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SHORT COMMUNICATIONS

Importance of 2-Aminoacetophenone to the Flavor of Masa Corn Flour Products

INTRODUCTION

A recent paper (Karahadian and Johnson, 1993) reported studies of the identification of volatile compounds of masa-type corn flour and of some of its products such as tortillas. They also carried out some sensory studies and identified a number of volatile aroma compounds. They reviewed fairly thoroughly previous work on these products.

We have also been carrying out studies on corn products. With corn flour and tortillas we found many of the same volatiles reported by Karahadian and Johnson (1993). In addition, we also characterized some compounds not mentioned by these authors. One of these was a component that we believe contributes much of the character of these products which we describe in this paper.

EXPERIMENTAL PROCEDURES

Materials. The corn flour was Quaker Masa Harina. Corn tortillas and taco shells were major brands purchased from local supermarkets.

Isolation of Volatiles. Two methods of preparing the product for the isolation were used. In the first, called the "neutral method", the corn flour or other product (25 g) was added to 150 mL of water saturated with NaCl (54 g) and the mixture blended for 30 s. The mixture was then transferred to a 1-L round-bottom flask containing an efficient magnetic stirrer. A suitable Pyrex glass head was then attached to the standard joint of the flask which allowed purified air (3 L/min flow rate) to pass over the rapidly stirred mixture and exit through a Tenax trap (Tenax GC, 60–80 mesh, 10 g, 14 cm × 2.2 cm i.d.). The isolation was carried out for 2 h at 25 °C and the trap then removed and eluted with 50–100 mL of freshly distilled ether (containing 0.001% of Ethyl Corp. antioxidant 330). The ether extract was then concentrated in the usual way on a warm water bath to ca. 20 μL. The trap was regenerated by passing a stream of purified nitrogen through the heated (180–200 °C) trap for 1 h.

With the second method of preparing the corn product, called the "basic method", Na_2CO_3 (7.5 g) was added along with the NaCl but otherwise the procedure was the same.

Capillary GC–MS Analysis. This was carried out using a HP 5890 gas chromatograph (GC) coupled with a HP 5970 quadrupole mass spectrometer. The column was a fused silica capillary (60 m long × 0.32 mm i.d.) coated with DB-1. The GC conditions used were as follows: hold at 30 °C for 25 min; temperature program at 4 °C/min to 200 °C; hold at 200 °C for a further 20 min. The carrier gas velocity at 30 °C was 22 cm/s, and the sample split ratio was 1/20.

Quantitative GC Analysis. The isolation method was as described above except that a measured volume (usually 1.00 mL) of a water solution of an internal standard (4-phenyl-2-butanone with the neutral method and quinoline with the basic method, each at 20.0 ppm) was added to the mixture immediately after blending and then the mixture blended again for 10 s. The GC conditions used were the same as described above except that the detection was by a flame ionization detector.

Authentic Samples. 2-Aminoacetophenone (99% pure) was obtained from Aldrich Chemical Co. and further purified by GC separation. Most other chemical compounds were also obtained from commercial sources or synthesized by established methods and their identities verified by spectral (MS or IR) means.

Odor Threshold Determination. This was carried out as previously described (Buttery et al., 1983) using a panel of 16–20 judges.

RESULTS AND DISCUSSION

The volatiles were isolated from the corn product using high-flow dynamic headspace sampling as described in detail under Experimental Procedures. Two main isolation procedures were used for comparison, one using neutral conditions and the other using slightly basic conditions. Bases such as 2-aminoacetophenone are more volatile in basic media. The corn products were mixed with water, and the solution was saturated with NaCl for the neutral method. The basic method used essentially the same procedure except that in addition some Na_2CO_3 was added along with the the NaCl. Capillary GC–MS analyses were carried out on the volatile concentrates from each of the corn products, i.e., corn flour (Masa Harina), tortillas, and taco shells. A prominent peak in the volatiles from corn flour showed a mass spectrum with molecular ion at 135 (58) and other ions at 120 (100), 92 (53), 65 (33), 39 (14), 52 (6), 77 (5), and 106 (4) and Kovats GC retention index of 1261 (DB-1). These data were consistent with

