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Journal of FOOD PROCESSING and PRESERVATION

Edited by
T. P. LABUZA

FOOD & NUTRITION PRESS, INC.
WESTPORT, CONNECTICUT 06880
USA

VOLUME 7, NUMBER 2 1983

JOURNAL OF FOOD PROCESSING AND PRESERVATION

All articles for publication and inquiries regarding publication should be sent to Prof. T. P. Labuza, University Minnesota, Department of Food Science and Nutrition, St. Paul, MN 55108 USA.

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One volume of four issues will be published annually. The price for Volume 7 is $65.00, which includes postage to U.S., Canada, and Mexico. Subscriptions to other countries are $77.00 per year via surface mail and $85.00 per year via airmail.

Subscriptions for individuals for their own personal use are $45.00 for Volume 7, which includes postage to U.S., Canada, and Mexico. Personal subscriptions to other countries are $57.00 per year via surface mail, and $65.00 per year via airmail. Subscriptions for individuals should be sent direct to the publisher and marked for personal use.

The *Journal of Food Processing and Preservation* is listed in *Current Contents/Agriculture, Biology & Environmental Sciences (CC/AB).*

The *Journal of Food Processing and Preservation* (ISSN: 0149-6085) is published quarterly by Food & Nutrition Press, Inc.—Office of Publication is 155 Post Road East, Suite 6, Westport, Connecticut 06880 USA. (Current Issue is June 1983).

Second class postage paid at Westport, CT 06880.

POSTMASTER: Send address changes to Food & Nutrition Press, Inc., 155 Post Road East, Suite 6, Westport, CT 06880.

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WESTPORT, CONNECTICUT 06880 USA

Food & Nutrition Press, Inc.
Westport, Connecticut USA

ISSN: 0145-8892

Printed in the United States of America

CONTENTS

DIRECT GAS SULFURING OF FRUITS FOR DRYING TO REDUCE AIR POLLUTION

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Received for Publication January 17, 1983
Accepted for Publication March 12, 1983

ABSTRACT

In using direct gas injection, less sulfur dioxide was wasted than in burning; 33-84% being absorbed by pears, peaches, and apricots compared to 5-34% by burning. Neither external fans nor heating of the gas before injection were necessary to obtain adequate dispersion throughout the house. An economical procedure was developed for modifying existing sulfur houses, so that bottled gas could be used. The operational cost of using this procedure should be similiar to the burning method. The direct gas sulfuring procedure provided better control and also minimized atmospheric air pollution.

INTRODUCTION

Sulfur dioxide has been used since antiquity in food processing and preservation. It has the unique property of retarding both enzymatic and nonemzymatic browning (Ingles 1966) and of providing antimicrobial protection at a low concentration (Skinner and Hugo 1976). It is also considered to be GRAS (U.S. Government 1978). In mammals, sulfur dioxide is enzymatically oxidized to the sulphate, and excreted (Gunnison 1981). The only known adverse nutritional effect is that it accelerates the degradation of thiamine; however, in turn it also retards the autooxidation of vitamin C.

Sulfur dioxide is currently the only material used commercially for retarding browning in dried cut fruits during processing and storage. All but a minor tonnage of dried apricots, peaches, pears and apples are treated in this way. These fruits are sulfured by exposing them to the fumes of burning sulfur (Mrak and Phaff 1949; Woollen 1969; von Loesecke 1955). The general procedure consists of putting the freshly cut fruit into a room where elemental sulfur is burned in an excess of oxygen to produce sulfur dioxide gas (SO_2). Since this burning requires

oxygen, vents are placed in the room. However, some of the gas also escapes into the atmosphere through these vents, thus creating a pollution problem. State and federal groups have recently set stringent limits for the concentration of certain gases in atmospheric air, and one of these gases is sulfur dioxide. Because of this, a low emission sulfuring procedure is needed.

Two major ways of attacking this problem seem to exist. One is to install a SO_2 scrubber on the existing chamber. The other is to develop a new system, as described in this report.

MATERIALS AND METHODS

The inside of a 2 by 2 by 4.5 m commercial sulfur house was sprayed with a foam insulation material to make it essentially gas tight. The conventional door was removed, and the front opening was covered with a sheet of 4 mil polyethylene film.

The film was nailed at the top and rolled up until the house had been loaded with fruit, at which time it was lowered and fastened on the sides with a "zip lock" type seal where the film edge was forced into a metal groove and held there with a rubber tubing (Fig. 1). The bottom was sealed using either loose sand or sand in tubes.

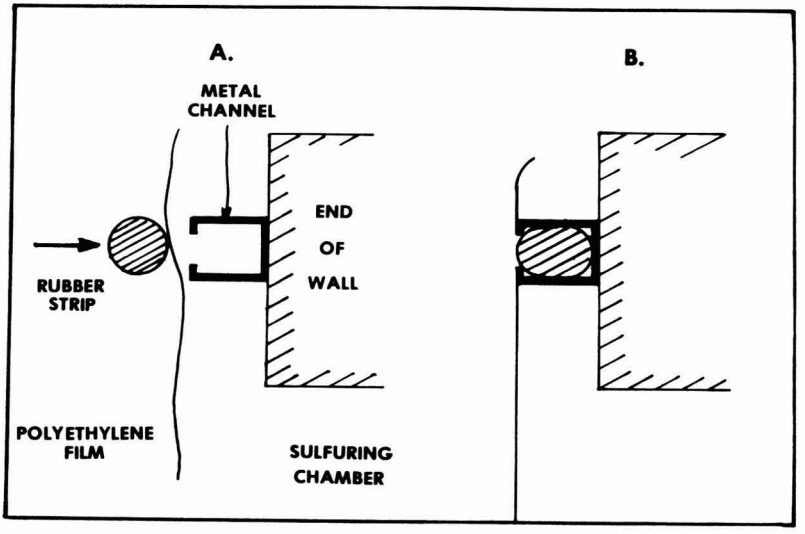

FIG. 1. TOP VIEW OF METHOD FOR ATTACHING FILM TO SIDE OF DOOR
A–before, B–after.

Sulfur dioxide gas was injected through a tube extending into the house, at a rate of approximately 16 kg/h. For preheating, the gas was routed through copper coils immersed in 96°C water. The gas cylinder was mounted on a scale so the amount of gas injected could be accurately determined.

Gas concentration inside the house was monitored by passing a sample of the atmosphere through a Pulsed Fluorescent Sulfur Dioxide Analyzer operating at a pressure of 0.5 kg/cm^2 and a gas flow of 0.29 m^3/h. The analyzer, which had a maximum reading of 5000 ppm, was calibrated with 4000 ppm standard gas.

Total and free SO_2 were determined by the method of Ponting and Johnson (1945). Appearance was measured objectively using a Hunter Color Difference Meter, where higher L, a, and b values indicate a higher degree of brightness, redness, and yellowness respectively.

The fruit consisted of Blenheim apricots, Fay Elberta peaches and Bartlet pears, which were picked the day before sulfuring. The fruit was usually commercially halved by cutting machines and spread cup-up on 0.9 × 1.8 m wooden trays. The trays were stacked on cars and loaded into the sulfuring chamber, which held four cars. Loading was usually done in the early morning. Quantities of fruit loaded into the house and the amount of gas injected or sulfur burned are indicated in Table 1.

Taste panel evaluation consisted of submitting the fruit to be tasted to a panel of 20 members at two different settings, using the Duo-Trio test (ASTM 68). In this procedure, the control comparison sample consisted of fruit held in frozen storage, which was compared to fruit stored at 32°C.

RESULTS AND DISCUSSION

A study was made to determine whether the heat evolved by burning the sulfur produced the "baked" appearance in the freshly sulfured fruit, in order to determine if a heating step would have to be incorporated when burning sulfur was not used. Thermocouples, placed at different locations inside the sulfur house and in the fruit, monitored temperatures during the 1.5 h burning of 8 kg of sulfur.

