2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone in Corn Products

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2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone (DHF) was identified (GC−MS) in canned, frozen (cooked), and fresh (cooked) sweet corn. It was also identified in corn tortilla chips and taco shells. The concentration of DHF was higher in canned (170−270 μg/kg) than in fresh (19 μg/kg) or frozen (27 μg/kg) sweet corn. Moderate concentrations of DHF occurred in tortilla chips (260 μg/kg) and taco shells (80 μg/kg). The DHF was isolated using a dynamic headspace method with anhydrous sodium sulfate blended with the corn products to remove water. DHF occurred at a concentration on the order of 5−10 times its odor threshold (in water) in the canned sweet corns and tortilla chips and also above this threshold in taco shells.

Keywords: *2,5-Dimethyl-4-hydroxy-3(2H)-furanone; Furaneol; sweet corn; tortilla chips; identification; concentration; dynamic headspace; sodium sulfate*

INTRODUCTION

2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone (DHF), also known as Furaneol, a well-known component of some fruits (Rodin et al., 1965; Re et al., 1973), was tentatively identified in popcorn by Waldrat et al. (1970) and later positively identified by Schieberle (1991) who found a concentration of 1.96 mg/(kg of popcorn) (Schieberle, 1992). The authors recently developed a relatively simple, relatively rapid method of analysis for water soluble volatiles in foods (Buttery and Ling, 1996a) and used this method to determine whether DHF also occurred in other corn products. Some of this work was recently presented (Buttery and Ling, 1996b).

EXPERIMENTAL PROCEDURES

Materials. Anhydrous sodium sulfate (>99% pure) and sodium dihydrogen phosphate (>99% pure) were heated at 150 °C for 4 h in clean glass containers to remove any possible volatiles and then allowed to cool. Diethyl ether was freshly distilled through a glass helix column, ca. 1−2 ppm Ethyl Corp. antioxidant 330 (1,3,5-trimethyl-2,4,6-tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene) was added to it, and it was stored in the dark. Authentic DHF was obtained from Aldrich Chemical Co. and recrystallized from ether−pentane.

Canned sweet corn, tortilla chips, taco shells, frozen corn (all major brands), and fresh corn (on cob with husks) were obtained from local supermarkets. At least two brands for each product were examined. All were from yellow corn. Tortillas were freshly cooked from tortilla flour. Frozen corn and fresh corn were cooked immediately before isolating the sample, the corn kernels being cut from the cob with a sharp knife after cooking.

Isolation of Volatiles. For canned, frozen, and fresh sweet corn and tortillas, samples (30 g) were weighed and placed in a Pyrex blending jar. With quantitative analysis 1 mL of internal standard was added (ethyl maltol 60 mg/kg water) at this point. The mixture was then blended for 30 s. (With tortilla chips and taco shells 30 g of the product was first blended dry and then 30 mL of water and the internal standard added). Sodium sulfate (100 g) was then added and the mixture blended until uniform (ca. 1 min). NaH_2PO_4 (2 g) was then added and the mixture blended again. The sodium sulfate mixture was then transferred to a 1 L beaker containing an additional 140 g of sodium sulfate and mixed thoroughly with a glass rod. The mixture was then placed in a Pyrex glass column 36 mm o.d. × 35 cm long containing a coarse fritted disk at the lower end and ground ball and socket joints for connection to the closed loop dynamic headspace system. The lower end of the column was attached to a large (ca. 10 g) Tenax trap. The outlet of the Tenax trap was connected by ball and socket ground glass joints through 6.4 mm o.d.Teflon tubing to the recirculating Teflon diaphragm pump. The outlet of the Teflon pump was connected via Teflon tubing to the upper part of the sample column. The complete system (placed behind a protective screen) was first flushed with nitrogen through the column, trap, pump, and tubing to displace the air before closing and starting the recirculating pump. The isolation was carried out for 3 h with the recirculating nitrogen moving at a flow rate of ca. 3−6 L/min. For efficient water absorption it is important that the product−Na_2SO_4 mixture remain at or less than ca. 25° C. The trap was then removed from the system and extracted with freshly distilled diethyl ether (50−100 mL). The ether extract was concentrated to ca. 50 μL using a warm water bath and micro-Vigreux distillation column. The diaphragm pump and Teflon tubing were cleaned between isolations by drawing hot (> 90 °C) distilled water (2 L) through the system using an aspirator (diaphragm pump off) and then drawing purified air (3L/min) through the system for 4−6 h.

