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The Relationship of Specific Carbonyl Compounds to Rancid Flavor [1/]

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The oxidative changes which occur in the lipids of meats and meat products when they are stored for any appreciable length of time are probably the most important of the chemical changes with which meat science and technology are concerned. These changes are the principal causes of deterioration in frozen meat and are responsible for both desirable and undesirable changes in the flavor and quality of cured meat. Many new types of preserved products, such as freeze-dried, irradiated, and precooked, frozen meats, suffer from problems of fat stability.

Our laboratory has been interested in several aspects of this problem, and we have extensively studied both the hydrolytic changes in fats which are induced by microorganisms and the products resulting

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1/ This paper was prepared for discussion at the 10th Meeting of the European Meat Research Workers. It should be regarded more in the nature of a progress report and as material for discussion than as a completed publication.

from chemical autoxidation of meat fats (1, 2, 3). The chemical changes consist of the formation of hydroperoxides and their subsequent breakdown into carbonyl compounds. The amount and distribution of the various fatty acid chains of the glyceride molecules largely determine the carbonyls which are produced, and a knowledge of glyceride composition will allow one to make rather accurate predictions of the carbonyls which will be found after oxidation. This we have proven by the development of accurate analytical methods for carbonyl identification and subsequent analyses of oxidation products of known substrates (4, 5, 6, 7, 8). One of our current interests is to discover which of the carbonyls known to occur in oxidized fat are actually responsible for the undesirable flavors commonly associated with rancidity. This paper is a progress report of the early phases of a study of these flavor effects. It is hoped that it may form the basis for a discussion of the importance of the fat oxidation problem, and that it may lead to some ideas for future experiments.

Experimental Methods. A group of six judges was repeatedly presented with three fat samples. One was a rancid control, one a fat base, and an experimental sample containing the fat base plus varying quantities of different aldehydes known to be present in rancid animal fats. Each judge was asked to indicate whether the test sample was similar to the rancid control with respect to both aroma and flavor, and to describe the aroma and flavor of the sample.

The rancid control was prepared by allowing a thin layer of mildly rendered lard to oxidize in air for 30 days at 23° C. The peroxide value reached was 24 meq/1000 g., and the flavor was regarded as typically rancid by several experienced judges. An analysis of the carbonyls present in the rancid control is shown in Table 1.

The fat base consisted of a proprietary hydrogenated vegetable oil prepared for use in the baking industry. It was chosen because of its ready availability and the impression that it was nearly tasteless. This proved to be a false impression, and, in future experiments, a deodorized lard will be used.

The test samples were made up by adding the carbonyl to the fat base just before tasting, and each carbonyl was tasted at least three times by each judge. The samples were presented to the judges at about 40° C.

Results. Table 2 shows the compounds tested and the responses of the judges. In addition to the compounds tested in Table 1, heptanal, octanal, and hexenal, which are often found in rancid samples, were tested. Undecenal, which was found in the rancid sample, was not available for testing at the time the organoleptic experiments were conducted. Tests were usually started with 1 or 2 ppm of the carbonyl, and increased until a majority of the judges could describe its presence in the test sample. This concentration is somewhat higher than the threshold level for the detection of the compound. The carbonyls used were either purchased or prepared in our Laboratory and were checked for purity by gas chromatography.

It is interesting to note that the contribution of carbonyls to rancidity seems to become greater with increasing chain length up to about 9 or 10 carbon atoms. Although present results are too fragmentary to more than hint at this, other workers have observed this to be true (9, 10, 11).

The fourth column of Table 2 indicates the number of "yes" answers to the question, "Was the aroma (or flavor) similar to the rancid control?" The judges, in answering the question affirmatively, often recognized a component of rancidity when they did not consider the sample exactly similar to the rancid control. In general, it can be concluded that all of these compounds have a somewhat objectionable aroma and taste. It was interesting, however, that there was greater agreement among the judges with respect to the character of the aromas and flavors of the saturated compounds than of the unsaturated compounds. A good example was nona-2,4-dienal, which was highly unpleasant to most judges, but pleasant to two.

Literature Cited

1. Gaddis, A. M., and R. Ellis. Volatile saturated aldehydes in rancid fat. Science 126, 745 (1957).

2. Sulzbacher, W. L., A. M. Gaddis, and R. Ellis. Oxidative rancidity in meat and meat products. Proc. 15th Amer. Meat Inst. Found. Res. Conf., p. 111, 1963.