The air temperature peaked after 1.5 h at 69°C in the front of the chamber where the sulfur was being burned. When the burning stopped the air temperatures quickly dropped (Fig. 2), and continued to decrease for 8 h until the house was in temperature equilibrium. During this time fruit temperature increased by only 3°C, while the outside air

Table 1. Cut-fruit sulfur dioxide adsorption efficiency

Fruit		Burn Sulfuring					Bottled Gas Sulfuring			
				Absorbed By Fruit				Absorbed By Fruit		
Variety	Weight m Ton	Sulfur Burned Kg/m Ton	Sulfur Dioxide Produced kg/m Ton	ppm	kg/m Ton	Percent	Sulfur Dioxide Injected kg/m Ton	ppm	kg/m Ton	Percent
Apricot	1.8	4.3	8.6	2900	5.7	34	3.8	3180	3.2	84
Peach	2.5	2.9	5.8	1400	1.4	24	3.2	1990	1.2	62
Pear	1.8	12.6	25.2	1300	1.3	5	13.0	4200	8	33

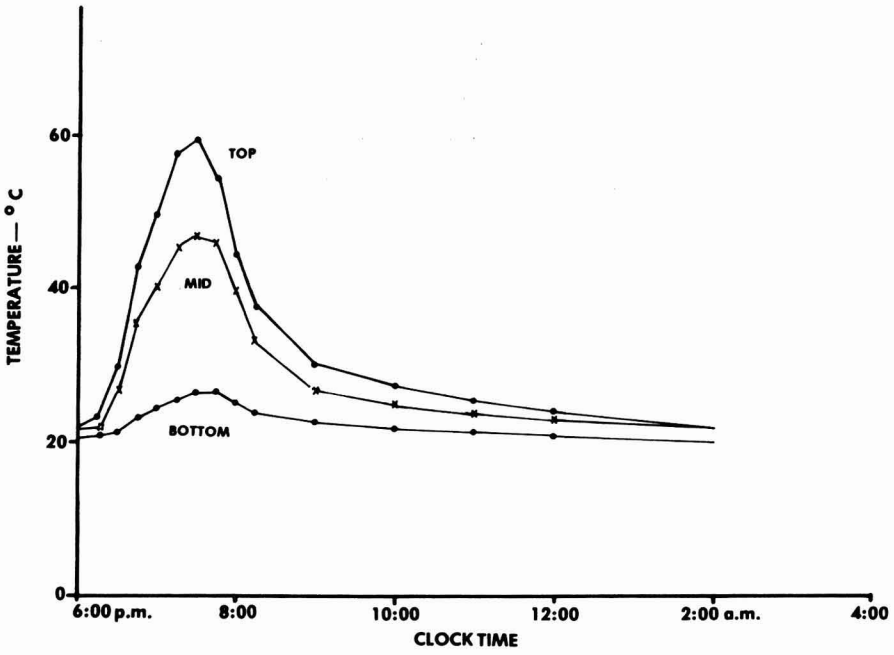

FIG. 2. AIR TEMPERATURE INSIDE HOUSE, MIDWAY TO BACK, AT TOP, MIDDLE AND BOTTOM LOCATIONS

temperature dropped from an initial 27°C down to 10°C. Granular and powdered sulfur had similar heat profiles, except that the former seemed to produce an earlier peak air temperature.

The greatest possible temperature increase was calculated to be 8°C, based on a heat value for sulfur of 290 kj (Washburn 1929). Therefore, no "baking" of the fruit occurred. The "baked" appearance of the freshly sulfured fruit is evidently caused by a sulfur dioxide initiated plasmolysis of the cells.

The absorption efficiency of the fruits varied considerably with sulfuring procedure. When sulfur dioxide is absorbed into the fresh fruit it dissociates depending on the pH medium. In these fruits, which are at pH 3.4-4.0, the main dissociation product is the bisulfite ion (HSO_3^-). Fruits sulfured by burning sulfur absorbed 5-34% of the gas produced (Table 1), whereas those treated with bottled SO_2 absorbed 33-84% of the gas. Unabsorbed sulfur dioxide represents atmospheric pollution.

Sulfur dioxide boils at −10°C; therefore, it has to be marketed in pressurized cylinders in the liquid form. The liquid, when withdrawn and brought to atmospheric pressure, absorbs heat, suggesting that the

atmospheric gas might need further heating to obtain adequate distribution within the sulfuring chamber.

Analysis of Variance (Table 2) of the sulfur dioxide and color data indicated no significant difference in sulfur dioxide absorption, whether the gas was heated or not, except for a small difference in the hue "a" value. However, the significant "heating x car" interaction suggests that a small difference between the samples might be masked. Duncan's multiple range test showed no significant differences in sulfur dioxide content of fruit among cars when the gas was not heated, but significant differences when the gas was heated (Table 3). A significant difference in sulfur dioxide absorption and retention occurred with respect to tray position (Table 2). Fruit on the top trays contained about 10% more sulfur dioxide, and were lighter (slightly higher L value) than the rest.

Table 2. Effects of various operating parameters on the variability of sulfur dioxide absorption and color of sulfured peaches

		Mean Squares ($\times 10^2$)				
	Degrees	Sulfur Dioxide		Color		
Variable	Freedom	Total	Free	L	a	b
Heating of gas	1	147	189	0.0167	0.0882*	0.0105
Moisture content	1	103000*	150000*	18.74*	0.3200*	7.78*
Car location	3	65.9	227	0.2000*	0.0731*	0.0327
Position of trays	1	1360*	841*	0.1910	0.0181	0.0528
Heating × moisture	1	232	15.7	0.0095	0.0181	0.0021
Heating × car	3	317*	81.8	0.0213	0.0194	0.0193
Heating × position	1	24.0	0.01	0.0026	0.0061	0.0091
Moisture × car	3	82.1	147	0.0262	0.0427	0.0055
Moisture × position	1	55.4	3.07	0.0639	0.0421	0.0253
Car × position	3	115	289	0.0520	0.0261	0.0040

*Significantly different at 0.05% level

Table 3. Variability in sulfur dioxide content of sulfured peaches among cars (ppm)

Car	Gas Heated	Gas Not Heated
1	1461 a	1339 a
2	1300 b	1354 a
3	1254 b	1337 a
4	1377 a b	1386 a

Means with different letters within a column are significantly different at the 0.05 level (Duncan's Multiple Range Test)

There was no significant variability in sulfur dioxide absorption and retention for either method of sulfured fresh peach halves because of car location within the sulfur house (Table 4). Color differences showed no consistent trend. The small difference (±125 ppm SO_2) due to tray position further indicated that the two treatment procedures were equally effective.

Gas concentration increased beyond the 5000 ppm limit of the measuring instrument a few seconds after injection was initiated, but a matter of minutes was required during burn sulfuring (Fig. 3). From extrapolation it appears that a maximum gas concentration of 0.6 to 2% is reached. Dahlenburg (1976) reported sulfur dioxide concentrations of 1-3% in sulfur houses in Australia. Gas concentrations were lower when the gas was heated before injection, presumably due to greater leakage.

The tray of hand-cut apricots that was not sulfured until 24 h after cutting had a brownish appearance because of the enzymatic darkening on the cut surface. However, after this fruit was sulfured with the bottled gas and dried, it was not significantly different in color from the fruit that was sulfured immediately after cutting.

Covering the stacks of sulfured fruit with sheets of polyfilm immediately after removal from the sulfuring house retarded sulfur dioxide loss by reducing the gradient of SO_2 in the atmospheric adjacent to the fruit to that on the fruit surface.

There was no visual difference initially between fruits sulfured by the two procedures to equal SO_2 levels, however, reflectance "L" values were slightly higher (lighter) for products sulfured with bottled SO_2.

