

after being placed in water in which these carrots had been boiled.

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FOOD FLAVOR CHANGES

Relationship between Monocarbonyl Compounds and Flavor of Potato Chips

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Eighteen monocarbonyl compounds have been identified in fresh potato chips and 19 in stale potato chips. The quantitative change of each individual carbonyl compound during storage has been investigated. Among saturated aldehydes the largest increase was in hexanal and next in pentanal; among 2-alkanones the important increase was in 2-pentanone and next in 2-propanone; and among 2-enals the largest increase was in 2-heptenal and 2-octenal. Only one 2,4-dienal—viz., 2,4-decadienal—was found in both fresh and stale potato chips. Its amount was greatly decreased during storage. The mechanism of the formation of these carbonyl compounds and their relationship to the flavor of potato chips are discussed.

CARBONYL compounds are an important group of compounds which contribute to both the savory and off-flavors of foods, particularly those rich in fat content. Potato chips contain 30 to 35% of their total weight in fat and possess a distinct, characteristic flavor, which, on storage, is gradually replaced by an unpalatable off-flavor. The chemical nature of the monocarbonyl compounds which might contribute to the fresh potato chip flavor and cause the development of this stale flavor have not been characterized.

Literature concerning the flavor components of potato chips is very scanty. Buttery (3, 4) studied the autoxidation of potato granules and identified acetaldehyde, propanal, 2-methylpropanal, butanal, 2- and 3-methylbutanal, pentanal, hexanal, octanal, 2-pentenal, 2-octenal, methane, ethane, propane, butane, and pentane as autoxidation products. Self, Rolley, and Joyce (28) investigated the volatiles of cooked potatoes and identified several carbonyl and sulfur compounds. In 1963 Dornseifer and Powers (8) reported the changes in volatile carbonyls

of potato chips during storage. They positively identified 2,3-butanedione and tentatively identified ethanal, propanal, 2-propanone, *n*-butanal, 2-pentenal, 2-hexenal, *n*-heptanal, and 2-heptenal. Their isolation technique involved the steam distillation of potato chips under vacuum.

Work by Gaddis, Ellis, and Currie (12) has indicated that a large number of the determinable carbonyls in rancid fat do not originally exist in the oxidized fat as free carbonyls. They are apparently produced through the breakdown of precursors under reaction conditions used in the isolation process. This fact was supported by Buttery (3). Furthermore, Crossley and Thomas (7), on the basis of their work on oil, stated that the carbonyl determinations used by many workers have estimated not only carbonyls but hydroperoxides as well.

Recently, Schwartz developed a procedure for the investigation of monocarbonyl compounds in an oil (26, 27). This method has several advantages over the conventional methods. Carbonyl compounds can be converted quantitatively into their 2,4-dinitro-

phenylhydrazones without the necessity of separating them from the oil; a carbonyl present in an oil in a concentration as low as 0.1 p.p.m. can be determined; and hydroperoxides of fat do not react with reactants under the chromatographic conditions. The present paper reports the use of this technique to study the relation between monocarbonyl compounds and flavor of potato chips.

Experimental

Materials. Potato chips used were made from Kennebec potatoes by frying in a mixture of 50% cottonseed and 50% corn oils at 365° F. The chips had a color of 4 to 5 according to the proposed color reference standard of the Potato Chip Institute. The freshly fried potato chips were packed in standard 2-pound coffee tin cans under an atmosphere of nitrogen containing only 1.70% oxygen and stored at -10° C. before using.

The fresh potato chips had an excellent flavor as evaluated by an expert taste panel. They were devoid of any harsh and burnt odor and had a clean, pleasant aftertaste. They had a moisture content of 1.70% as determined by TAPPI (Technical Association of the Paper and

Pulp Industry) official method No. 484.

Fresh potato chips from the same lot were exposed to air by opening the lid of the can and were aged at room temperature in the same container by covering the can with two layers of cellophane paper. After 8 weeks, the stale potato chips had a moisture content of 2.05 to 2.10% and a stale but not rancid flavor.

Isolation of Flavoring Compounds.

One kilogram of potato chips was ground in a glass mortar, transferred into an all-glass Soxhlet apparatus of 1-kg. capacity, and extracted with 2.5 liters of carbonyl-free hexane. The residual chips possessed only a slight potato chip and starchy odor. The hexane extract of the fresh potato chips had an excellent potato chip odor and that of the aged chips had a stale, but not rancid, odor.

