

# FATTY ACID COMPOSITION OF OIL FROM DAMAGED CORN AND WHEAT<sup>1</sup>

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## ABSTRACT

The fatty acids from the oils of commercial samples of corn and wheat were analyzed by gas chromatography to study the differences in composition among different types of damage found in the grain. The chromatographic patterns were similar for fatty acids of increasing chain length from lauric to linolenic. In the area of the chromatogram where caproic to capric acid methyl esters appear, a number of unresolved peaks indicated a complex mixture. This lower-molecular-weight material appeared more prevalent in the free fatty acids from corn damaged by artificial drying, cob-rot, or blue-eye mold and in wheat damaged by heat.

Earlier studies of the fat acidity of grain show that the amount of free fatty acids in the oil is related to the degree and type of damage present in the grain (1,2,5). While it is known that deterioration causes fatty acids to be released from the glyceride molecule, it is not known whether they are released in the same proportions in which they are combined in the oil. If a certain type of damage caused the release of one fatty acid more readily than another, then the free fatty acid composition of the oil from damaged grain would differ from the total fatty-acid composition of the oil from sound grain. The purpose of the present study was to determine whether the different types of damage occurring in grain were reflected in the free fatty acid composition of the oil. The investigation was directed toward the fatty acids having 10 to 18 carbon atoms, since the fatty acids found in grain oils are mainly of the higher carbon-chain lengths.

## Materials and Methods

Commercial samples, classed as yellow corn and hard red winter wheat under the U.S. Official Grain Standards, were obtained from the General Field Headquarters of the Grain Division, Agricultural Marketing Service. Each sample was chosen as representing one type of damage frequently found in commercial samples and the amount of damage was determined by regular grain inspection methods. The

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types of damage represented by these samples can be considered storage damage, with the exception of the samples of corn which were believed to be damaged by artificial drying. The fatty acid composition of the oil from the damaged samples was analyzed by gas chromatography. Samples of oil from sound corn and wheat were similarly prepared and analyzed.

The oil was extracted from 100 g. of the ground samples of grain by petroleum ether, boiling range 35°–59°C. (Skellysolve F), in a Soxhlet extraction apparatus. The extraction time was at least 18 hours. The free fatty acids were separated from the oil by shaking the concentrated petroleum ether solution of the oil with 1% sodium carbonate in a separatory funnel. After the sodium carbonate solution of the fatty acid salts was separated from the petroleum ether solution of the oil, the acids were recovered by acidifying the sodium carbonate solution and extracting it with petroleum ether. After removal of the free fatty acids, the neutral oil was then saponified by boiling with alcoholic potassium hydroxide. The mixture was cooled, diluted with water, and the unsaponifiable material extracted with petroleum ether. Then the alkaline solution was acidified and the fatty acids recovered by extraction with petroleum ether. Two sets of acids were thus obtained for each sample of damaged grain: 1) the free fatty acids, and 2) the fatty acids hydrolyzed from the neutral oil. A set of acids from sound grain was also obtained by saponification of the oil. All sets of acids were converted to the methyl esters by esterification with diazomethane in ethyl ether solution. The solvent was evaporated under a stream of nitrogen, leaving the methyl esters. Two to five samples of each type of damage were prepared for analysis.

A Perkin-Elmer gas chromatograph (Model 154C) was used to analyze the methyl esters. The column was composed of a succinate polyester of diethylene glycol supported on Chromosorb R. The operating temperature was 210°C. with a helium flow rate of 70 cc. per minute. Three  $\mu$ l. of the methyl esters were introduced into the chromatograph with a microliter syringe. A standard mixture containing known amounts of the methyl esters of caproic, caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, and linolenic acids was chromatographed directly ahead of each set of samples. The chromatograms of the samples were identified by comparison with the chromatograms of the standard mixture.

The moisture content, fat acidity value, and percentage of oil extracted by the petroleum ether were determined on the grain. Iodine numbers were determined on the oil.

### Results and Discussion

Chromatograms of the standard mixture show distinctly separate peaks for the esters of caproic, caprylic, and capric acids. Some of the chromatograms of the methyl esters from the free fatty acids show a number of unresolved peaks in this area, which indicates a complex mixture of shorter carbon-chain acids. The amount of this mixture does not appear as large in the fatty acids from the neutral oils or the sound grain oils as it is in the free fatty acids from some types of damage. In corn oil, these unresolved peaks are of greater area in samples damaged by artificial drying, cob-rot, or blue-eye mold. In wheat, these shorter carbon-chain acids are most prevalent in the heat-damaged samples. The appearance of these peaks in the free fatty acids may indicate a breakdown of some longer chains by certain types of damage.

The chromatographic patterns of the free fatty acid methyl esters of increasing carbon-chain length, from lauric to linolenic, are similar for all types of damage and are similar to the patterns produced by the fatty acid methyl esters from neutral oils and sound-grain oils. The similarity of patterns indicates that the relative amounts of lauric, palmitic, stearic, oleic, linoleic, and linolenic acids remain very nearly the same in the free fatty acids released by damage. Since the relative amounts of these acids are also similar to those of the sound oil, it is apparent that the free fatty acid composition, at these carbon-chain lengths, is not indicative of a particular type of damage. Linoleic acid appears as the predominating fatty acid, a fact already shown by other studies (3). Oleic and palmitic acids appear next in significance.