The processed and unprocessed fruits subjected to accelerated storage (32%) showed that SO_2 losses and darkening rates were not dependent on the sulfuring procedure (Fig. 4), however, SO_2 binding was. In peaches, 90% and 94% of the SO_2 respectively, was free

Table 4. Variability in total and free SO_2 content and color of direct gas sulfured peaches among cars immediately after treatment

Car	Sulfur Dioxide		Color			
	Total (ppm)	Free (ppm)	L	a		b
1	1754 a	1617 a	57.0 a	10.8 a	b	34.0 a
2	1789 a	1617 a	56.6 a	10.7 a	b	34.0 a
3	1755 a	1643 a	53.8 a	11.5 a		32.2 b
4	1730 a	1609 a	53.3 a	9.2	b	31.6 b

Means with same letters in the same columns are not significantly different at 0.05 (Duncan's Multiple Range Test)

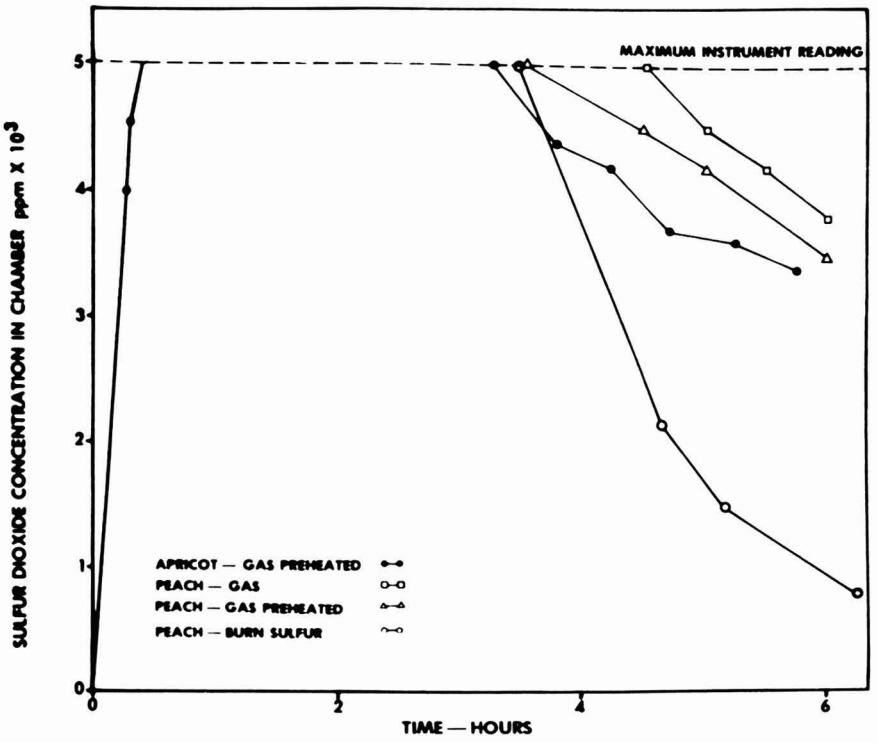

FIG. 3. SULFUR DIOXIDE GAS CONCENTRATION INSIDE THE SULFUR HOUSE DURING SULFURING OF FRUIT

immediately after burn and direct gas sulfuring. However, the burn and direct gas sulfured peaches contained 67% and 55% free SO_2 respectively, after drying. Also, the percentage of bound sulfur dioxide increased during storage. Taste panel evaluation of fruits sulfured by both procedures and stored for 3-6 months at 32°C indicated no significant effect of treatment on flavor, texture or aroma.

Economics

Operating sulfuring costs appear to be similiar for the two methods. Liquified sulfur dioxide costs about 36.5 cents per kg in bulk. Powdered sulfur for burning costs 38.7 cents per kg. One kg of burned sulfur produces two kg of sulfur dioxide; but, because of sulfur dioxide losses in this procedure, more than one kg of sulfur is required to produce two kg of effective SO_2 in the fruit. A higher initial cost would be incurred with the bottled gas procedure, since it would be necessary to have both a fairly gas tight house, and a gas distribution system.

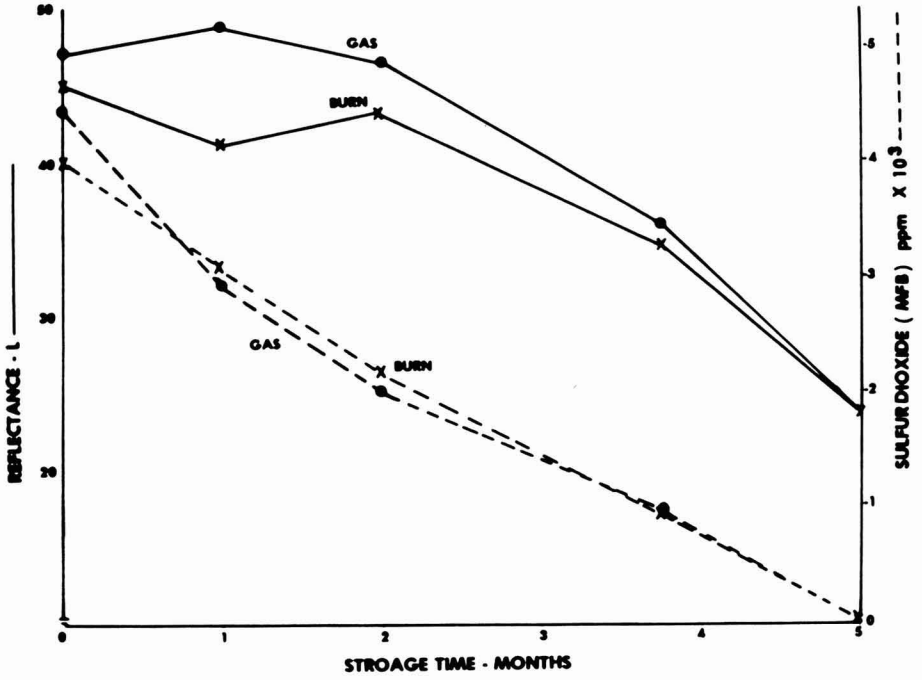

FIG. 4. SULFUR DIOXIDE AND COLOR CHANGES IN DRIED PEACHES DURING STORAGE AT 32°C

In conclusion, injection of the SO_2 gas directly into a sealed chamber containing fruit to be sulfured appears to be a viable alternative to burning sulfur. This procedure reduces sulfur dioxide emission resulting in more efficient use of the gas, safer and more pleasant working conditions for personnel, and reduced exposure of adjacent property and people. Dried product quality is equal to or better than that of products sulfured traditionally. This new procedure provides better control over the amount of sulfur dioxide absorbed by the fruit.

ACKNOWLEDGMENT

Appreciation is gratefully expressed to Dr. Bruce Mackey for biometric evaluation.

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A LABORATORY MICROWAVE STERILIZER AND ITS POSSIBLE APPLICATION TOWARD IMPROVING TEXTURE OF STERILIZED VEGETABLES[1]

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Received for Publication August 26, 1982
Accepted for Publication April 12, 1983

ABSTRACT

A microwave-permeable chamber was constructed for high temperature sterilization of foods in glass containers at overpressures up to 50 psig. Temperatures could be monitored satisfactorily in the microwave field using stainless steel shielded type T thermocouples if the metal sheath were grounded. Percent fracturability did not differ between potato samples sterilized by microwave energy (1000 W output) and steam. Extrapolation of kinetic data indicated that although fracturability retention is quite low at temperatures below 150°C (<15%), it should increase dramatically above 160°C (>60%). Verification of this will require a higher microwave output (>1000 W) than was available in these experiments.

INTRODUCTION

More than three decades ago, Jackson (1947) demonstrated distinct possibilities for the use of microwave energy as a rapid means of providing heat uniformly throughout a container of food, thereby achieving sterilization temperature after only a relatively short come-up time. Microwave heating appears to be the most promising and economically feasible means of achieving commercial sterility of large vegetable pieces, such as broccoli or asparagus spears, without inducing excessive softening. In addition to these obvious benefits, certain microwave applications in food processing have halved energy requirements and have reduced labor time and space needs by 75% (Smith 1977).