Capillary GC−MS. The capillary column was fused silica 60 m long × 0.25 mm i.d., coated with DB-WAX (J and W Scientific Co., Folsom, CA). The column was held at 30° C for the first 4 min and then heated at 2 °C/min to 170° C and held at this temperature for a further 25 min. The injector temperature was 170 °C and was used with a 1/20 split. The gas chromatograph was a HP 5890 instrument directly coupled to a HP 5971 quadrupole mass spectrometer.

Quantitative Analysis. The gas chromatography conditions used for the quantitative analysis were similar to those described for GC−MS except that the capillary column had an i.d. of 0.32 mm. The internal standard was ethyl maltol (2-ethyl-3-hydroxy-4-pyranone), which was used as a solution in water at a concentration of 60 mg/ kg. Flame ionization detection peak areas were used for the determination. Each isolation and GC analysis was replicated 3 or more times and the mean of the results obtained.

RESULTS AND DISCUSSION

Identification and Quantitative Analysis. DHF was identified in fresh and frozen corn, canned sweet corn (both kernel and creamed), tortilla chips, and taco shells by comparison of the mass spectrum (ions (intensities in parentheses) at 128 (72), 85 (22), 72 (9), 57

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Table 1. Concentrations of 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone (DHF) Found in Some Corn Products[c]

corn product	conc DHF μg/kg[a]	corn product	conc DHF μg/kg[a]
fresh corn (cooked)	19	corn tortilla chips	260
frozen corn (cooked)	27	corn taco shells	80
canned sweet corn (kernel)	170	tortilla	<5[b]
canned sweet corn (creamed)	270		

[a] μg of DHF per kg of corn product (ppb). [b] Not detectable by mass spectrometry. [c] The values shown are the means from at least three different isolations and GC analyses and are probably only accurate to the correct order of magnitude.

(61), 55 (24), 45 (12), 43 (100), 29 (46)) and capillary GC retention time (K.I. = 2030, DB-WAX) with those of an authentic sample. DHF could not be detected by GC−MS in tortillas. Table 1 lists the concentrations found. Although they were determined as carefully as possible, they are probably only accurate to the correct order of magnitude.

The compound maltol (3-hydroxy-2-methyl-4-pyranone) was also identified (GC−MS) in the fried products tortilla chips and taco shells at roughly the same order of concentration as DHF.

Isolation Method. The method for isolating DHF using excess Na_2SO_4 was described previously by the authors (Buttery and Ling, 1996a,b). The method included use of high flow dynamic headspace isolation in a closed loop arrangement where the sweep gas was recycled by means of a noncontaminating Teflon diaphragm pump in an arrangement where all internal surfaces were Teflon or glass. The closed loop Teflon diaphragm pump method has also been described previously by the authors (Buttery and Ling, 1995) in a study of flavor components of corn tortillas and related products. In this 1995 study the sample (blended with a saturated aqueous salt solution) was placed in a flask. In the present study the dry sample−sodium sulfate mix powder was packed into a large column that replaces the flask used in the previous study. Blending and mixing of the sodium sulfate with the product give a powder roughly of 30−80 mesh, which is similar to the particle size used for gas chromatography preparative column packing and gives good contact of the sweep gas with the volatiles supported on the sodium sulfate and also allows a high sweep flow rate. Any adsorption of volatiles on the sodium sulfate, glass, and Teflon surfaces seems to be readily overcome (eluted) by the high flow rate of the sweep gas in a way analogous to that in gas adsorption chromatography.

