Some Unusual Volatile Carbonyl Components of Potato Chips

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Combined capillary gas chromatography–mass spectrometry analysis of the carbonyl fraction of the volatile oil of potato chips detected a number of unusual aldehydes which were shown to be 4-methylpent-2-enal, 4-methylhex-2-enal, 2-isopropylbut-2-enal, 2-methylmercaptomethylbut-2-enal, 2-methylmercaptomethyl-4-methylpent-2-enal, 2-phenylbut-2-enal, 2-phenyl-4-methylpent-2-enal, and 2-phenyl-5-methylhex-2-enal. These compounds are probably formed in the potato chips during the frying by aldol-type condensations. Other compounds also characterized included 2-methylhexa-4,5-dione, acetophenone, hepta-*trans*,-*trans*-2,4-dienal, and octa-*trans*,*trans*-2,4-dienal.

A number of aldehydes have been previously characterized in potato chips (Buttery and Ling, 1972; Chang, 1967; Mookerjee *et al.*, 1965) but these have generally been of the commonly encountered straight-chain saturated, monounsaturated, and diunsaturated types. In previous work by this laboratory (Buttery, 1971) some unusual aldehydes were detected but at that time could not be characterized. The aim of the present work was to characterize these unusual compounds which were suspected to be aldol condensation products. Some aldol condensation products have been reported previously in other heated products, notably roasted cocoa beans (van Praag *et al.*, 1968).

EXPERIMENTAL SECTION

Materials. Good quality potato chips were obtained from a local market and used within a day or two of purchase. Authentic samples (other than aldol condensation compounds) were synthesized by well established methods.

Isolation of Volatile Carbonyl Fraction. Potato chips (1100 g) were placed in a 12-l. flask with odor-free triple-distilled water (4 l.). This was then connected to a steam distillation continuous extraction head of the type described by Nickerson and Likens (1966). Attached to the solvent arm of this head was a 500-ml flask containing purified hexane (200 ml), and Girard T reagent (5 g) in water solution (50 ml). The mixture in the solvent flask was stirred continually with a magnetic stirrer. The isolation was carried out under vacuum (100 mm pressure) with the aqueous potato chips at a temperature of about 50°. The condenser was cooled with ice water. The isolation was carried out for 3 hr. The aqueous Girard T extract was then separated from the hexane layer and washed with purified pentane (50 ml, 1×). The Girard T solution was then placed in a flask with pentane (100 ml). Dilute hydrochloric acid (200 ml, 4 *N*) was then added and the mixture was stirred under a nitrogen atmosphere at room temperature for 2 hr. The pentane layer was then separated and the aqueous layer was extracted with more pentane (2 × 50 ml). The pentane extract was washed with saturated sodium bicarbonate solution (1 × 50 ml) and then dried over sodium sulfate. The extract was then concentrated to a volume of about 100 μl using low holdup distillation columns. This concentrate was stored at −30°.

Capillary Gas–Liquid Chromatography (glc)–Mass Spectral Analysis. This was carried out in a similar way to that described by the authors for other products (Buttery *et al.*, 1969). The column was a 1000-ft long by 0.03-in. i.d. stainless steel capillary coated with Carbowax 4000 containing 5% Igepal CO-880. The column was temperature programmed from 25 to 80° at 2° per min and then from 80 to 170° at ½° per min and held at the upper limit. The effluent from the column was led to a silicone membrane molecular separator attached to a modified Consolidated 21-620 mass spectrometer.

Synthesis of Aldol Condensation Compounds. These were all synthesized in a similar way by mixing the two aldehydes involved and catalyzing their condensation with 25% aqueous potassium hydroxide solution. General methods have recently been described for aldol condensations (Nielson and Houlihan, 1968). In the present work the unsaturated aldehydes were isolated directly by the method used. No appreciable amounts of the intermediate aldol alcohols were detected.