[1] Scientific Journal Series Paper No. 13,036 Minnesota Agricultural Experiment Station, St. Paul, MN 55108

Many comparisons of the effects of microwave versus conventional heating methods upon food product quality can be found in the literature. Most of these studies have been carried out using domestic microwave ovens whose heat distribution patterns are generally less uniform than those of industrial units. These comparisions have almost always ignored the kinetics of various quality changes during cooking. For example, Crespo & Ockerman (1977) claimed that the conventional oven is more effective than the microwave oven in inactivating bacteria in meat while cooking it to a final temperature of 75°C. Schrumph and Charley (1975) studied the textural properties of broccoli and carrots cooked conventionally (100°C for 12 and 20 min) and in a microwave oven (1600 W, 2450 MHz, for 5 and 8 min). These heating times were apparently chosen arbitrarily. Kylen *et al.* (1961) were unable to obtain a consistently superior product by either microwave or conventional cooking.

Bollman *et al.* (1948), Bowman *et al.* (1971), and Schrumph and Charley (1975) observed surface dehydration, tough texture and extensive weight loss in vegetable samples microwave-cooked at atmospheric pressure. Copson (1962), Goldblith and Pace (1967), Fenton (1957), and Armbruster and Haefele (1975) all suggested that foods be covered during microwave cooking in order to retain steam, minimize uneven heating and reduce quality and nutritional losses (thiamin and ascorbic acid).

These studies were all similar in that (1) all comparisons were flawed by ignoring the kinetics of various food quality changes and (2) all experiments were conducted at atmospheric pressure and at temperatures lower than those normally used for sterilization. The studies were directed toward preparation of food for the table rather than toward long term preservation. Their conclusions, therefore, have only limited application toward studying effects of microwave sterilization (MS) upon food quality.

In general, improved color, flavor, and texture can be expected for high-temperature short-time (HTST) processed products versus low-temperature long-time (LTLT) processed products, if comparisons are made on a fair basis. Decareau (1968) provided a historical perspective for MS. Landy (1965) and Long *et al.* (1966) discussed methodology and packaging materials for MS. Jeppson and Harper (1967) suggested a method for continuous MS using pressure to maintain a hydrostatic head. In 1971, Kenyon *et al.* demonstrated MS at 121°C; it is unfortunate that HTST treatment by MS was not explored further in their experiments. The U.S. Army Natick Laboratories successfully designed, constructed and tested a unit for continuous microwave sterili-

zation of foods packaged in plastic pouches (Ayoub *et al.* 1974). Linke (1976) conducted a study in which fruit and vegetable pastes were sterilized using a continuous HTST microwave process.

This work was undertaken to design and construct a microwave sterilizer suitable for laboratory use in an environmental microwave oven similar to that of Hung, Davis and Gordon (Hung, 1980; Wei *et al.* 1981) and to evaluate the possibility of using pressurized microwave heating to improve the texture of shelf stable vegetable products. Potato was chosen as the experimental material.

MATERIALS AND METHODS

Potatoes

Russet Burbank potatoes were cut into 2 × 2 cm cylindrical samples as described by Loh and Breene (1981).

Microwave Sterilizer

The microwave sterilizer (Fig. 1) consists of 3 major sections, namely, a microwave generation and transmission system, a microwave cavity and a sterilization chamber. Figure 2 is a schematic of the whole system with individual components identified.

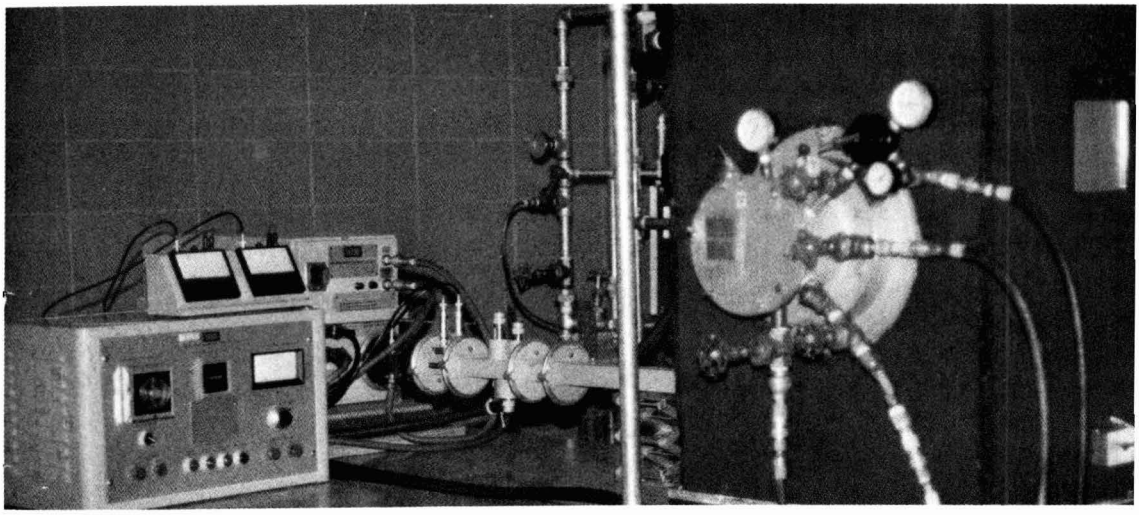


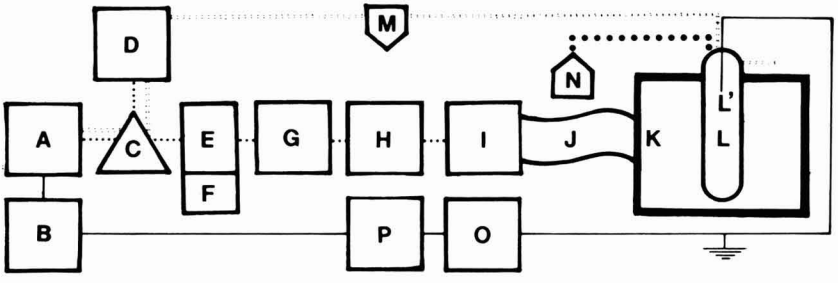
FIG. 1. OVERALL VIEW OF THE HUNG-DAVIS-GORDON HYBRID OVEN WITH STERILIZING CHAMBER IN PLACE

Microwave Cavity

The microwave cavity was built and described in detail by Hung (1980). It was constructed from 6.4 mm thick heavy aluminum sheets. The external dimensions are 61 × 61 × 91 cm. It was separated with 2 sheets of 2.2 cm thick perforated aluminum (hole diameter, 3.2 mm) to give a 61 × 61 × 61 cm usable space inside the cavity. The microwaves enter the cavity through a 7.2 × 3.4 cm rectangular hole at the center of a side wall. A cavity opening (30.5 cm diameter) was designed to allow the insertion of the sterilization chamber which is secured by 12 equally-spaced screws on the cavity wall.

Microwave Sterilization Chamber

Figure 3 shows the chamber. Its main body was made from a 61 cm long cylindrical fiberglass-reinforced epoxy tube which is commercially available (A.O. Smith Inland Inc., Little Rock, Arkansas). This tube has a pressure rating of 150 psig and a temperature tolerance of 165°C. Its low lossiness, high mechanical strength and high temperature tolerance have been proven safe by Kenyon (1971). Detailed specifications of the power unit, sterilization chamber and its accessories can be found elsewhere (Loh 1979; Hung 1980).