3. Alford, J. A., D. A. Pierce, and W. L. Sulzbacher. Microbial lipases and their potential importance to the meat industry. Proc. 15th Amer. Meat Inst. Found. Res. Conf., p. 11, 1963.

4. Ellis, R., A. M. Gaddis, and G. T. Currie. Paper chromatography of 2,4-dinitrophenylhydrazones of saturated aliphatic aldehydes. Anal. Chem. 30, 475 (1958).

5. Gaddis, A. M., and R. Ellis. Paper chromatography of 2,4-dinitrophenylhydrazones. Resolution of 2-alkanone, n-alkanal, alk-2-enal, and alk-2.4-dienal derivatives. Anal. Chem. 31, 870 (1959).

6. Ellis, R., and A. M. Gaddis. Paper chromatography of 2,4-dinitrophenylhydrazones. Estimation of 2-alkanone, n-alkanal, alk-2-enal, and alk-2,4-dienal derivatives. Anal. Chem. 31, 1997 (1959).

7. Ellis, R., A. M. Gaddis, and G. T. Currie. Carbonyls in oxidizing fat. IV. The role of various fatty acid components in carbonyl generation. J. Food Science 26, 131 (1961).

8. Gaddis, A. M., R. Ellis, and G. T. Currie. Carbonyls in oxidizing fat. V. The composition of neutral volatile monocarbonyl compounds from autoxidized oleate, linoleate, linolenate esters and fats. J. Am. Oil Chemists' Soc. 38, 371 (1961).

9. Lea, C. H., and P. A. T. Swoboda. The flavor of aliphatic aldehydes. Chem. and Ind. 4, 1289 (1958)

10. Forss, D. A., E. A. Dunstone, and W. Stark. The fishy flavour in dairy products. II. The volatile compounds associated with fishy flavour in butterfat. J. Dairy Res. 27, 211 (1960).

11. Day, E. A., D. A. Lillard, and M. W. Montgomery. Autoxidation of milk lipids. III. Effect on flavor of the additive interactions of carbonyl compounds at subthreshold concentrations. J. Dairy Sci. 46, 291 (1963).

Table 1. - Monocarbonyl Composition of Rancid Control

Compound		pm/10 g.	% of monocarbonyls found	Acid source
Alkanal:	C_2	.0401	3.86	
	C_3	.0476	4.59	linolenic
	C_6	.2025	19.51	linoleic
	C_9	.4026	38.78	oleic
	C_{10}	.1102	10.61	
Total alkanal		.8030	77.35	
2-Enal:	C_7	.0179	1.72	linoleic
	C_8	.0227	2.19	linoleic
	C_9	.0585	5.64	linoleic
	C_{10}	.0401	3.86	oleic
	C_{11}	.0217	2.09	oleic
Total 2-enal		.1609	15.50	
2,4-Dienals:	C_7	.0244	2.35	linolenic
	C_9	.0141	1.36	linolenic
	C_{10}	.0357	3.44	linoleic
Total 2,4-dienal		.0742	7.15	

Table 2. - Responses of Judges to Some Carbonyl Compounds

Compound	Concentration[1/] ppm	Number of judgments	Number times scored rancid: Aroma	Number times scored rancid: Flavor	Descriptive terms used by judges
Ethanal	2	17	2	6	alcohol, fruity, grassy, yeasty, metallic, stale
Propanal	2	16	4	8	yeasty, grassy, fruity, sour
Hexanal	4	21	13	12	grassy, rancid, pungent, stale, oily, tallowy
Heptanal	5	16	10	15	grassy, green, acid, rancid, metallic
Octanal	4	22	8	18	grassy, green, citric, bitter, metallic, rancid
Nonanal	5	42	9	18	green, grassy, stale, pungent, metallic, bitter
Decanal	5	19	2	10	tallowy, acid, oily, painty, bitter
2-Hexenal	2	18	2	2	sweet, fruity, tallowy, spicy, puckery, acidic
2-Heptenal	5	18	6	7	acrid, acidic, grassy, astringent
2-Octenal	6	17	8	11	grassy, green, spicy, rancid, metallic
2-Nonenal	4	18	4	10	tallowy, painty, medicinal, bitter
2- Decenal	7	18	3	5	grassy, metallic, sharp, acidic
Hepta-2,4-dienal	15	12	3	6	fruity, sour, puckery, stale, soapy
Nona-2,4-dienal	4	18	10	15	grassy, tallowy, pungent, acrid, rancid
Deca-2,4-dienal	6	18	8	12	grassy bitter, acidic, acrid, soapy

1/ The minimum concentration of the aldehyde which was considered describable by a majority of the judges.