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Chemical Changes Which Take Place in an Edible Oil During Thermal Oxidation[1,2]

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Previous studies on the nature of the chemical changes which take place in fats and oils and fatty acid esters during oxidation have usually been carried out at temperatures ranging from 0 to 100°C. (2, 5, 11). At these temperatures it has been shown that the peroxide value increased rapidly and large amounts of carbonyl compounds were formed. Polymeric material was produced, possibly through carbon to oxygen linkages (2).

Studies at higher temperatures (250°–300°C.) have generally been carried out in inert atmospheres and have shown that molecular weight and viscosity increase, resulting partially from the formation of polymers through the Diels-Alder type of condensations (3, 10, 13). Cyclic monomers were also believed to be produced under these conditions (12).

To date the combined effects of oxidation and thermal treatment have not been studied extensively. Although changes in acid value and iodine value have been reported, the effect of specific conditions, *e.g.*, temperature, aeration, and the length of the heating period on the nature of these changes has not been studied. The present study was designed to provide information on the effect of thermal treatment at a temperature of 200°C. when aeration and the time of thermal treatment were varied.

Methods

The thermal oxidation (aeration) was carried out in a five-liter, stainless steel beaker. The apparatus was similar to that used in our previous studies (5). The sample of oil was heated to 200°C., and the aeration was begun when the oil had reached the desired temperature.

The saponification, free fatty acid, and Wijs iodine values were determined by official methods (9). The peroxide determination was made according to the modification of Wheeler (14), and the mixed fatty composition was determined by the spectrophotometric method of Brice *et al.* (1). Carbonyl values were obtained by using a modification of the procedure suggested by Lappin and Clark (7). The solvent used was a 1:1 mixture of carbonyl-free methanol and ethanol, and decyl aldehyde was used as standard. The carbonyl value was expressed as milliequivalents per kilo of oil.

A standard set of conditions was selected for the initial experiment. Further experiments were then carried out, using variations in the time, temperature, and amount of aeration from these following four standard conditions: a) sample weight, 1,500 g. of commercially refined corn oil; b) temperature, 200° C. ± 10°; c) time of treatment, 24 hrs.; and d) rate of aeration, 150 ml. of air per kilo of oil per minute.

Results

The iodine value of corn oil decreased at a relatively constant rate during the first 10 to 12 hours of treatment under the standardized conditions (Figure 1). As the iodine value decreased, a corresponding decrease was observed in the amount of nonconjugated dienoic acids present. A marked increase in the percentage of conjugated diene in the oil indicated that at least part of the dienoic acid was conjugated before further reactions took place. A careful comparison of the decreases in iodine value and linoleic acid content indicated that the linoleic acid decreased more rapidly than the total unsaturation. The percentage of monounsaturated fatty acids in the corn oil increased from 26.1% in the fresh corn oil to 39.9% in oil which had been heated for 24 hrs. This suggested that only one of the double bonds of linoleic was attacked or utilized during the initial period.

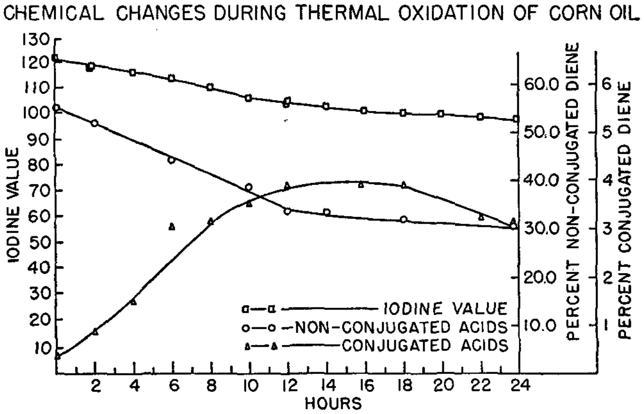

Fig. 1. Chemical changes during thermal oxidation of corn oil.

The total oxygen content of the oil increased during the first 10 to 12 hrs. and then began to decrease

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during the next four hours of heating. Following this decrease, the oxygen content again started to increase. As part of the increase in oxygen was caused by the formation of oxygen containing functional groups, the oil was carefully analyzed for the groups which might be formed. Only low and insignificant values for peroxide and carboxyl were found (Figure 2). However the carbonyl content of the oil increased greatly during heating and then decreased at approximately the same time that the total oxygen content decreased (Figure 3). The carbonyl groups present were in part α,β-unsaturated carbonyls since the oil had an absorption peak in the ultraviolet spectra at 224 mμ (6). The treatment of the oil with dilute alkali in 75% ethanol produced an absorption at 275 mμ, again suggesting unsaturated carbonyl compounds.

