

THE NUTRITIONAL EFFECT OF POLYMERS
ISOLATED FROM THERMALLY OXIDIZED
CORN OIL ^{1,2}

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INTRODUCTION

In a recent report from the National Research Council (Gortner, '58) it was stated that "Chemical alterations produced in fats during heating should be defined and studies should be made of the heated oils produced in food processing and under home cooking conditions." The chemical alterations which occur in an unsaturated oil at commercial food frying temperatures of approximately 200°C have already been reported elsewhere (Perkins et al., '58; Johnson and Kummerow, '57). The length of time a specific triglyceride molecule of the oil is exposed to this temperature is dependent on the turnover rate of the oil. As this rate is governed by the amount of oil absorbed on the "cooked" food item, the turnover rate is variable. In order to eliminate variables in the composition of oil samples and to note only the effects of temperature on the

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nutritional value of an edible oil heated for a specific period of time, corn oil was heated continuously at 200°C for 48 hours in the present study. The heated oil was subjected to urea fractionation and molecular distillation and various fractions fed to weanling rats for 21 days.

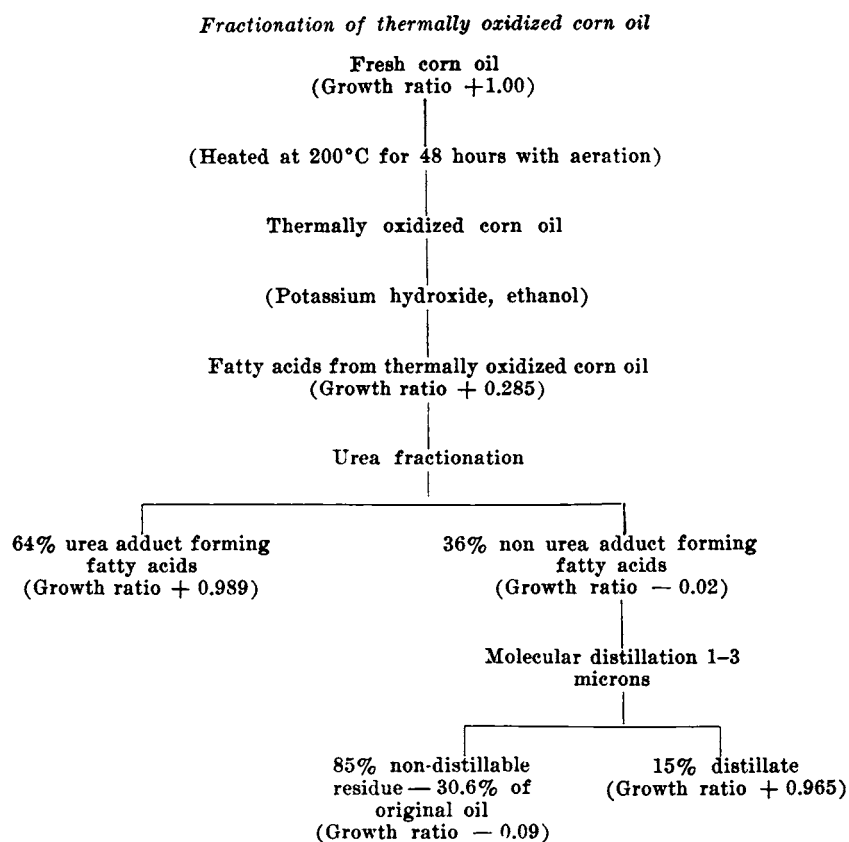
EXPERIMENTAL

A basal diet which consisted of 50% glucose,⁴ 31% casein, 5% Wesson ('32) salt mix and 14% fat was used in all the feeding experiments. The test fat or fatty acid fraction represented 12% and fresh cottonseed oil 2% of this 14% of fat. Two grams of a water-soluble vitamin mix were added to each kilogram of food. This mixture was composed of choline chloride 93.5 mg, thiamine hydrochloride 1.24 mg, riboflavin 1.24 mg, pyridoxine hydrochloride 1.24 mg, calcium pantothenate 2.48 mg, folic acid 0.30 mg, and 1.9 gm of glucose. The fat-soluble vitamins were given by dropper once each week.⁵ Groups of 7 animals each were kept in single cages, weighed daily and all animals arbitrarily restricted to the same amount of food intake as those fed the non-urea-adduct-forming acids.