As an example, 2-methylmercaptomethylbut-2-enal was synthesized as follows. Potassium hydroxide solution (0.6 ml, 25% in water) was added dropwise over ½ hr to a stirred, ice-cooled mixture of acetaldehyde (0.4 g) and methional (0.2 g). The mixture was stirred for 2 hr longer at 0° and then for 2 hr at room temperature. Ether (50 ml) was then added and the aqueous layer was separated in a separatory funnel. The ether solution was washed with ice cold 10% sulfuric acid (20 ml, 1×) followed by saturated sodium bicarbonate solution (20 ml, 1×). The ether extract was then dried over sodium sulfate and filtered, and the ether was removed on a steam bath. Glc separation was carried out using a 10-ft by ¼ in. o.d. column packed with 60–80 mesh Chromosorb P coated with 10% Silicone SF96 (350) at 160°, and with an inlet pressure of 15 psi. This showed a major peak at 16 min whose mass and proton magnetic resonance (pmr) spectra were consistent with that expected of 2-methylmercaptomethylbut-2-enal. Yield based on methional and calculated from glc peak areas was 25%.

In general, yields varied with the type of condensation. Good yields (>50% based on phenylacetaldehyde) were obtained with the condensation of acetaldehyde or 3-methylbutanal with phenylacetaldehyde. Here the aliphatic aldehydes were used severalfold in excess. The methylene group between the ring and the aldehyde group in phenylacetaldehyde is particularly active for this type of condensation. Low yields (*ca.* 5%) were obtained with the condensation of 3-methylbutanal and acetaldehyde to give 2-isopropylbut-2-enal. Even lower yields were obtained with the condensation of 2-methylpropanal with acetaldehyde. This is probably due to the steric hindrance of the branched aldehydes.

Good yields of 4-methylpent-2-enal and 4-methylhex-2-enal were obtained using a malonic acid condensation synthesis similar to that described previously for 5-methylhex-2-enal (Buttery and Ling, 1972). 4-Methylpent-2-enal had been synthesized previously by Jutz (1958).

Proton Magnetic Resonance (pmr) Spectra. These were measured in deuterated chloroform at 100 MHz using a Varian HA-100.

RESULTS AND DISCUSSION

Table I lists the compounds found in the present work that were not previously reported by the authors (Buttery

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Table I. Unusual Aldol-Type Compounds and Other Compounds Found in the Volatile Carbonyl Fraction of Potato Chips

Aldol condensation type compounds[a,b]
4-Methylpent-2-enal (I) MS, RT
4-Methylhex-2-enal (II) MS, RT
2-Isopropylbut-2-enal (III) MS, RT
2-Methylmercaptomethylbut-2-enal (IV) MS, RT
2-Methylmercaptomethyl-4-methylpent-2-enal (V) MS, RT
2-Phenylbut-2-enal MS, RT
2-Phenyl-4-methylpent-2-enal MS, RT
2-Phenyl-5-methylhex-2-enal MS, RT

Other compounds[a,b]
2-Methylhexa-4,5-dione MS, RT
Hepta-*trans,trans*-2,4-dienal MS, RT
Octa-*trans,trans*-2,4-dienal MS, RT
Acetophenone MS, RT

[a]MS, RT = mass spectral and glc retention evidence, respectively. [b]Evidence cited is consistent with that of an authentic sample obtained on the same instrument.

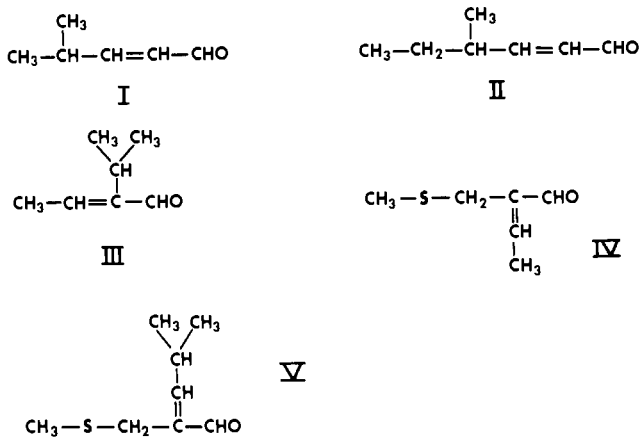

Figure 1. Structures of unusual aldol condensation type aldehydes.

and Ling, 1972). Figure 1 shows the structures of the aliphatic aldol-type aldehydes.

Particular care was taken to minimize the chance of interaldehyde condensation during the isolation of carbonyls from potato chips. This included the use of Girard T reagent to bind the aldehydes as soon as possible after the extraction and the use of dilute solutions (the "concentrate" contained less than 5% of total carbonyls in pentane). The use of vacuum steam distillation continuous extraction would allow very little acetaldehyde to occur in the extract. Acetaldehyde is one of the major aldehydes needed to form the aldol condensation aldehydes listed in Table I.