A microwave generator
B microwave power control
C three port circulator
D dummy load
E directional control
F dual power monitor
G triple stub tuner
H test tube coupler
I slotted waveguide
J flexible waveguide
K microwave cavity
L sterilization chamber
L' temperature sensor
M cooling water control
N air pressure control
O temperature recorder
P on/off relay

FIG. 2. SCHEMATIC OF THE MICROWAVE UNIT—MODIFIED AFTER HUNG (1980)

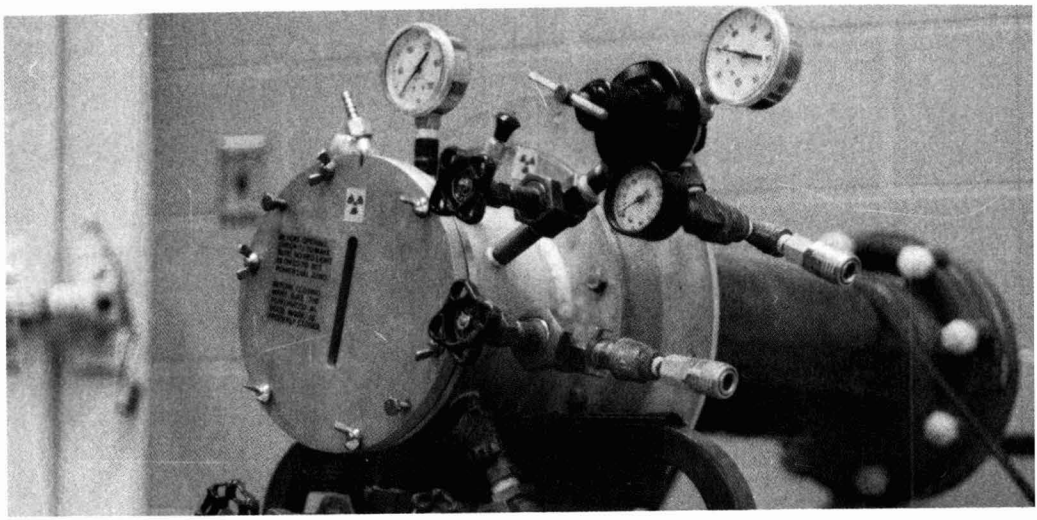


FIG. 3. FRONT VIEW OF THE STERILIZING CHAMBERFrom top (clockwise): pressure guage, safety valve, pressure regulator, overflow valve, cooling water inlet and drain valve. Thermocouple inlet is not visible.

Pressurizing, water-cooling and temperature measuring systems were attached to the portion of the sterilization chamber outside the microwave cavity. A perforated aluminum door prevents microwaves from escaping. The aluminum door was secured during operation by 8 bolts with wing nuts. A glass window at the center of the door was designed to permit checking of the water level. The built-in pressurizing system was capable of providing a predetermined overpressure up to 50 psig. A quick pressure releasing valve and safety valve set at 60 psig were also attached.

The water cooling system provided 70 psig water pressure which permitted rapid flow of 15°C tap water into the chamber to cool the sample at the termination of the heating cycle while remaining under the overriding air pressure. Fill time was less than 0.5 min. The cold water flowed into the chamber from the bottom under a 6.4 mm thick bottom stage (aluminum outside the cavity; nylon inside the cavity with six 1.9 cm diameter holes at one end) and circulated back through the chamber above the stage. Overflow and drain valves were also installed to properly control the cooling process. A check valve in the water line at the entrance to the chamber prevented backflow of water. Pressure gauges and regulators were used to monitor the pressurizing system. A model 8000M dual set point on/off relay (Omega Engineering, Inc., Stanford, Connecticut) was used as a safety device to

automatically turn the microwave transmission system on or off according to the pre-set temperature so that overheating or burning of the sample as well as explosion of the container could be avoided.

Containers and Temperature Sensor

Rigid glass containers were chosen for this study in order to explore the possibility of using existing glass jar filling lines. A microwave-permeable nylon screw cap was used to replace the traditional metal (microwave reflecting) one. Figure 4 illustrates the container and the design allowing the thermocouple to be placed into the container, while at the same time resisting pressure exerted from either side of the cap top. This container should provide better protection against mechanical stress, gas permeation and edge overheating problems (Ayoub *et al.* 1974) than pouches. Stainless steel shielded type T thermocouples were used; the metal sheaths were grounded (Fig. 4) to prevent heating, arcing and material breakdown at output wattages higher than 200 W. Each thermocouple consisted of an ungrounded junction sealed with melted polyester. Ideally, an ungrounded metal-sheathed thermocouple with the sheath grounded should be used. At the time of this experi-

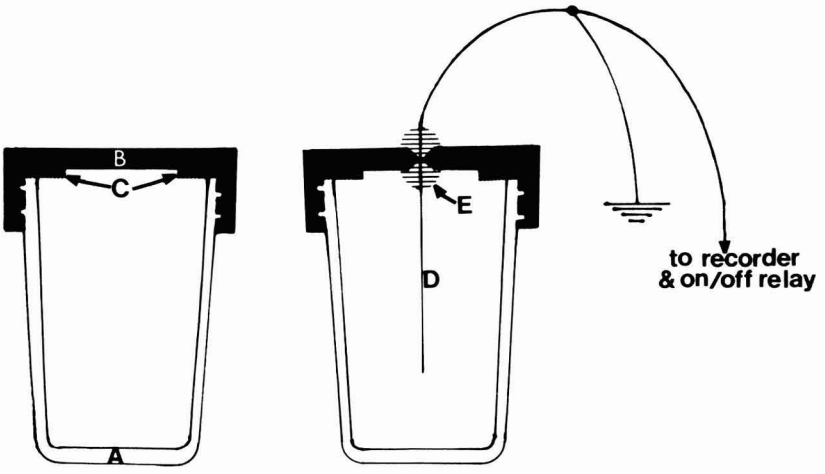


FIG. 4. CONTAINER AND TEMPERATURE SENSOR

mentation, however, such thermocouples were not conveniently available in a length sufficient (approximately 0.9 to 1.2 m) to place the plastic connector outside the microwave cavity.

Thermocouple Calibration

The described thermocouples were calibrated to ensure that correct temperatures were recorded inside the microwave cavity. This was accomplished by first measuring the boiling temperatures of aqueous glycerol solutions with a mercury thermometer outside the cavity and then recording the boiling temperatures of identical solutions as indicated by thermocouples inside the cavity at 200, 500 and 1000 W microwave power. The calibration curves are shown in Fig. 5. Temperatures recorded by thermocouple were consistently higher than actual temperatures and this deviation increased with increasing microwave power wattage.

Conventional Retort Sterilization

One cylindrical potato sample (2 × 2 cm) was placed in a standard container which was then filled with water to a total volume of 150 ml and sterilized in a miniature vertical still retort having 57 liter capacity.

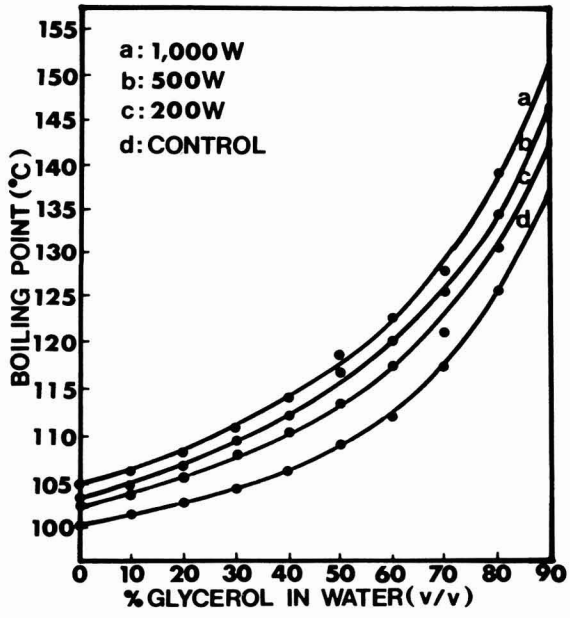


FIG. 5. CALIBRATION CURVES FOR THERMOCOUPLE ACCORDING TO THE BOILING POINTS OF GLYCEROL/WATER MIXTURES

A thermocouple was positioned at the geometric center of the cylinder at the slowest heating point (cold spot). The heating time required to achieve a "12 D" (or $F_0 = 3$ min) process was determined according to the general method of Bigelow *et al.* (1920). Heating for 38.7 min (retort temperature: 121.1°C) followed by immediate cooling to below 25°C was equivalent to a "12 D" process. This procedure was replicated four times to construct an average heating/cooling curve.