The thermally oxidized oil was prepared by heating fresh corn oil continuously for 48 hours at 200°C with agitation in the presence of air. The oil was then saponified with 4% potassium hydroxide in 95% ethanol, acidified with dilute hydrochloric acid, the lipids extracted with Skellysolve F and subjected to urea fractionation (Johnson et al., '57). The crystalline urea adducts of the straight chain fatty acids were removed by filtration and the adducts decomposed in warm water according to the scheme on opposite page.

⁴ Cerelese.

⁵ One drop per rat of the following vitamin mixture was administered once each week: Five grams vitamin A (200,000 U.S.P. units, courtesy of Distillation Products), 0.0054 gm vitamin D, and 2.535 gm vitamin E (mixed tocopherols) in 100 ml of olive oil.



The fatty acids were extracted from the aqueous phase with Skelly-solve F and freed from solvent. The non-urea-adduct-forming fraction was freed of urea and solvent and subjected to molecular distillation under 1 to 3 μ pressure at 150°C in a small falling film type still.

RESULTS

Weanling rats which had been fed the non-distillable residue from the non-urea-adduct-forming fatty acids of thermally oxidized corn oil all died within 7 days (fig. 1). These animals had lost approximately 7 gm, while those on the fatty acids of fresh corn oil had gained an average of 16 gm in weight on

the same amount of food intake during this 7-day period. Dilution of the non-urea-adduct-forming fatty acids with an equal volume of the fatty acids from fresh corn oil assured survival of the animals for the 21-day test period, but counteracted

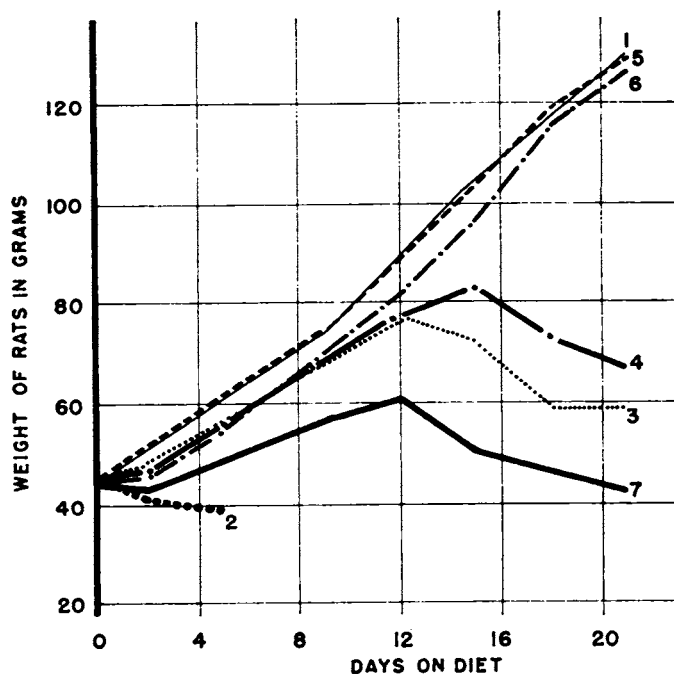


Fig. 1 Change in weight of rats fed various fractions of thermally oxidized corn oil. (1) Fatty acids from fresh corn oil; (2) Non-distillable residue from non-adducting acids from thermally oxidized oil; (3) 6% non-distillable residue, 6% fatty acid from fresh corn oil; (4) Thermally oxidized fatty acids; (5) Urea-adduct-forming acids from thermally oxidized oil; (6) Molecular distillate of non adducting acids from thermally oxidized oil; (7) Non-urea-adduct-forming acids from thermally oxidized oil.

only partially the growth depressing effect of the non-urea-adduct-forming fatty acids. The animals which had received this mixture had gained only 14 gm, while those on the fatty acids of fresh corn oil had gained approximately 85 gm in weight during the 21-day test period.

The major portion of the fatty acids in the thermally oxidized corn oil did not seem to be damaged by the severe heat treatment. Although the fatty acids from thermally oxidized oil depressed growth significantly, the rats fed the urea-adduct-forming fatty acids, which represented 64% of the oil, gained as much weight as those on the fatty acids of fresh corn oil. Furthermore, the molecular distillate from the non-urea-adduct-forming fatty acids, which represented 15% of this fraction, also did not depress growth significantly. It is evident, therefore, that only a minor portion of the fatty acids in the triglycerides of corn oil is susceptible to heat damage.