The condensation products with phenylacetaldehyde have been previously reported as volatile constituents of roasted cocoa beans (van Praag *et al.*, 1968) and roasted peanuts (Johnson *et al.*, 1971; Walradt *et al.*, 1971). The mass spectra of these compounds were also reported by van Praag and coworkers. The mass spectra found for other aldol-type compounds in Table I (using a modified Consolidated 21-620 cycloidal-type instrument) are listed below (intensities in parentheses with base peak taken as 100, two most intense ions every 14 mass units above m/e 34, *cf.* systems of Herz *et al.* (1971), molecular ion is underlined).

4-Methylpent-2-enal (I), 39 (38), 41 (100); 53 (14), 55 (44); 69 (40), 70 (8); 79 (4), 83 (32): 97 (5), 98 (38).

4-Methylhex-1-enal (II), 39 (46), 41 (70); 55 (100), 56 (28); 69 (17), 70 (9); 83 (70), 84 (11); 94 (4), 97 (26); 111 (2), 112 (9).

2-Isopropylbut-2-enal (III), 41 (100), 43 (55); 53 (11), 55 (52); 67 (11), 69 (29); 79 (10), 83 (38); 97 (33), 98 (35); 112 (71), 113 (7).

2-Methylmercaptomethylbut-2-enal (IV), 39 (48), 45 (37); 53 (49), 54 (95); 69 (2), 71 (1); 82 (100), 83 (24); 96 (1), 97 (3); 115 (5), 116 (1); 130 (47), 131 (5).

2-Methylmercaptomethyl-4-methylpent-2-enal (V), 39 (56), 41 (82); 53 (20), 55 (37); 67 (64), 69 (11); 81 (42), 82 (21); 95 (75), 96 (11); 109 (14), 110 (100); 121 (3), 125 (3); 143 (8), 144 (1); 158 (58), 159 (4).

As far as the authors could determine, III, IV, and V had not previously been reported in the literature. Molecular weights found for these compounds using a high-resolution Consolidated 21-110B double-focusing mass spectrometer were as follows.

2-Methylmercaptomethylbut-2-enal, found 130.0445 ($C_6H_{10}OS$ requires 130.0451). 2-Methylmercaptomethyl-4-methylpent-2-enal, found 158.0738 ($C_8H_{14}OS$ requires 158.0764). 2-Isopropylbut-2-enal, found 112.0883 ($C_7H_{12}O$ requires 112.0887). The mass spectral fragmentation patterns were consistent with the structures named. Pmr spectra were also consistent.

Only one aldol condensation aldehyde (V) would be expected (and was found) from the condensation of 2-methylpropanal and methional. Two aldol condensation aldehydes might be expected from methional and acetaldehyde, but only one (IV) could be isolated from the synthetic work.

One compound reported by the authors previously (Buttery and Ling, 1972), which probably also belongs to this group, is the compound 5-methylhex-2-enal which could result from the aldol condensation of acetaldehyde and 3-methylbutanal. Two related compounds found in the present work are II (which could result from the condensation of acetaldehyde and 2-methylbutanal) and I (from acetaldehyde and 2-methylpropanal). Both aldol condensations give very poor yields for the synthesis of these compounds in the laboratory, possibly because of the steric hindrance caused by the 2-methyl group. It is surprising that any of these compounds are formed in the chips, although the high temperature (*ca.* 170°) of the frying process may facilitate this.

Theoretically the aldol condensation 2-enals can exist in cis and trans forms. Only one form was found in the present work with all aldol compounds in Table I. This is probably the more stable trans form, which is normally the case with 2-enals.

Although the aldol condensation products found represent possible condensations between the major aldehydes, there has seemed to have been some selection. Some aldehydes present in reasonable amounts in the steam volatile oil, such as hexanal, and deca-2,4-dienal did not seem to have undergone any aldol-type condensations, whereas the compound methional, which is present in smaller amounts, has. It may be that the aldol condensation products that we see reflect what aldehydes are "free" during the frying process. Possibly fat breakdown products such as hexanal are not free during the frying but are bound in some way in the oil. They may also accumulate during storage from gradual breakdown of oxidized fat. The eventual contact with water probably also catalyzes this breakdown.

All of the aldol-type compounds and particularly the sulfur-containing compounds had interesting aromas and probably contribute to some extent to the total aroma of the potato chips. Sensory evaluation of these compounds will be carried out in the near future.