Identification of Carbonyl Compounds. The technique used for the identification of the monocarbonyl compounds consisted of essentially five steps: (1) passing the hexane extract of potato chips through a Celite column, which was homogeneously impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid, in order to convert all the carbonyl compounds in the oil quantitatively into their 2,4-dinitrophenylhydrazones; (2) removing the oil from the solution with a Seisorb-Celite column; (3) removing the decomposition products and 2,4-dinitrophenylhydrazones of ketoglycerides with an alumina column; (4) separating by adsorption chromatography the 2,4-dinitrophenylhydrazones of monocarbonyl compounds into four classes—viz., saturated 2-alkanones, saturated aldehydes, 2-enals, and 2,4-dienals—and (5) finally identifying the individual components in each class of compounds by R_f values of liquid-liquid partition chromatography. A detailed description of this procedure has been published (22).

A typical liquid-liquid partition chromatogram is shown in Figure 1. Each peak represents the presence of one saturated aldehyde. The area under the peak represents the amount present.

Results and Discussion

Relationship between Carbonyl Compounds and Potato Chip Flavor. Monocarbonyl compounds increased slightly when the potato chips became stale (Figure 2)—4 μ moles per kg. of potato chips. This slight increase in monocarbonyl compounds might have led to the misunderstanding of the relationship between carbonyl compounds and flavor of potato chips if the investigation had not included the change in each class of carbonyl compounds. As shown in Figure 2, there was an increase of saturated aldehydes, saturated ketones, and 2-enals, but a large decrease in 2,4-dienals in stale potato chips. This indicated that the development of a stale flavor was due not simply to the formation of undesirable carbonyl compounds but also to the disappearance of the desirable