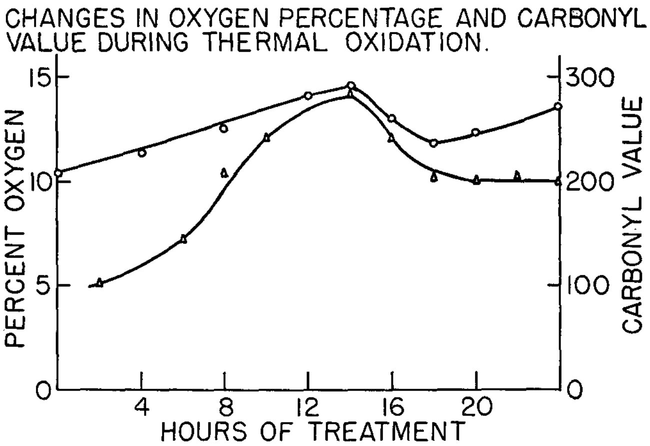

FIG. 2. Changes in total oxygen content and carbonyl value during thermal oxidation of corn oil.

The changes in refractive index and viscosity of the oil suggested that polymeric materials were present (Table I). The solubility of the oil in an ethyl alcohol-isopropyl alcohol mixture (2:1) decreased from 10.35 g. per 100 ml. at the start of the heating period to 8.5 g. after 24 hrs. The viscosity increased rapidly after 12 to 16 hours of heating. Thus changes in the oil during the initial hours of treatment may produce materials which will then polymerize after 12 hrs. of heating. Continuation of the heat treatment to 48 hrs. produced a further decrease in iodine value and a very marked increase in viscosity. The refractive index also increased, but only about one-fourth of the increase observed in the first 24 hrs.

TABLE I
Chemical Changes in Corn Oil Thermally Oxidized at 200°C.

Constants	Time of treatment in hrs.				
	Fresh oil	8	16	24	48
Iodine value	122	115	108	102	90.0
Peroxide value	1.1	1.6	1.7	2.0	—
Acid value	.20	.42	1.23	1.44	1.60
Sap. value	186	196	200	200	—
Ref. index 25°C.	1.4730	1.4760	1.4788	1.4797	1.4814
Viscosity (poises) 25°C.	.65	.85	1.25	3.00	7.55

It is of interest to compare the chemical changes in samples of corn oil thermally oxidized for 24 hrs. at 120°, 160°, and 200°C. in order to see what effect temperature had on the types of changes produced (Table II). The oils were aerated at 150 ml./min./kilo. The low peroxide value of the oils which had been heated to 160° and 200°C., compared with that of the oil treated at 120°C., indicated that these peroxides were not heat-stable. While the iodine value was affected slightly less in the samples treated at 120°C., the decrease in iodine values in the samples treated at 160° and 200°C. was almost equal. The increases in refractive index parallel the increase in polymeric material which is produced in heated or oxidized oils (8). The greatest increase in viscosity and refractive index was observed in the oil treated at 200°C., suggesting that the polymer formation was greatest in this sample.

TABLE II
Effect of Temperature on Chemical Changes During Oxidation for 24 Hours. (Air flow: 150 ml./min./kilo of oil)

	Temperature of oxidation			
	Fresh corn oil	120°C.	160°C.	200°C.
Iodine value	122	105	102	100
Peroxide value	1.0	81.0	6.0	2.0
Acid value	.16	1.90	1.8	1.3
Saponification value	186	198	198	200
Refractive index (25°C.)	1.4730	1.4752	1.4762	1.4792
Viscosity (poises, 25°C.)	.65	1.00	1.65	2.50

The rate of aeration also played an important part in the changes which took place during thermal oxidation. Five samples of corn oil, A, B, C, D, and E, were aerated at various rates at 200°C. for 24 hrs. The rate of aeration was 0, 200, 600, 1,200, and 2,400 ml. per minute per kilo of oil for samples A through E, respectively (Figure 3). The viscosity of the samples increased in proportion to the rate of aeration, and the final viscosity of the samples, in poises, ranged from 1.4 for sample A to 6.3 for sample E. The decrease in iodine value in these samples was least in sample A, and greatest in sample E. The final iodine value in sample E was 90, which was equal to that observed in the sample treated for 48 hrs. at 150 ml. per minute per kilo. The iodine values of samples A to D were 111, 101, 98, and 95, respectively. The carbonyl values of the samples after 24 hrs. were 173, 191, 222, 244, and 232 milli-

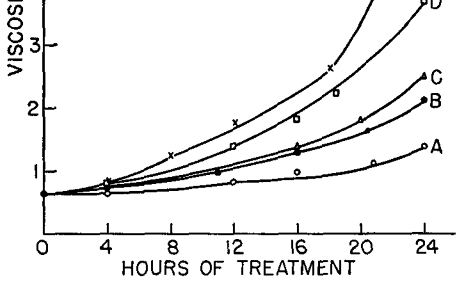

FIG. 3. Changes in viscosity of corn oil thermally oxidized at 200°C. with varying rates of aeration (at 25°C.).

