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Received for review July 5, 1985. Accepted November 27, 1985. This work was supported by the Swedish Board for Technical Development.

Products Identified from Photosensitized Oxidation of Selected Furanoid Flavor Compounds

Tony A. Mensah,* Chi-Tang Ho, and Stephen S. Chang

Singlet oxygen was generated photochemically and used to oxidize furfural, 2-ethylfuran, furfuryl acetate, and furfurylacetone. Major products were identified and reaction pathways were proposed. In all reactions, singlet oxygen adds into the furan ring by 1,4-cycloaddition to form an unstable ozonide. This then reacts with the solvent and rearranges to form the identified products. The exocyclic double bond of furfurylacetone does not appear to be involved in the reaction.

INTRODUCTION

Furfural occurs naturally in essential oils, roasted coffee, and rum (Furia and Bellanca, 1975). Maga (1979) reviewed the extensive occurrence of this and many other furanoid flavor compounds in such varied foods as alcoholic and nonalcoholic beverages, fruits, meat and poultry products, milk products, oil seed products, and vegetables.

Many of these foods contain photosensitizers like chlorophyll and hemoglobin that can generate singlet oxygen (Clements et al., 1973). Singlet oxygen thus generated may oxidize furanoid flavor compounds and affect the quality of food. First, the total flavor of the food may become unbalanced due to the loss of furanoid flavor compounds. More importantly, the oxidation products may impart undesirable flavor notes to the food.

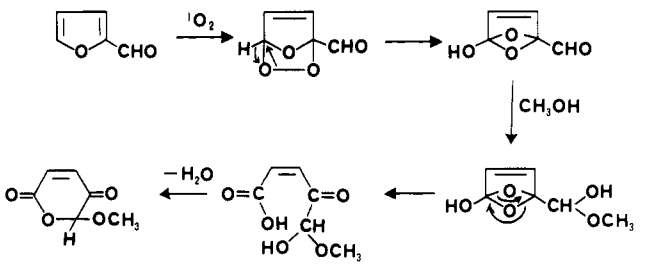
In this work, products from singlet oxygen reactions with selected furanoid flavor compounds were identified to propose reaction pathways.

EXPERIMENTAL SECTION

Materials. Reagent-grade furfural, furfuryl acetate, and ethylfuran were purchased from Aldrich Chemical Co. (Milwaukke, WI). Reagent-grade furfurylacetone was obtained from Pfaltz and Bauer, Inc. (Stamford, CT). Chlorophyll (99%) from spinach was purchased from Sigma Chemical Co. (St. Louis, MO). Methanol was UV spectroscopic grade (J. T. Baker Chemical Co., Phillipsburg, NJ).

Photosensitized Oxidation. Photosensitized oxygenation was carried out in a 150-mL reaction tube (4 cm i.d. × 20 cm) containing a given furanoid flavor compound and chlorophyll dissolved in methanol at 10^{-2} and 10^{-4} M concentrations, respectively. The tube was suspended in a trough of ice-cold water. Oxygen was bubbled through the solution at a flow rate of 30 mL/min under illumination from two 150-W lamps placed about 5 cm from reaction tube. The reaction was stopped after 60 min, and the solution was concentrated 10-fold by vacuum distillation. The reaction conditions were chosen to ensure adequate formation of products for NMR and/or GC-MS identification (Mensah, 1984).

Scheme I. Furfural Reaction Pathway



GC-MS Analysis. The concentrated samples were analyzed by GC-MS using a Finnigan 3300 mass spectrometer coupled with a Varian 3700 gas chromatograph. The GC was fitted with a 30 m × 0.32 mm i.d., 1-μm film, DB-1 fused silica capillary column (J&W Scientific, Inc., Rancho Cordova, CA). The column oven temperature was held at 100 °C for 1 min and then programmed to 300 °C at 8 °C/min. Mass spectra were obtained at 70 eV and a source temperature of 200 °C.

Proton NMR Analysis. A packed 10% OV-17 column (12 ft × $^1/_8$ in. o.d.) was used to collect major peaks from a Hewlett-Packard 5700 gas chromatograph for NMR determination. The peaks were dissolved in $CFCl_3$ and identified at ambient temperature on a Varian SL-100 NMR spectrometer at 40 rps using 1500-Hz sweep width and 3-s sweep time.