Table 1. Comparison of Concentration of 2-Aminoacetophenone Found in Different Masa Corn Flour Products and of Log_{10} Odor Units for This Compound

product	concn in product, ppm[a] neutral method	basic method	log odor units[b]
corn flour (Masa Harina)	0.40	0.34	3.2
tortilla	0.12	0.15	2.9
taco shells	0.32	0.33	3.2

[a] Parts (mL) of 2-aminoacetophenone per 10^6 parts (g) of corn product. [b] For basic method.

that for an authentic sample of 2-aminoacetophenone. The presence of this compound was also confirmed by GC–MS analyses of the other two corn products.

Determination of the concentration of 2-aminoacetophenone was carried out using internal standards which were measured amounts of 20.0 ppm water solutions of 4-phenyl-2-butanone for the neutral method and quinoline for the basic method. These were added to the corn product mixture before the volatiles were isolated by the high-flow dynamic headspace method. Combined recovery and response factors relative to 4-phenyl-2-butanone and quinoline were determined using known concentrations of 2-aminoacetophenone in water following otherwise the same isolation procedures as for the corn products.

Table 1 compares the concentrations of 2-aminoacetophenone found in these three products under both neutral and basic conditions, which are in reasonable agreement. The values shown are the means of at least three determinations.

Odor Threshold and Odor Units. An odor threshold of 2-aminoacetophenone was measured using methods previously described (Buttery et al., 1983). The sensory panels' judgments were 86% correct at 0.4 ppb (96 total judgments), 74% correct at 0.2 ppb (112 total judgments), and 67% correct at 0.1 ppb (112 total judgments). Plotting this and similar data from eight other concentrations indicated a threshold point of 0.2 ppb. This is reasonably consistent with the value of 0.5 ppb reported previously by Parks (1967).

Using this value and the concentration data, we can calculate the number of odor units [cf. Buttery et al. (1983)] present for this compound in each product. This is the ratio of the compound's concentration divided by its threshold and gives the number of odor threshold concentrations present for that compound. This is shown in the last column of Table 1 for the basic method concentrations. Of all compounds identified in corn flour and tortillas, 2-aminoacetophenone showed the largest amount of odor units and was among the compounds with the most odor units for taco shells. This compound is undoubtedly important to the aroma and flavor of these products.

In qualitative sensory studies [cf. Buttery et al. (1983)] the judges were first asked to describe the odor of 200 ppb of water solutions of 2-aminoacetophenone. Using the five most frequently used terms, the judges were then asked to score (from 1 to 5) the odor's similarity to each term (these were floral, flour, grape, tortilla, and vegetable). The description tortilla was scored the highest.

Presence of 2-Aminoacetophenone in Other Foods. One of the first reports of 2-aminoacetophenone in foods was that of Parks (1967), who found it as an off-flavor in milk products. It is chemically related also to the grape flavor component methyl anthranilate and has been reported to cause the "foxy" aroma of Labruscana grapes and to occur in the anal sac of the Japanese weasel, itatsi (Acree et al., 1990). Some judges in our sensory studies noted its odor resemblance to methyl anthranilate. It is interesting that the 2-aminoacetophenone has an amino group located near an acetyl group and so shows some analogy to compounds such as 2-acetyl-1-pyrroline which have cracker-like odors [cf. Buttery et al. (1983)]. None of the sensory panelists, however, described its odor as cracker-like. For comparison, the odor threshold of 4-aminoacetophenone was determined, where the amino group is far away from the acetyl. It proved to be a very much weaker odorant, with an odor threshold of 100 000 ppb.

Possible Origin. Parks (1967) noted that Spacek (1954) had observed that 2-aminoacetophenone can result from alkaline degradation of tryptophan. This then provides an explanation for its presence in masa-type corn flour because of the treatment of the corn with calcium hydroxide in the normal production of the masa flour.

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