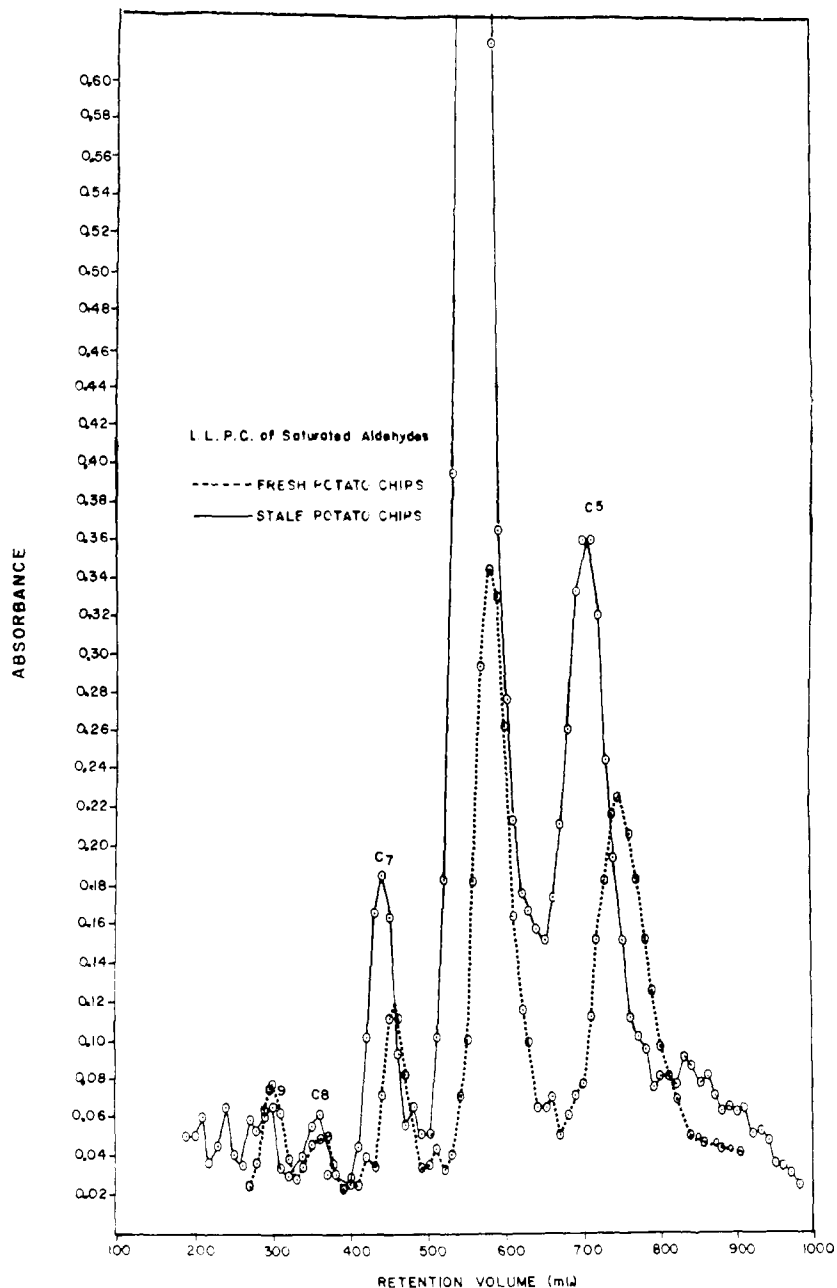


Figure 1. Determination of saturated aldehydes in fresh and stale potato chips by liquid-liquid partition chromatography

2,4-dienals, which contributed to the fresh potato chip flavor.

Nineteen monocarbonyl compounds have been identified, out of which five were saturated aldehydes, seven were saturated ketones, six were 2-enals, and one was a 2,4-dienal. The relative concentration of these compounds in fresh and stale potato chips is shown in Table I. Among saturated aldehydes, the largest increase was in hexanal, and next in pentanal. Among saturated ketones, the largest increase was in 2-pentanone, and next in 2-propanone. Among 2-enals, the largest increase was in 2-heptenal, and next in 2-octenal. Only one 2,4-dienal, 2,4-decadienal, was found in both fresh and stale potato chips. Its amount decreased from 10 μ moles per kg. in fresh potato chips to 1.6 μ -

moles per kg. in stale ones. When the concentration of each individual component was converted into parts per million, the amount of monocarbonyl compounds in stale potato chips appeared to be 0.19 p.p.m. less than in fresh potato chips because the 2,4-decadienal, which was greatly decreased, had a larger molecular weight than those carbonyl compounds which were increased.

Origin and Disappearance of 2,4-Decadienal. The 2,4-decadienal constituted about 55% of the total monocarbonyl compounds in fresh potato chips, but only about 7% in stale potato chips. It originated mainly from the decomposition of linoleic acid under conditions of deep fat frying, although arachidonic acid might also be its precursor. Patton (23) identified 2,4-decadienal

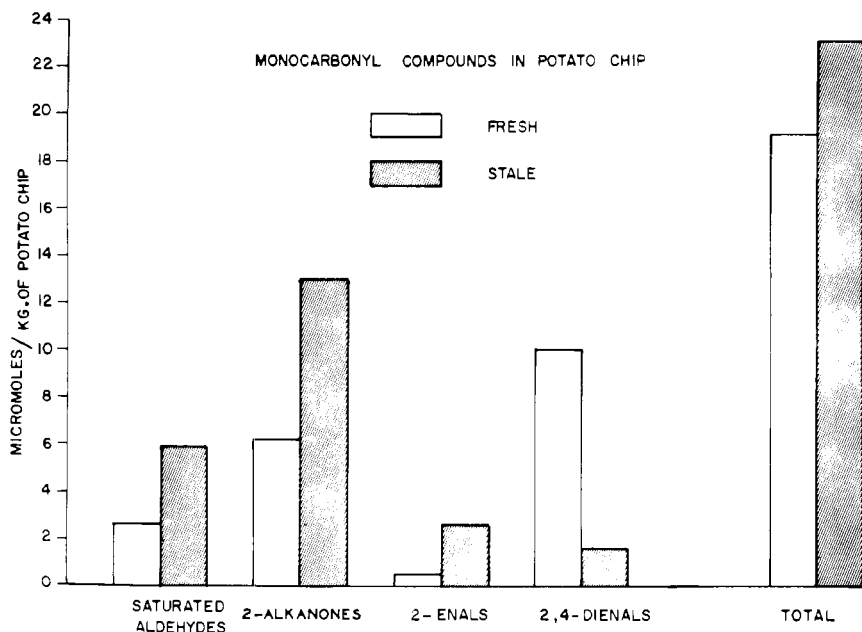


Figure 2. Monocarbonyl compounds in fresh and stale potato chips

as the major carbonyl compound in the deodorization distillate of cottonseed oil and soybean oil and heat decomposition of methyl linoleate. Flavor and odor qualities of this dienal were described by Patton as "deep fried." The 2-*trans*-4-*trans*-decadienal with a deep fried fat odor and 2-*trans*-4-*cis*-decadienal with a sweet aldehydic odor were also isolated from oils containing linoleic acid, such as palm and peanut oils, by Hoffman and Keppler (17). 2,4-Decadienal is an amazingly potent flavor compound; its flavor threshold value in water was determined to be 0.5 part per billion. Since 2,4-decadienal plays an important role in the fresh potato chip flavor, it is evident that oils used for frying potato chips should contain a certain amount of linoleic acid.