Microwave Sterilization

One cylindrical potato sample (2 × 2 cm) was placed in a standard container with 5 ml water. A thermocouple was positioned in each potato sample at the cold spot. Two containers were processed at a time at the center position of the sterilization chamber. Air overpressure was set at 50 psig to prevent lids from being blown off the containers. Heating/cooling curves (composite of four replicate runs) were constructed from corrected temperatures obtained using the calibration curves in Fig. 5. By using the same general method (Bigelow *et al.* 1920), the heating time equivalent to a "12 D" process was determined to be 10.2 min at 1000 W output.

Objective Texture (Fracturability)

The General Foods Texture Profile Analysis parameter of fracturability was determined on the Instron TM-M at a crosshead speed of 1 cm min^{-1} as described earlier (Loh and Breene 1981). Percent retention of fracturability after sterilization and cooling was based on mean values for 8 replicate determinations for heated as well as for control samples.

RESULTS AND DISCUSSION

Temperature Measurement

One of the major accomplishments of this work was the establishment of a reliable and reproducible temperature monitoring system.

Difficulties in accurate temperature measurement at relatively high microwave power have been a major deterrent to the application of microwave energy in the food industry. Thermocouples or thermistors are probably still the most simple and convenient temperature measurement sensors. Other temperature sensing systems for use in microwave fields, which include a glass thermometer filled with low lossiness

materials (e.g., dioxane and benzene) (Copson 1962), a thermometer employing a manometer to measure the pressure change (Copson 1973), and a nonperturbing sensor employing a liquid crystal/optic fiber system (Rozzel *et al.* 1974), are expensive.

The heating effect caused by concentration of the electric field around the thermocouple wire or metal sheath produces a large error (Watanabe *et al.* 1974; and Ma 1976) even when measurement is made after the microwave power switch has been turned off. Watanabe *et al.* (1974) presented methods for preventing such heating by using a metal or low dielectric loss material (polyphenylene oxide) as a shield for the temperature sensing elements. Ma and Arsem (1975) investigated the relative magnitude of the heating effect on shielded thermocouples. They found the major heating effect to be due to radiative heating. Due to the high power levels involved in microwave sterilization, the application of their techniques to temperature measurements may require considerable modification.

Figure 5 shows that as wattage was increased in this study, the deviation and the magnitude of the temperature readings also increased. However, the temperature as sensed by a thermocouple having its sheath grounded was rather stable ($\pm 1°C$, only if the same thermocouple was used) and consistent at a given condition. On the other hand, a similar thermocouple having its sheath ungrounded produced hundreds of degrees of variation at a given condition, thus rendering it completely useless in a high wattage situation.

The more complete the sealing of an individual thermocouple, the better was its overall performance; therefore, thermocouples must be thoroughly tested before using. Ungrounded metal-sealed thermocouples with sheath grounded should be used in the future. It is recommended that the fluoroptic thermometer with fiber optic probe (Luxtron, Mountain View, CA 94043) which recently became commercially available should be used to provide direct temperature measurement in a microwave field. The improved thermocouple-temperature measuring system used in the present investigations was satisfactory, however, for studying the texture changes occurring in vegetables during microwave sterilization.

Temperature Distribution in the MS Chamber

The field distribution inside the pressure chamber at 1000 W power output was surveyed by heating three 100 ml quantities of distilled water in standard containers located at three different zones inside the chamber (near each end and at the center) and then cooling them by

Figure 6. These results indicated that the microwave intensity was higher at the center than at the ends of the chamber. Therefore, only 2 containers located at the center of the pressure chamber were processed at a time.

Temperature Distribution Within Containers

Temperature readings at different locations within any specific container filled with water and heated at 1000 W were not significantly different, probably owing to convective currents.

Temperature Distribution Within Potato

Foods of the nonfluid type are most likely heated by conduction; therefore, localized heat generation and temperature are highly dependent on position because of the unevenness of the field distribution and power reduction due to penetration loss. Figure 7 shows heating and cooling curves for cylindrical potato samples (Russet Burbank) 3.3 cm in diameter and 4.0 cm high stood on end in the container and heated in the center of the chamber followed by cooling with cold tap water. In standard containers with 5 ml added water and for sterilization purposes, the reference point (cold spot) within the container for designing a thermal process is about 2±0.1 mm above the bottom of the cylindrical potato sample. This should apply also to other foods.

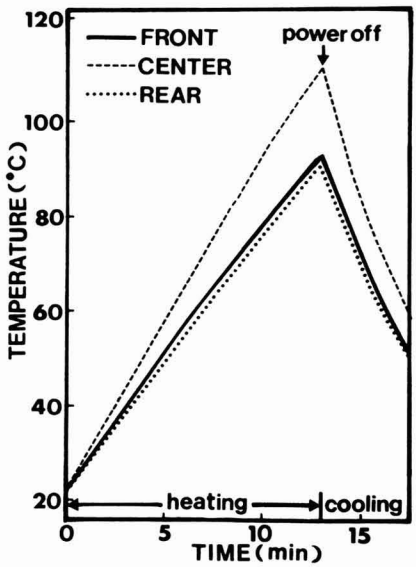


FIG. 6. INFLUENCE OF POSITION WITHIN THE MICROWAVE CAVITY UPON HEATING AND COOLING RATES OF WATER IN STANDARD CONTAINERS

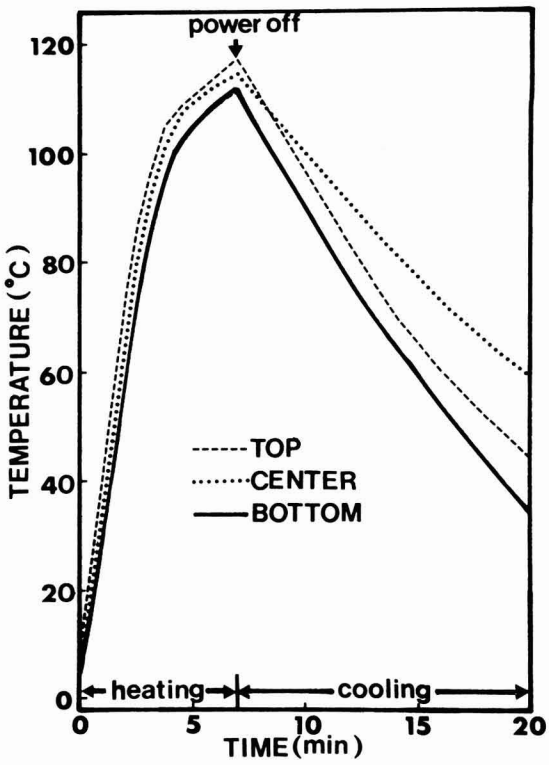


FIG. 7. INFLUENCE OF POSITION OF THE THERMOCOUPLE WITHIN A CYLINDRICAL (3.3 CM DIAMETER × 4 CM) POTATO SAMPLE UPON HEATING AND COOLING RATES

Water apparently either has a greater heat capacity than potato tissue or is less lossy than potato tissue, because it heated more slowly than potato tissue. Surface dehydration became quite serious even when the containers were tightly sealed and pressurized. The addition of 5 ml of water practically eliminated the drying problem, yet still maintained a high heating rate, since the added water quickly provided a moisture-saturated environment preventing moisture loss from samples.

Degree of Sterility

In order to make a fair comparison between the fracturability retentions of steam sterilized and microwave sterilized potato, the degree of sterility must be defined. For low acid foods, Esty and Meyer (1922) suggested an F value of 3.0 min with a D (121.1) value of 0.26 min and a Z value of 10°C giving an approximate 12 log reduction, or "12 D" process.