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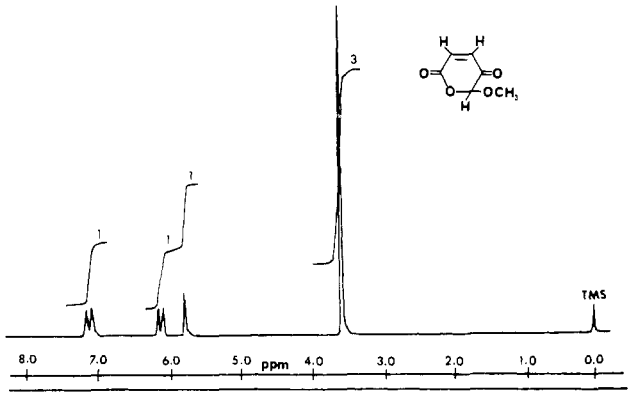


Figure 1. NMR spectrum of furfural photodecomposition products.

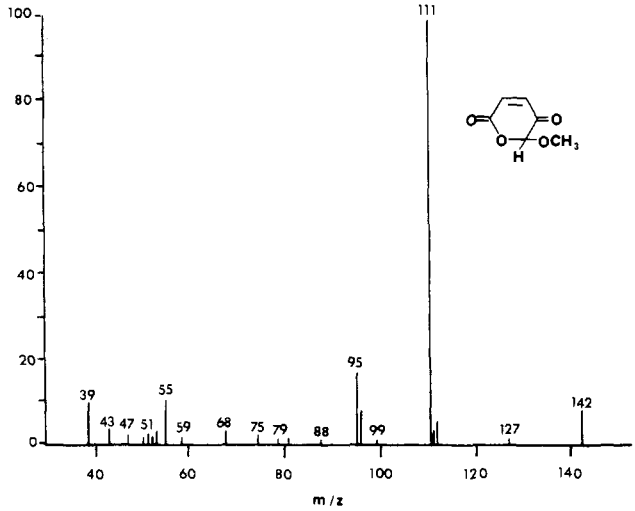


Figure 2. Mass spectrum of furfural photodecomposition products.

RESULTS AND DISCUSSION

Furfural Reaction. Gas chromatographic analysis of photooxidized furfural solution showed one major product. The NMR spectrum of this product is shown in Figure 1. There was no aldehydic proton signal. This suggests a reaction pathway involving the aldehydic group. The singlet at δ 3.4 suggests a methyl group attached to an ether carbon. The two doublets represent two vinylic protons. The more deshielded proton (δ 5.8) is closest to the ether oxygen of the α,β-unsaturated lactone (4-oxo-5-methoxy-2-penten-5-olide) shown in Figure 1. The mass spectrum of this photodecomposition product is shown in Figure 2. The base peak corresponds to the loss of a methoxy group from the parent ion.

As shown in Scheme I, 4-oxo-5-methoxy-2-penten-5-olide is formed by initial 1,4-cycloaddition of singlet oxygen onto the furan ring. The ozonide thus formed undergoes ring expansion, after reaction with the solvent, methanol, to produce the identified α,β-unsaturated δ-lactone.

2-Ethylfuran Reaction. Like the furfural reaction, 2-ethylfuran reaction showed one major gas chromatographic peak. Figures 3 and 4 show its NMR and mass spectra, respectively. The triplet and quartet signals in Figure 3 represent the methyl and methylene protons, respectively, of the ethyl group. The singlet at δ 3.0 is due to the three methoxy protons. Two vinylic protons appear as doublets. The one closest to the ring oxygen is more deshielded and appears at δ 7.0. This photodecomposition product of 2-ethylfuran is therefore identified as 5-ethyl-5-methoxy-2(5*H*)-furanone. The parent ion of this identified γ-lactone is absent from the mass spectrum

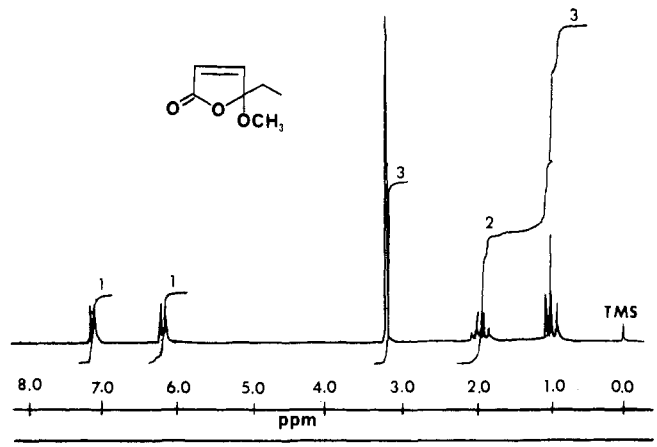


Figure 3. NMR spectrum of ethylfuran photodecomposition products.