The disappearance of 2,4-decadienal is probably due to either polymerization among themselves or autoxidative decomposition to other carbonyl compounds. Pippen and Nonaka (24) reported that 2,4-decadienal, on exposure to air at room temperature, develops first stale and then rancid odors. Thus, this compound may contribute to desirable aroma but also be an immediate precursor of stale or rancid odors. Without conclusive data nothing can be predicted about the fate of the compound. But the fact that 2,4-decadienal decreases on storage will serve as the stimulus for further investigation of its chemistry.

Origin of Carbonyl Compounds Identified. The products identified seem to arise mainly from autoxidation of the unsaturated oleic and linoleic acids, which are the main constituents of triglycerides of cottonseed and corn oils used for frying potato chips. By considering the autoxidation theory of Farmer (17) and its extension to the α -methylene group outside the non-

conjugated 1,4-pentadienoic system, the formation of all saturated aldehydes, 2-enals, and 2,4-dienals except 2-hexenal could be presumed from the autoxidation of the two unsaturated fatty acids (Table II). However, the formation of heptanal, nonanal, 2-heptenal, 2-nonenal, and 2-decenal could be explained only by unusual double bond shifts (29) or the presence of unknown precursors. It has been reported that shifts of double bonds resulted from the tendency to form thermodynamically more stable compounds before or after hydroperoxide decomposition (16). Identification of all these carbonyl compounds from the autoxidation products of oleate, linoleate, and linolenate by various workers (7, 13, 16, 18, 19) further proves the possibility of double bond shifts. Gas chromatographic analyses indicated the presence of less than 1% of linolenic acid in corn oil. This unsaturated fatty acid may well be the precursor of 2-hexenal through double bond shift.

The presence of 2-alkanones in autoxidized fats and oils has been reported by various workers. Chang (5) reported the presence of 2-heptanone in reverted soybean oil. Endres, Bhalerao, and Kummerow (10) presented evidence for the presence of methyl ketones in thermal oxidations of synthetic triglycerides. Crossley, Heyes, and Hudson (6) found homologous series of 2-alkanones in heated pure triglycerides. The formation of homologous series of 2-alkanones in reverted soybean oil without heat treatment was first reported by Mookherjee and Chang (22). In the present investigation homologous series of 2-alkanones have also been found in stale potato chips. Their amount is relatively larger than the other classes. Moreover 2-propanone constituted more than one third of the ketones found in fresh and stale potato chips.

The mechanism for the formation of 2-alkanones, however, is more difficult to postulate. According to Ellis (9), 2-alkanones could be formed by the addition of water across the double bond next to a keto group which is produced

Table I. Monocarbonyl Compounds Identified in Potato Chips

	Fresh, $\mu\text{moles/Kg.}$	Stale, $\mu\text{moles/Kg.}$
Pentanal	1.0	1.8
Hexanal	1.0	3.4
Heptanal	0.3	0.5
Octanal	0.1	0.2
Nonanal	0.2	0.1
2-Propanone	1.9	4.4
2-Butanone	1.8	2.2
2-Pentanone	0.8	4.0
2-Hexanone	0.4	0.9
2-Heptanone	0.1	0.3
2-Octanone	0.2	0.3
2-Nonanone	0.1	0.1
2-Hexenal	0.0	0.2
2-Heptenal	0.1	0.9
2-Octenal	0.1	0.8
2-Nonenal	0.1	0.3
2-Decenal	0.1	0.2
2-Undecenal	0.1	0.2
2,4-Decadienal	10.1	1.6
Total	18.4	22.4

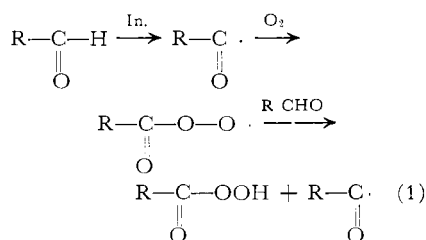
Table II. Origin of Carbonyl Compounds from Autoxidation of Unsaturated Fatty Acids

