1140

Volatile Saturated Aliphatic Aldehydes in Rancid Fat

A great deal of attention has been given in recent years to the isolation and identification (*1*) of aldehydes, ketones, and dicarbonyls in food and natural products. These compounds are recognized as influencing quality and flavor. Little is known concerning the carbonyl compounds present in rancid fats. Klose (*2*) found hexanal to be the major volatile carbonyl and probably the major carbonyl compound in oxidized turkey fat. A complete qualitative determination of volatile saturated aldehydes in rancid tissue fats has not been previously described. This report deals with the identification of volatile saturated aliphatic aldehydes present in rancid (*3*) pork fat.

Carbonyls volatilized by steam for 22 min from 10.0 g of mildly rendered (< 100°C) fat were collected in an excess of 2,4-dinitrophenylhydrazine in 2*N* HCl. After standing overnight, the cloudy solution of 2,4-dinitrophenylhydrazones (DNPH) was extracted with carbon tetrachloride and then benzene. Chromatography on 20-percent hydrated alumina (*4*) yielded monocarbonyl and dicarbonyl DNPH fractions from the carbon tetrachloride and a monocarbonyl DNPH fraction from the benzene extract. The monocarbonyls from the carbon tetrachloride extract were separated into from two to four apparently different classes (*5*) [depending on peroxide values (1 to 86), temperature of storage, and whether the sample was cooked] on untreated Whatman No. 3 filter paper by ascending development with a petroleum ether fraction boiling at 37° to 40°C. Description of the method of separation into classes, and studies of the variations in proportions of the classes with oxidation and processing will be reported elsewhere (*6*). These class fractions, on the basis of their absorption maxima in carbon tetrachloride of 343 to 346, 349 to 352, 360 to 365, and 370 to 380 mμ, appeared to be DNPH's of saturated aldehydes, saturated ketones or a mixture, 2-enals and 2,4-dienals, respectively. The dicarbonyl DNPH class had a maximum absorption at 370 to 390 mμ (*6, 7*).

Propanal and hexanal DNPH's have been separated and identified from the fraction with an absorption maximum at 343 to 346 mμ. The compounds were separated on Whatman No. 3 paper impregnated with 20 percent propylene glycol by ascending development with 96 percent Skellysolve C and 4 percent methanol, a rapid, new method for separating C_1 to C_{14} DNPH's of saturated aliphatic aldehydes (*8*). Similarly, methanal and ethanal DNPH's were separated and identified in the monocarbonyl fraction from the benzene extract. This fraction was also found to contain acetone and methyl ethyl ketone DNPH's. Ethanal DNPH was isolated in two polymorphic forms. These were identified by comparison with two forms from a low-melting preparation of authentic ethanal DNPH (*8*).

Identification was made by comparison of R_F values with those of authentic derivatives, nonseparation on filter paper when mixed with authentic derivatives, maxima in carbon tetrachloride, fading rate in alcoholic alkali (*8*) of major maxima at 430 to 434 mμ, and a disappearing secondary maximum at 520 mμ which distinguishes saturated aldehyde DNPH's from saturated ketone and 2-enal DNPH's (*9*).

Screening of the other monocarbonyl DNPH fractions gave no indication of other saturated carbonyls. In the samples of rancid fat examined thus far, saturated carbonyl compounds with a carbon chain greater than six do not appear to be present. The chances of such compounds being mixed with other carbonyl classes seem remote since authentic higher-molecular-weight saturated compounds added to the monocarbonyl fraction separated only in the saturated class. Therefore, the separation of monocarbonyls into classes (*6*) is remarkably precise. The second monocarbonyl fraction with maximum at 349 to 352 mμ, which was at first thought to be a saturated ketone or a mixture of classes, is evidently a separate class. Six components were found in this class; these appeared to be C_6 to C_{11} carbonyls. Their spectral properties did not agree with any of the classes studied by Jones *et al.* (*9*); the absence of secondary maxima indicated unsaturation, but the major maxima were intermediate between saturated carbonyl and 2-enal DNPH's. It is tentatively suggested that they may be unconjugated unsaturated compounds such as have been detected in milk fat (*10*). The 2-enal class had five components and the 2,4-dienal class had three components that were apparently C_6 to C_{12} compounds.

In a sample of unheated rancid pork fat (peroxide 86), the saturated aldehydes had the following proportions; 93.6 percent hexanal, 5.8 percent propanal, 0.4 percent ethanal, and 0.2 percent methanal. The saturated aldehyde class is the major one in uncooked rancid tissue fat. Heating at 165°C, which approximates the temperature of cooking, produces large increases in total carbonyls (*11*), monocarbonyls, and the proportion of the conjugated unsaturated classes (*6*). Ethanal, propanal, and hexanal were identified as saturated compounds lost during cooking. The predominance of saturated carbonyls in unheated fat is therefore considerably modified when the fat is cooked. Methanal was not detected in cooked fat tissue.

A. M. GADDIS
REX ELLIS
Eastern Utilization Research and Development Division, Agricultural Research Service, Beltsville, Maryland

References and Notes

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