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does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

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New Sweetening Agents: *N'*-Formyl- and *N'*-Acetylkynurenine

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N'-Formyl- (**6**) and *N'*-acetylkynurenine (**7**) are approximately 35 times sweeter than sucrose. The kynurenine derivatives elicit a sweet taste sensation immediately on contact with the taste buds. The sweetness of the acetyl derivative is linearly comparable to sucrose in concentrations up to 2.5 mg/ml. A sweetness comparison of sucrose and the formyl analog is linear to 1.6 mg/ml. An off-flavor at higher levels of **6** may account for the lack of comparability to **7** and sucrose at higher concentrations. A new synthesis for DL-kynurenine is described.

The need for a low or noncaloric sweetener needs no reiteration. A compound which is a normal metabolite and is sweet may offer potential in this area. Several amino acids as well as several dipeptides containing aromatic groups are known to be sweet (Yamaguchi *et al.*, 1970a,b). Yamaguchi *et al.* (1970a,b) have reported D-tryptophan to be 25 to 50 times sweeter than sucrose. L-Tryptophan (Solms *et al.*, 1965) exhibits a bitter flavor half as intense as caffeine. Mazur *et al.* (1969, 1970) have reported various dipeptides and aspartic acid amides to be sweet.

Kynurenine, a tryptophan metabolite, and various derivatives of kynurenine have been synthesized previously from tryptophan (Dagliesh, 1952; Knox and Mehler, 1950). Our studies were undertaken to evaluate the sweetness of kynurenine derivatives and to devise syntheses for kynurenine and related artificial sweeteners from inexpensive starting materials.

EXPERIMENTAL SECTION

Evaluation of Sweetness. A five-member panel compared the sweetness of five samples of kynurenine solutions of varying concentrations to a sucrose solution of a given concentration. The panelists ranked the sweetness of the kynurenine solutions equivalent to the sucrose solution. Results in Table I are expressed in milligrams of kynurenine derivative judged to produce equivalent sweetness.

Synthetic Experiments. A synthetic route to kynurenine (**5**) is outlined in Figure 1. *o*-Chloroaniline (Eastman) was converted to a Grignard reagent at 85° (Spencer and Stokes, 1908). The reaction flask was then cooled in crushed solid carbon dioxide while 5% maleic anhydride in tetrahydrofuran was added dropwise, as described by Newman and Smith (1948). The intermediate product (**4**) was not isolated but put into a Paar bomb, which was then evacuated and charged with ammonia. The mixture was kept under 14 lb of pressure for 16 hr. Kynurenine was then precipitated as described by Auerbach and Knox (1957).

Anal. Calcd for $C_{10}H_{12}N_2O_3$ (mol wt 208.22): C, 57.68; H, 5.81; N, 13.46. Found: C, 58.27; H, 5.95; N, 13.44.

N'-Acetylkynurenine was made as follows. One gram of kynurenine was dissolved in 15 ml of 90% acetic acid. Acetic anhydride (30 ml) was then added and the reaction mixture was stirred for 2 hr. Adding diethyl ether precipitated the product. The yield was 60% after recrystallization from 90% acetic acid with ether (mp = 189°). *N'*-Formylkynurenine was synthesized according to Dagliesh (1952).

RESULTS AND DISCUSSION

The elemental analyses as well as spectroscopic and nuclear magnetic resonance (nmr) data support the structure for the synthetic kynurenine. The ultraviolet spectrum of the synthetic compound shows three peaks which correspond to the literature values (Knox and Mehler, 1950) for kynurenine (**4**): λ 360 (ε 4500), 257 nm (ε 7500), 230 nm (ε 18,900). The 100 Hz nmr spectra of synthetic and commercial kynurenines are shown in Figure 2. Both ultraviolet and nmr spectra of commercial and synthetic kynurenines are

Table I. Comparison of Sweetness of Sucrose and *N'*-Formyl- and *N'*-Acetylkynurenine

	Sweetness[a,b]	
Sucrose, %	*N'*-Formylkynurenine	*N'*-Acetylkynurenine
2.5	0.7	0.6
5.0	1.5	1.4
10.0	3.0	3.0

[a] Milligrams of kynurenine derivative equivalent to sucrose standard. [b] Based on 25 judgments at each of seven levels of kynurenine derivative for each sucrose level. Each figure is the average concentration where 50% of the judges said a level of sweetener was sweeter than the sucrose concentration.

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