For quantitative analysis ethyl maltol was used as the internal standard. It has a retention time ca. 1 min before DHF using the DB-WAX capillary. Experiments were carried out to determine the absolute recovery of DHF and ethyl maltol under the conditions of the method using standard solutions of these compounds in water. An internal standard (2,5-dimethylpyrazine) was added to the ether extract eluted from the Tenax trap. This (taking into account relative detector response factors) showed that the absolute recovery of DHF was 44% and that of ethyl maltol 56%. The absolute recoveries, under these conditions, of the related compound maltol was 46% and that of the related sotolone (4,5-dimethyl-3-hydroxy-2(5*H*)-furanone) was 31%. The recovery depended considerably on the pH conditions. A small percentage of NaH_2PO_4 was used to keep the mixture slightly acidic (pH ca. 4.5−5.5). The NaH_2PO_4 was added after the first portion of the sodium sulfate because if a solution of NaH_2PO_4 was formed first, the absorption of the water by Na_2SO_4 would not be efficient. It was also important to prevent the Na_2SO_4 mixture from becoming too warm, since the decahydrate of this salt is known to melt and lose water at 32° C. A temperature near 25° C was satisfactory.

As with many dry foods, both tortilla chips and taco shells show very low concentrations of volatiles for the dry material. During the process of chewing, volatiles are released when the product comes in contact with saliva in the mouth. For this study an equal weight of water was added to these dry products during the blending process to approximate the conditions in the mouth.

Probable Origin of DHF. The highest concentrations of DHF were found in the products, which during their manufacture are heated well above 100° C, such as the oil-fried tortilla chips and taco shells and the canned sweet corn, which are heated to sterilization temperatures during canning.

Schieberle (1992), in relation to popcorn, bread, etc. volatiles, conducted a thorough study of the mechanism of the formation of DHF and concluded that “in heat-processed foods containing hexoses furaneol (DHF) will always be formed”. He also isolated a low molecular weight fraction from an aqueous extract of corn flour (which was shown to contain relatively high amounts of the C6 sugars glucose and fructose) and found that this fraction gave relatively low amounts of DHF if heated in water solution at 100° and 150° C but gave much larger amounts when heated in the dry state. This could explain the formation of DHF in the dry tortilla chips and taco shells and its absence in the relatively moist tortilla. The formation in canned sweet corn may result from decomposition of sugar phosphates, which Schieberle (1992) showed was a more likely mechanism with aqueous systems. Canned sweet corn, however, also contains added sugar. This fact could be another reason (besides the higher canning temperatures) for the larger amounts of DHF found in the canned products.

The use of calcium hydroxide in the normal preparation of tortilla flour may have an adverse effect on the presence of DHF in tortillas because it is known that DHF is less stable under alkaline conditions (Hirvi et al., 1980).

Probable Contribution to Aroma. The threshold of DHF determined previously at the authors' laboratory (Buttery et al., 1995) was 20−60 μg/kg in water solution depending on the pH. This indicates that the concentration of DHF in canned sweet corn would be ca. 5−10 times its threshold and it very probably contributes to the canned corn flavor and aroma, but it is only at a borderline concentration in the cooked fresh and frozen corn. The concentrations of DHF in tortilla chips and taco shells are also reasonably well above the threshold in water solution, but the medium involved in these oil-cooked foods is more complex. DHF does not seem to be released from these foods until they come into contact with moisture such as saliva as they are placed in the mouth. Because oil does not have a high affinity for the polar DHF, it seems likely that its concentration in the vapor in the mouth would probably be enough for it to contribute. DHF possesses a sweet aroma character that is important in fruits, but it may also enhance the flavor of some of these corn products.

The concentration of maltol also found in tortilla chips and taco shells was below its threshold in water (2500

μg/kg), and it seems unlikely to contribute to the odor and flavor of these products.

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