More research is needed to verify adequate sterilization for microwave-heated low acid foods. Published reports differ considerably as to the lethal effects of microwaves on various microorganisms. However, it is reasonable to assume that the lethal effect of microwaves in MS processes due to temperature alone can provide adequate assurance of product safety regardless of any possible radiation effect. An F value of 3.0 min at 121.1°C, a commonly used process standard, was chosen for this study to assure adequate sterility of processed samples. This is not only the most commonly used process standard but it also provides a great margin of safety at processing temperatures above 121.1°C.

Microwave Versus Steam Heating/Cooling Curves

Heating/cooling curves for microwave and steam sterilized potato samples are given in Fig. 8. For both methods the heating curves were very consistent among replicates, but the cooling curves were less reproducible. Temperature of the microwave-heated samples rose almost linearly at the initial stage. The heating curve broke at slightly above 100°C and showed a plateau before the temperature again rose at a slower rate than initially, presumably due to evaporation of the water. When water alone was heated under the same conditions, the curve did not exhibit the plateau, but there was a gradual decrease in the heating rate at slightly above 100°C. Further studies of the heat transfer properties of foodstuffs under high temperature (above 100°C) microwave heating are necessary to provide a valid explanation for this phenomenon.

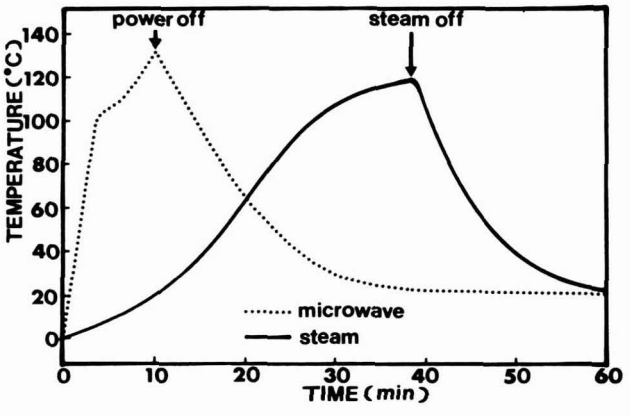


FIG. 8. HEATING/COOLING CURVES FOR CYLINDRICAL (2 × 2 CM) POTATO SAMPLES STERILIZED BY MICROWAVE AND STEAM HEATING

Influence of Heating Method on Fracturability

Final fracturability values for potato sterilized by the two methods were not significantly different ($p \leq 0.01$). Only 1.3% and 1.8% of the original fracturability remained after a "12 D" process in microwave and steam sterilized potato tissue, respectively. This suggests that the equilibrium texture was reached after those heat treatments (Loh and Breene 1981).

Fracturability loss in potato tissue appeared to take place more rapidly than spore inactivation at a given average processing temperature. Therefore, in spite of the greater Q_{10} of spore inactivation, rapid microwave heating will not improve fracturability retention in potato tissue unless a more rapid heating rate and higher heating temperature can be achieved by increasing the wattage of microwave output. The cooling rate after microwave heating can be increased by complete submersion of the solid potato sample in water within a container. However, this will involve a trade-off with heating rate which was observed to be slower at a greater water to solid sample ratio within a container.

The Q_{10} of fracturability loss (2.8) is approximately 3.5 times smaller than the Q_{10} of spore inactivation (10). However, the rate of fracturability loss is about 3–7 times greater than the rate of spore inactivation at 100°C. Calculations were based on D (100) values of 20-40 min for *Clostridium botulinum* spores (Perkins *et al.* 1975). As a consequence, if the food temperature can be brought up to 140, 150 and 160°C instantaneously the retained fracturability in potato after a "12 D" microwave process will be 10%, 15% and 60% of the initial fracturability, respectively. The advantages of HTST microwave sterilization of vegetable material in improving fracturability retention are slight and likely not practically significant below 150°C, but should increase drastically above 160°C.

CONCLUSIONS

A sterilization chamber for microwave processing of foods at high temperatures can be constructed of readily available stock materials. Stainless steel shielded type T thermocouples are satisfactory for temperature monitoring in a microwave field provided it is properly calibrated and the sheath is grounded. Although improvement of fracturability retention in potato tissue could not be attained in a "12 D" process limited to microwave heating at 1000 W power output and cooling with 15°C water, considerable improvement appears possible at

higher wattages and with more rapid cooling. Similar pressurized microwave heating systems may also be useful to "pasteurize" chunky acid vegetables such as pickled cucumbers without excessive damage to textural quality.

ACKNOWLEDGMENTS

We are grateful to Drs. E.A. Davis, J. Gordon, and C.C. Hung for their assistance and cooperation in incorporating the pressure sterilization chamber into the overall design of their experimental microwave oven and for allowing us to use it in their oven. We also thank Mr. Jack Madigan of the University of Minnesota Electrical Shop for his kind advice and assistance.

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SULPHUR DIOXIDE AND CARBON MONOXIDE GAS TREATMENT OF APPLES FOR ENZYME INHIBITION PRIOR TO FREEZING

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Accepted for Publication April 27, 1983

ABSTRACT

The present most common method for inactivating enzymes prior to freezing is thermal blanching which is energy intensive, involves losses of nutrients and soluble solids and causes waste disposal problems. The feasibility of applying sulphur dioxide and carbon monoxide gases, as enzyme inhibitors, to apples prior to freezing was evaluated.

Using catalase and polyphenoloxidase, CO gas was found to be ineffective as an enzyme inhibitor. Treatment of apples with SO_2 was found to inhibit enzyme activity as effectively as thermal blanching. This inhibition was maintained during 195 days storage at −8 and −18°C. Losses in soluble solids were considerably lower than in blanched samples. Hunter color "b" values were different indicating that the SO_2 treated apples were yellower and the blanched ones greener. No significant sensoric preference was found for either sample after baking despite the obvious difference in soluble solids content and color. Residual SO_2 in apples could be reduced to below 50 ppm.

INTRODUCTION

All fruits and vegetables are blanched prior to freezing to inactivate enzymes which might result in off-flavor development and consequent quality changes. Blanching is carried out in hot water at 87-98°C or in steam. The time and temperature are regulated in such a manner that the detrimental enzymes are inactivated. After blanching, vegetables are quickly frozen. The disadvantages of this method include losses of soluble solids and nutrients, high energy costs and waste disposal problems. All of the above provoked interest to find new methods for enzyme inactivation which require less energy and losses of soluble solids.

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Journal of Food Processing and Preservation 7 (1983) 93-104.

A method that uses SO_2 and CO as bactericidal and enzymodcidal gases was tested by Kramer *et al.* (1980). The purpose was to replace thermal preservation energy consuming methods to obtain "fresh-like products." These authors showed substantial reduction in energy requirements and increase in retention of nutrients and solids.

The objective of this work was to test the feasibility of applying sulphur dioxide and carbon monoxide gases, as enzyme inhibitors, to apples prior to freezing and evaluate the product in comparison to thermally treated ones.

Materials

Apples of the Grand Alexander variety were obtained from the local market in Haifa, Israel.

Various fruits and vegetables: cauliflower, potatoes, apples, apricots and peaches.

Packaging Materials used were low density polyethylene bags, 0.1 mm thick.

Gases employed were: (a) Sulphur dioxide gas (SO_2) 99.97% pure from Fluka AG, Buchs SG, Switzerland. (b) Carbon monoxide (CO) 99% pure from Galim-Gordon Gas Co., Tel Aviv, POB 1589.

Equipment

Vacuum sealing machine manufactured by Woodward Research Co. Inc. Model MO-VAC II with a chamber, in which vacuum is made by a Hyvac 14 vacuum pump from Cenco Inc., was used. A three way valve was installed in order to break the vacuum by the injection of any desired gas.