Name of Compound	Precursor Acid	Position of Double Bond between C-Atom	Position of Hydroperoxide at C-Atom	Splitting of Bond between C-Atom
Pentanal	Linoleic	12-13	14	13-14
Hexanal	Linoleic	11-12	13	12-13
Heptanal	Oleic	10-11	12	11-12
Octanal	Oleic	9-10	11	10-11
Nonanal	Oleic	8-9	10	9-10
2-Hexenal	Linolenic	14-15, 11-12	13	12-13
2-Heptenal	Linoleic	13-14	12	11-12
2-Octenal	Linoleic	12-13	11	10-11
2-Nonenal	Linoleic	11-12	10	9-10
2-Decenal	Oleic	10-11	9	8-9
2-Undecenal	Oleic	9-10	8	7-8
2,4-Decadienal	Linoleic	10-11, 12-13	9	8-9

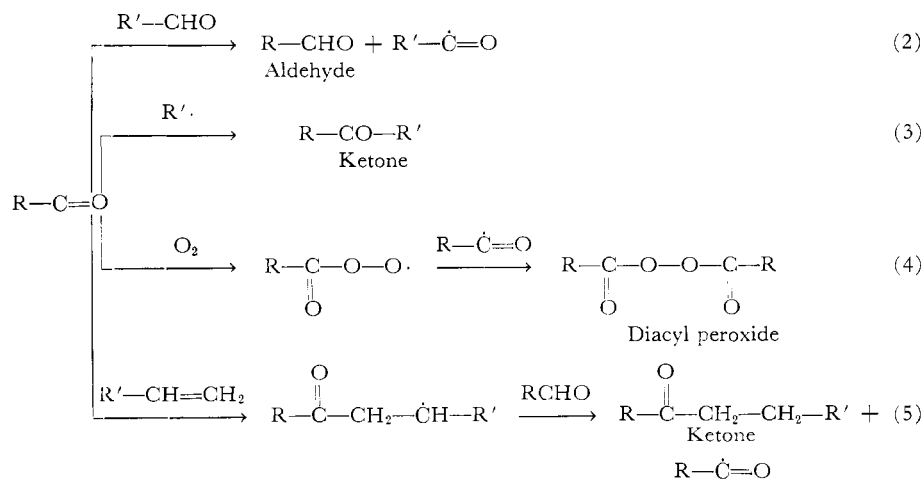
from a hydroperoxide by the mechanism of Bell *et al.* (2). Another mechanism for the formation of 2-alkanones was the decarboxylation of β -keto acids (30). Crossley (6) proposed a mechanism for ketone formation in heated triglycerides. It consisted of two parts: oxidative scission in the neighborhood of double bond to form vinyl ketone, and production of 2-alkanone by the oxidation of vinyl ketone.

These mechanisms do not completely explain the increase of 2-alkanones in potato chips during storage at room temperature. Although the formation of 2-alkanones could be explained by the combined mechanisms of Ellis and Bell, it is doubtful that the addition of water across the double bond could take place to such an extent at room temperature. Furthermore, acetone, which had the highest increase during storage of potato chip at room temperature, could originate only from linolenic acid which was present in the frying oil only in trace amount. Therefore, a free radical mechanism is postulated.

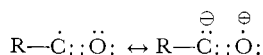
The autoxidation of aldehydes proceeds with ease, even at room temperature, to form acyl free radical (14).



The acyl free radical may participate in the following reactions to produce various compounds:



The assumption that an acyl free radical has sufficient lifetime to participate in all these reactions has been deduced from the resonance structure of this free radical (15).



This structure also suggests that acyl radical may be appreciably nucleophilic because of the drift of electron density from oxygen to the "trivalent" carbon. This nucleophilic character explains the fact that acyl free radical has less tendency to attack an electron-rich center.

Equations 3 and 4 give rise to saturated 2-alkanones. For the formation of 2-alkanones according to Equation 3, methyl free radical is required. The latter could be easily formed by the formation of C₁₇ hydroperoxide in the linolenic acid chain and scission of bond between C₁₈ and C₁₇, or the decomposition of acetyl peroxide formed by Equation 4. Rembraum (25) showed that acetyl peroxide decomposed spontaneously, producing virtually quantitative yields of carbon dioxide and methyl free radical. For the formation of 2-alkanones according to Equation 5, terminal olefins are required (27). The latter could be produced from the autoxidation of unsaturated fatty acids and aldehydes. The mechanisms of formation of terminal olefin could be readily understood from some recent work of Kerr and Trotman-Dickenson (20), who showed that peroxide-catalyzed free radical degradation of pentanal gave propene as one of the major products.

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