The proportion of non-urea-adduct-forming material and the molecular weight seem to represent a better index of nutritional value (table 1) than the iodine value (Melnick, '57; Melnick et al., '58). The urea-adduct-forming fatty acid had an iodine value of 62 as compared to 126 for the fatty acids of fresh corn oil, yet both gave similar weight gains. Characterization of the non-distillable residue from the non-urea-adduct-forming material indicated that this fraction contained polymers with molecular weights ranging from 692 to 1600. These polymers contained oxygen in the form of hydroxyl as well as carboxyl groups and double bonds which resisted hydrogenation (Perkins and Kummerow, '59).

It has been reported previously that heat and oxygen damaged the nutritional value of an edible oil at 95° (Kaunitz et al., '55) as well as at 275° (Crampton et al., '51). Differences in the temperature of heating and the presence or absence of oxygen can alter the rate and the type of polymerization which may occur but it is evident that heat damage is not limited to any specific temperature between 95 and 275°. The length of time that an oil is exposed to heat and oxygen and the percentage of heated oil in the diet also influence the nutritional value of the oil (Johnson et al., '56).

An oil heated for 6 hours at frying temperature may not be damaged enough to cause significant growth depression (Deuel et al., '51). However, the enlarged livers in rats fed oil which had been heated for 48 hours (Johnson et al., '57) seems to

TABLE 1
Comparison of constants and biological response to various fractions of the fatty acids from fresh and thermally oxidized corn oil¹

DIET SUPPLEMENT	CONSTANTS OF TEST FATTY ACIDS			LINOLEIC ACID CONTENT	CHANGE IN WEIGHT IN 21 DAYS	PERCENTAGE OF LIVER/BODY WEIGHT
	Non adduct	Iodine value	Molecular weight (East)			
	%					
Fatty acids from fresh corn oil	5	126	294	55.4	+ 84.9 ± 6.9 ²	4.8 ± 0.7
Urea-adduct-forming acids from T.O. oil	0	62	300	3.5	+ 84.0 ± 0.3	4.3 ± 0.3
Non-urea-adduct-forming acids from T.O. oil	74	83	512	9.5	- 2.0 ± 0.0	8.2 ± 1.4
Molecular distillate of non-adducting acids from T.O. oil	0	113	320	33.6	+ 82.1 ± 0.3	5.5 ± 0.2
Non-distillable residue from non-adducting acids from T.O. oil	100	70	692	6.0	- 7.6 ± 0.3 ³	8.7 ± 1.2
Thermally oxidized fatty acids	36	71	454	10.0	+ 21.9 ± 0.9	7.1 ± 0.2
6% non-distillable residue + 6% fatty acids from fresh corn oil	50	98	460	31.7	+ 14.2 ± 1.0	8.1 ± 0.9

¹ Corn oil heated for 48 hours at 200°C with 150 ml of aeration per min./kg oil.

² Standard error of the mean.

³ All died in 7 days.

imply that such oils do elicit a biological response. Whether thermally oxidized oil will manifest biological activity may depend on the amount of dietary protein (Witting et al., '56), the presence of sufficient amounts of pyridoxine or other vitamins and possibly other factors.

The present data cannot be projected to predict whether a specific unsaturated oil will be damaged sufficiently during commercial frying operations to be harmful to human consumers, as fresh oil is continually introduced into the frying vat, and the "used" oil adsorbed on the fried product and withdrawn. However, small amounts of thermally oxidized oils, similar in character to the one used in the present study, are sometimes added to salad oils as crystallization inhibitors, in order to prevent the crystallization of higher melting triglycerides from the oils. The present study indicates that the use of such oils for this purpose may not be desirable from a nutritional point of view.

SUMMARY

Weanling rats were fed for 21 days a diet composed of 50% glucose, 31% casein, 5% Wesson salt, 2% fresh cottonseed oil, 12% of the test fat or fatty acid fraction, and all of the known required water- and fat-soluble vitamins. Those fed the non-distillable residue from the non-urea-adduct-forming fatty acids of corn oil which had been heated at 200°C for 48 hours and represented approximately 30% of the original oil all died within 7 days. Dilution of the non-urea-adduct-forming fatty acids with an equal volume of the fatty acids from fresh corn oil assured survival of the animals for the 21-day test period, but counteracted only partially the growth depressing effect of the non-urea-adduct-forming fatty acids. The major portion of the fatty acids in the thermally oxidized corn oil did not seem to be damaged by the severe heat treatment. Although the fatty acids from thermally oxidized oil depressed growth significantly, the rats fed the urea-adduct-forming fatty acids, which represented 64% of the oil, gained as much weight as those on the fatty acids of fresh corn oil.

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