

Determination of Dirichlet's Series Satisfying a Functional Equation.—Hecke (*Math. Annalen*, 112 Band, V Heft, pp. 661–699) has solved a very general problem (the particular case of the Riemannian Zeta-function being determined from its functional equation had been solved earlier by Hamburger), concerning the determination of functions satisfying a functional equation analogous to that of the Riemannian Zeta-function and some regularity conditions. Let λ, k , be +ve constants and $r = \pm 1$. Let $\phi(s)$ be such that $(s-k)\phi(s)$ is an integral function of finite order; and $\left(\frac{2\pi}{\lambda}\right)^s \Gamma(s) \phi(s) = R(s) = rR(k-s)$; and let $\phi(s)$ be expansible as a Dirichlet series of the special form $\sum \frac{a_n}{n^s}$ which is convergent for some value of s . Each of such functions $\phi(s)$ is said to belong to the signature $\{\lambda, k, r\}$. The problem he has handled is the determination of the number of linearly independent ϕ 's. To each such function ϕ , another function $f(\tau)$ is made to correspond. $f(\tau)$ is defined in the

along the line $R(s) = \sigma_1$, $\{\phi(s)$ converges abso-

lutely for $s = \sigma_1\}$; and $C_k = \left(\frac{2\pi}{\lambda}\right)^{-k} \Gamma(k)a$, where

a = the residue of $\phi(s)$ at k . Then $f(\tau) = rC_k + F(-i\tau)$ where $x = -i\tau$. The conditions which are satisfied by $\phi(s)$ give rise to corresponding conditions which should be satisfied by $f(\tau)$. The conditions (regularity conditions are omitted) are

$$(1) f(\tau + \lambda) = f(\tau) \quad (2) \frac{f\left(-\frac{1}{\tau}\right)}{(-i\tau)^k} = r f(\tau).$$

[The equations are analogous to those satisfied by elliptic modular transcendentals for $\lambda = 1$.] He has shown in a natural way that the problem for ϕ is identical with that of f . The results that he obtains do not assume the acquaintance of the general theory of automorphic functions; he only uses simple theorems on conformal representation. The results he obtains are the following:

I. when $\lambda > 2$, there exists an ∞ of linearly independent ϕ .

II. when $\lambda = 2$, the number of linearly independent $\phi = \left[\frac{k}{4} \right] + 1$, for $r = 1$, and $= \left[\frac{k-2}{4} \right] + 1$ for $r = -1$. [for $k < 2$ no such ϕ exists.]

The case when $0 < \lambda < 2$ is very interesting

following manner. Let $F(x) = \sum_1^\infty a_n e^{-\frac{2\pi n x}{\lambda}}$

Then by means of Mellin's integral it is also $= \frac{1}{2\pi i} \int \frac{R(s)}{x^s} ds$ where the integral is taken