One sample of "sick" wheat and one sample of sprout-damaged wheat showed unusually large amounts of lauric acid in the free fatty acids, which could not be explained, but which suggests that factors other than damage may cause differences in fatty acid composition. This study does not consider possible differences in composition among varieties and among geographic locations of growth. One must also remember that these were commercial samples on which the damage had been determined only by visual examination. Only one type of damage was assumed to be present in each sample, but there may have been small and varying amounts of other types of hidden damage. All these factors would contribute to variations among a set of samples.

The efficiency of the column in the gas chromatograph was noted to decrease with use. Variations between successive runs may be experimental error or may be characteristic of the column. These variations, along with possible variations among the samples, discouraged calcula-

tion of the fatty acid composition on a quantitative basis.

In Table I are results of other tests made on the grain and oil. The

TABLE I  
IDENTIFICATION OF CORN AND WHEAT SAMPLES FROM WHICH FATTY ACID METHYL  
ESTERS WERE PREPARED

GRAIN AND TYPE OF DAMAGE		AMOUNT OF DAMAGE	FAT ACIDITY VALUE <sup>a</sup>	MOIS- TURE CONTENT	OIL CONTENT	IODINE NUMBER OF OIL
		%		%	%	
CORN						
Rancid germ	-1	10.0	40	10.4	4.7	126
	-2	12.5	44	10.4	4.9	126
	-4	17.5	45	10.2	4.6	126
	-5	20.0	47	10.3	4.6	126
Heat	-1	10.0	36	11.3	4.5	119
	-2	12.5	34	11.2	4.8	125
	-3	15.0	35	11.4	4.6	118
	-5	20.0	38	11.3	4.6	117
Artificial dryer	-1	10.0	36	10.8	4.7	116
	-2	12.5	38	10.8	4.9	113
	-3	15.0	37	10.1	4.7	116
	-4	17.5	44	10.6	4.8	110
	-5	20.0	39	10.7	4.7	115
Cob rot	-1	10.0	54	11.4	5.0	114
	-2	12.5	59	11.3	4.3	118
	-3	15.0	68	11.2	4.8	116
	-4	17.5	71	11.4	4.6	116
	-5	20.0	69	11.4	4.8	114
Blue-eye mold	-1	10.0	51	10.6	4.9	113
	-2	12.5	62	10.8	4.6	102
	-3	15.0	54	10.8	4.7	110
	-4	17.5	66	10.9	4.7	116
	-5	20.0	68	11.2	4.5	114
Sound corn	-1	0	12	11.8	4.6	128
	-2	0	10	12.1	3.8	114
WHEAT						
Heat	-1	10.0	28	11.3	1.8	114
	-3	15.0	30	11.3	1.8	91
	-4	17.5	30	11.1	1.9	91
	-5	20.0	32	11.2	1.8	99
"Sick" (germ)	-1	10.0	27	11.3	2.9	99
	-2	12.5	28	11.4	3.0	103
	-4	17.5	28	11.3	3.0	104
Sprout	-2	12.5	23	10.8	1.7	129
	-3	15.0	23	10.9	1.6	135
Sound wheat	-1	0	14	11.6	1.9	...
	-2	0	15	11.2	1.9	...

<sup>a</sup>No. of mg. of potassium hydroxide required to neutralize the free fatty acids in 100 g. of dry grain.

fat acidity values were fairly high, but not as high in some cases as might be expected for the amount of damage indicated. The iodine numbers gave little or no indication of any relation to the amount or type of damage.

Within the scope of this study, it has been learned that the free fatty acids, released by damage to grain, do not show a marked difference in composition in the longer carbon-chain lengths from lauric acid to linolenic acid. The composition, at these longer carbon-chain lengths, is similar among different types of damage and is similar to the fatty acid composition of sound-grain oil. However, the appearance of a complex mixture of shorter carbon-chain acids in the free fatty acids from some types of damage may be significant. These lower-molecular-weight acids were not prominent in the sound-grain oil. There are also indications that variations in the free fatty acid composition may be caused by factors other than damage. This limited study may open doors to other avenues of exploration.

#### Literature Cited

1. BAKER, DORIS, NEUSTADT, M. H., and ZELENY, L. Application of the fat acidity test as an index of grain deterioration. *Cereal Chem.* **34**: 226-233 (1957).
2. BAKER, DORIS, NEUSTADT, M. H., and ZELENY, L. Relationships between fat acidity values and types of damage in grain. *Cereal Chem.* **36**: 308-311 (1959).
3. ECKEY, E. W. *Vegetable fats and oils*. Reinhold: New York (1954).
4. PECSOK, R. L. *Principles and practice of gas chromatography*. Wiley: New York (1959).
5. ZELENY, L., and COLEMAN, D. A. Acidity in cereals and cereal products, its determination and significance. *Cereal Chem.* **15**: 580-595 (1938).