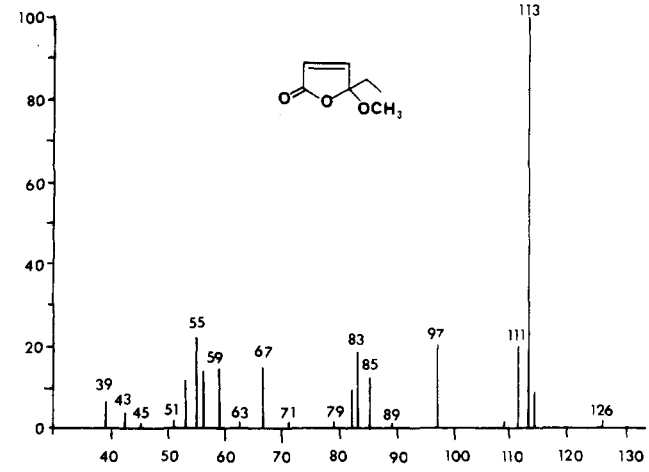
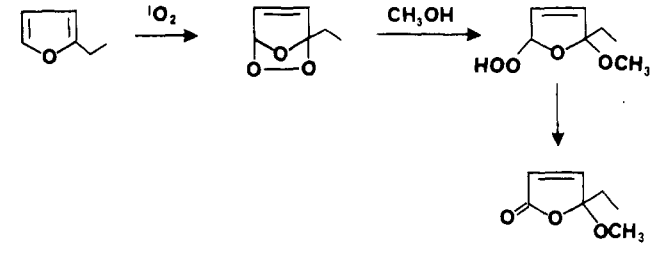


Figure 4. Mass spectrum of ethylfuran photodecomposition products.

Scheme II. 2-Ethylfuran Reaction Pathway



(Figure 4) due to the rapid loss of the ethyl group to form the ion of base peak at m/z 113. The other major fragmentation ion at m/z 111 is formed from the loss of methoxy group.

Scheme II summarizes the pathway for the formation of the identified α,β-unsaturated γ-lactone.

Furfuryl Acetate Reaction. Two product peaks were observed in the gas chromatogram of photooxidized furfuryl acetate solution. One was identified as acetic acid, which may be a solvolysis product rather than a photooxidation product of furfuryl acetate.

The other photodecomposition product was identified from the mass spectral data (Figure 5) as 5-methoxy-5-(acetoxymethyl)-2(5*H*)-furanone. Fragmentation of the acetoxymethyl group on C-5 of an unstable parent (m/z 186) ion produced the three major peaks in the mass spectrum. Thus, ion m/z 43 corresponds to the acetyl ion and the acetoxy ion explains the m/z 59 peak. The base peak (m/z 113) is due to the complete loss of the acetoxymethyl group.

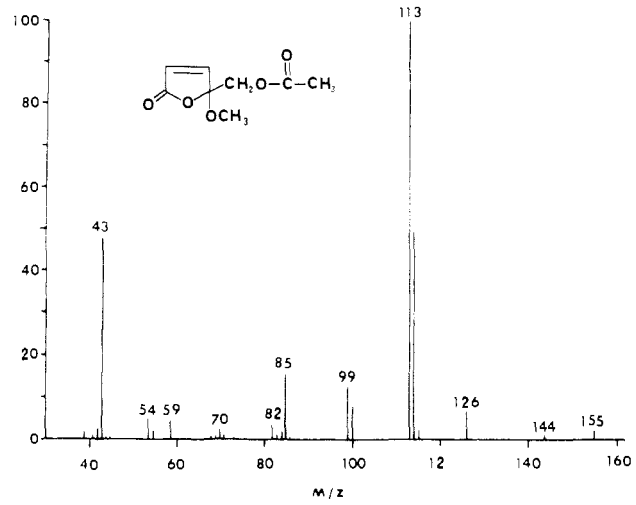


Figure 5. Mass spectrum of furfuryl acetate photodecomposition products.