Rate of aeration:	Ml. air/minute/kilo oil
A. 0	D. 1,200
B. 200	E. 2,400
C. 600	

moles per kilo. The maximum value for sample B was 212 after 16 hrs. while the maximum for samples C, D, and E was 242, 286, and 325 after 12 hrs. Sample A showed a continuous increase in carbonyl and did not exhibit a maximum concentration in carbonyl on continued treatment as found in samples B to E.

Discussion

It was shown that the thermal oxidation of corn oil at 200°C. caused a decrease in iodine value and increases in refractive indices and viscosity. The linoleic acid content of the oil decreased from 53% to 30% during a 24-hr. treatment. However during the treatment the monounsaturated acid content of the oil increased from 26% to 39.9%, suggesting that only one double bond of the linoleic acid was involved in part of the reactions.

Since only one oxygen containing functional group, *e.g.*, carbonyl, was produced in any substantial amount, it was possible that this group played some part in secondary reactions. It is doubtful that the many changes which took place during the twelfth to sixteenth hour of heating were mere coincidence. Increased aeration during heating appeared to produce a more pronounced change but did not appear to change the type of reaction. Even samples which had not been aerated were found to decrease 10% in iodine value.

In the sample aerated at 2,400 ml. per minute per kilo the decrease in iodine value was greatest during the first 14 hours. and was least during the final ten hrs. In addition, the rise and decline of the carbonyl value paralleled that of samples B through D. It appears that the changes produced during the first 12 to 16 hrs. differ from those produced later. It has been suggested that the initial decrease in iodine value might be caused by the formation of cyclic monomers (12). However the presence of air or oxygen might give rise to other reactions which could also give a decrease in iodine value. Previous studies (3, 8) have been carried out in the absence of air or oxygen. The changes noted in the present study were carried out in the presence of oxygen and therefore could differ from those in which the production of cyclic monomeric material has been reported.

Initially the oil was attacked by the oxygen to produce carbonyl groups. Part of this attack was at the double bonds, but some changes must have occurred at methylene groups since the presence of α,β-unsaturated carbonyl groups was indicated (6). Other reactions involving the double bonds were also taking place, including conjugation. Some of the products of this initial period are easily polymerized, and when these have built up to a certain concentration, after 12 to 16 hrs. of treatment, polymerization increases, producing the final products.

Summary

The thermal oxidation of corn oil proceeds in two steps, an initial period of 12 to 16 hrs., characterized by a decrease in iodine value and a rapid increase in carbonyl value, and a second phase in which a slower decrease in iodine value, a slight decrease in carbonyl value, and a rapid increase in viscosity occurred. Increasing the rate of aeration caused greater magnitude in changes but did not alter the over-all two-phase reaction.

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The Analysis of Nitrogen in the Smalley Oilseed Meal Series, 1955-56

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CANADA PACKERS' RESEARCH LABORATORY entered the Smalley Oilseed Meal Series in August, 1955. The nitrogen analyses were performed by the rapid Kjeldahl procedure (4) developed by this laboratory because this is the method in routine use by our control laboratories. This method requires a digestion time of about 15 min. on 1-g. samples, and the temperature of the digestion and concentration of mercury are considerably higher than that obtained in the official A.O.C.S. Method (2). From the beginning it was apparent that our nitrogen analyses were consistently higher than the Smalley median value used in scoring the series, and our problem was to establish whether these higher nitrogen analyses were true or false.

In order to increase the accuracy of our work the following precautions were taken.

1. Weight burette technique was used in all titrations, including standardization of solutions.
2. The accuracy of our Gram-atic balance was checked against one-piece weights bearing a certificate from the National Physical Laboratory, England.
3. The sulfuric acid used for titrating the ammonia was standardized against sodium carbonate, mercuric oxide, and sodium hydroxide solution which had been standardized (by weight) against acid potassium phthalate obtained from the U. S. National Bureau of Standards.
4. The reagent blanks were measured both by the usual digestion with sugar and directly by the use of Nessler reagent. They were found to be insignificant.
5. To assure complete recovery of ammonia a new solid glass still was designed. A glass leg was blown onto the end of the trap. Inside the leg is a long, glass, cold finger which eliminates condensation on the outside surface.

The end of the condenser dips directly into the receiving acid. At the end of each distillation the cooling water is turned off. In approximately 30 seconds steam issues from the end of the condenser, eliminating the retention of traces