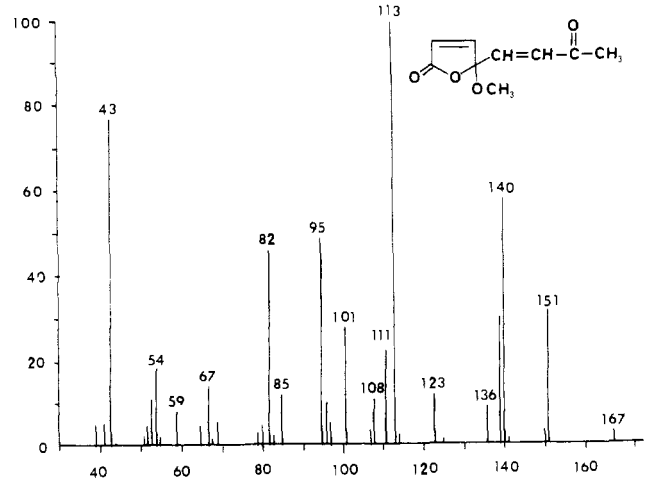


Figure 6. Mass spectrum of furfurylacetone photodecomposition products.

Pathway for the formation of this, α,β-unsaturated γ-lactone is similar to that shown in Scheme II for ethylfuran.

Furfurylacetone Reaction. Furfurylacetone is an interesting reactant for the photooxidation reaction since it contains an exocyclic double bond in addition to the furan ring double bonds. Conceptionally, singlet oxygen could undergo 1,2-cycloaddition onto the exocyclic double bond to produce dicarbonyl compounds without involving the furan ring.

A gas chromatogram of the photooxidized furfurylacetone solution showed one product peak. The mass spectrum (Figure 6) suggests it to be 5-methoxy-5-(but-1-en-3-one)-2(5*H*)-furan, an α,β-unsaturated γ-lactone. Again, the unstable parent ion was not observed. Some of the identified peaks included acetyl ion (m/z 43). Simultaneous loss of methoxy and but-1-en-3-one groups on C-5 produces ion m/z 82. Ion at m/z 151 is formed from the loss of the methoxy group of the parent ion. Like the mass spectra of the photodecomposition products of ethylfuran and furfuryl acetate, the base peak (m/z 113) in this spectrum is due to the loss of but-1-en-3-one group.

Again, the data suggest an α,β-unsaturated γ-lactone formed by similar reaction pathways as shown in Scheme II. This photooxidation product does not suggest the involvement of the exocyclic double bond in the reaction.

Discussion. Our results show that photosensitized oxidation of furanoid flavor compounds in methanol proceed via 1,4-cycloaddition of singlet oxygen onto the conjugated ring double bonds to form an unstable ozonide. In the case of furfural, the ozonide undergoes intramolecular proton transfer and then reacts with the solvent to form a hemiacetal. This hemiacetal forms an α,β-unsaturated δ-lactone by ring expansion. Ozonides from the other furanoid compounds studied undergo solvolysis to form methoxy hydroperoxides that rearrange, at room temperature and above, to produce α,β-unsaturated γ-lactones.

Similar reaction pathways will be expected in other alcoholic solvents like ethanol. However, reactions in nonalcoholic solvents may show different pathways leading from the unstable ozonide to product formation.

These products can be formed in alcoholic beverages containing furanoid flavor compounds. In fact, the literature contains many examples of α,β-unsaturated γ- and δ-lactones identified in the aromas of various foods like raspberries, roasted filberts, milk, fried onions, roasted coffee, beer, and many others (Maga, 1976; Vernin, 1982). Most of these foods contain dye sensitizers and significant levels of furan compounds that, as suggested above, may undergo photosensitized oxidation to produce α,β-unsaturated γ- and δ-lactones. Thus, a possible connection may exist via photosensitized oxygenation, between furanoid flavor compounds and α,β-unsaturated lactones in foods.

ACKNOWLEDGMENT

New Jersey Agricultural Experiment Station Publication No. D-10501-1-85 supported by state funds and General Foods Corp. This work is part of a Ph.D. thesis written by T.A.M.. We are grateful to Ron Belanger for his analytical help on the MS analysis. We thank Joan B. Shumsky for her secretarial aid.

Registry No. Furfural, 98-01-1; 2-ethylfuran, 3208-16-0; furfuryl acetate, 623-17-6; furfurylacetone, 699-17-2; 2-methoxy-3,6(2*H*)-pyrandione, 99798-63-7; 5-ethyl-5-methoxy-2(5*H*)-furanone, 86799-55-5; 5-methoxy-5-(acetoxymethyl)-2(5*H*)-furanone, 99798-64-8; 5-methoxy-5-(but-1-en-3-one)-2(5*H*)-furan, 99798-65-9.

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Received for review July 26, 1985. Accepted November 15, 1985.