Gas chromatograph, manufactured by Becker, model 406, equipped with thermal conductivity detectors, was used for gas analyses. The column of oxygen and nitrogen separation was $6' \times 1/4''$ packed with molecular sieve 5A 60/80, and for CO_2 analysis–a $6' \times 1/4''$ packed with Porapack Q.

Methods

Hunter color measurements were determined on a Hunter Lab Color Difference Meter D25-2. The reference plate was light yellow, having the following values: L = 78.8, a = −1.7 and b = 23.8. The readings were made on apple puree (one part of apples was blended with five parts of water for one minute) in a lucite transparent dish.

Browning was measured according to Meydav *et al.* (1977). Pulp removal by centrifugation was followed by 1:1 dilution with ethyl

alcohol for flocculation of remaining cloud particles and filtration through filter paper Whatman #42. Absorbance at 420 nm was evaluated in a Bausch and Lomb Spectronic 21 spectrophotometer.

Sulphur dioxide was determined on mashed apples before and after baking according to AOAC (1980) (Modified Monier-Williams Method). This method is based on distillation of the sample under acid conditions and absorption of SO_2 with excess of oxidizing agent which converts it into sulphuric acid. SO_2 concentration was determined by titration with sodium hydroxide. (Results are given in ppm SO_2.)

pH determinations were carried out on a digital pH-meter PBS-710 from El-Hama Instruments. Accuracy of the instrument was ±0.01 pH units.

Soluble solids of thawed and baked samples were determined on the Abbe '60' Refractometer from Bellingham and Stanley Ltd. Accuracy of readings were ±0.02° Brix.

Quantitative Enzymatic Assays

Catalase activity was measured according to AOAC (1980). This method is based on the determination of H_2O_2 equivalent by iodine titration. Catalase activity was determined from the slopes of the curves obtained by plotting H_2O_2 equivalents versus time. Activity remaining is reported as the ratio of slopes of treated sample and the fresh product.

Polyphenoloxidase activity was determined according to Luh and Phitakpol (1972). The principle of the method is the development of brown color due to reaction between the enzyme in the sample and the substrate (Catechol). Absorbance of the solution was evaluated at 420 nm on a Bausch and Lomb Spectronic 21 spectrophotometer and plotted against time in minutes. Enzyme activity was evaluated as in paragraph a.

Sensory Evaluations

For tasting purposes the sliced apples from both treatments and storage temperatures were baked in an oven at 200°C for 20 min. The taste panel consisted of 10-14 partially trained members from the department. The scoring preference test was used. (Larmond 1977). At each session the panelists were presented the 4 different samples, in replicates, and were asked to rate them according to their texture and taste. The ratings (excellent, good, fair and poor) were given numerical values from 1 to 4 (1 being the highest), averaged and analyzed statistically.

EXPERIMENTAL

Deaeration

The time required to remove the intratissue gases of the apples was determined in the vacuum sealer. The apples were packed in the P.E. bags which were placed in the machine, evacuated for different times and injected with carbon dioxide. The residual air was monitored by injecting a sample of headspace from the bag into the gas chromatograph.

Preparation of samples

Based on preliminary experiments, the apples were treated according to the scheme in Fig. 1.

RESULTS AND DISCUSSION

Deaeration

The time required to remove the intratissue gases in the MOVAC II vacuum sealer was found to be 5 min. This time was used in all experiments.

Gas Treatments

Carbon Monoxide Treatment. Cauliflower, potatoes, apples, pears, apricots and peaches were exposed to CO according to the scheme in Fig. 1. The products were exposed to CO for periods up to 3 min. In some experiments apples were exposed to CO for up to 10 min but no inhibitory effect was noticed on any of the product tested as regards catalase and polyphenol oxidase activity. These results are in contradiction with claims made by Kramer *et al.* (1980) who showed inactivation with this gas. However, examination of their data indicate that they never reported an enzyme inactivation of CO by itself. This gas was always used by them in combination with SO_2.

Based on these results no further experiments were done with this gas.

Sulphur Dioxide. Bisulfate solutions of 200 ppm at 40°C were initially tried for treating the products. Alternating atmospheric and partial vacuum conditions were applied with no success. Only when SO_2 concentration was increased to 10,000 ppm was a significant reduction of enzyme activity observed. Since this concentration, or a longer time

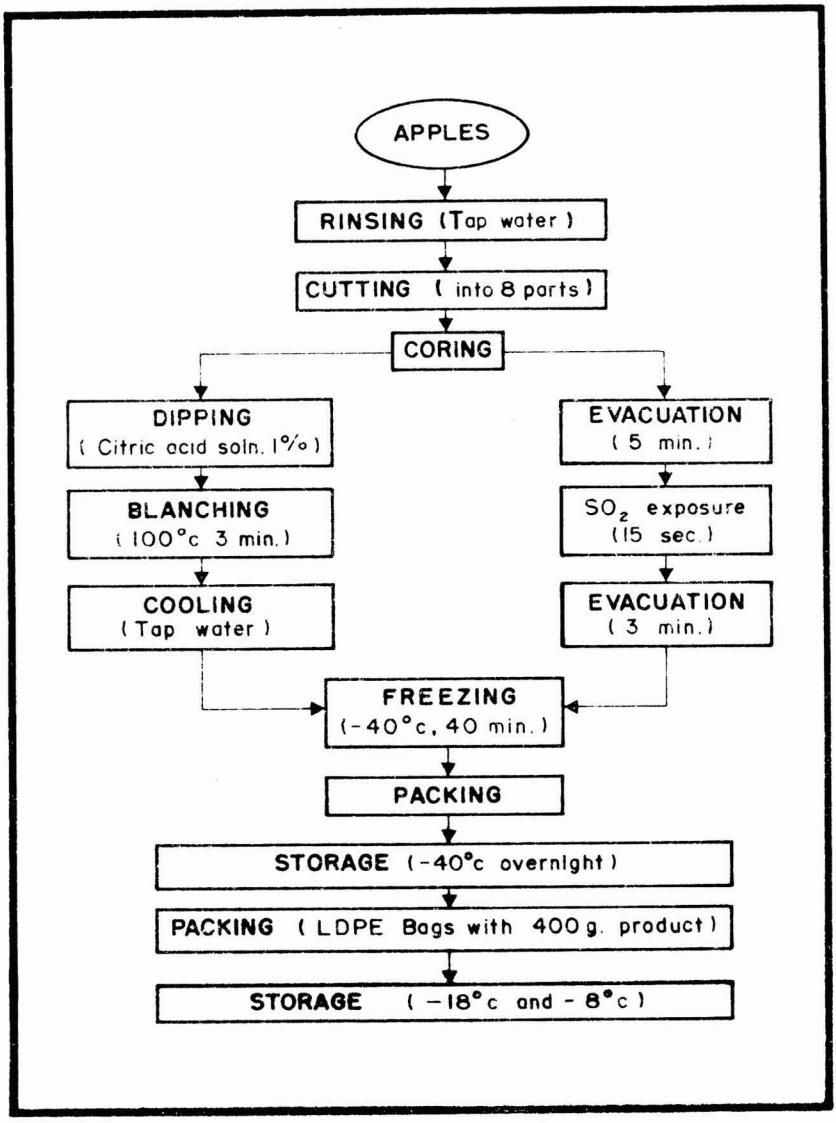

FIG. 1. FLOW DIAGRAM FOR THERMALLY AND GAS TREATED APPLES

at lower concentrations, did not seem practical, further experiments were made only with pure SO_2 gas according to the flow diagram shown in Fig. 1.

Mixtures of Sulphur Dioxide and Nitrogen. Gas mixtures of SO_2 and N_2 at the following ratios were prepared by mixing the suitable volumes: SO_2/N_2; 75/25%; 50/50%; 25/75%.

Packaging. After treatment and packaging, the apples were stored at −8° and −18°C, respectively, and analyzed periodically for Hunter color, browning, pH, soluble solids, residual SO_2, enzyme activity and sensory quality. All analyses were carried out at least in duplicate.

Hunter color values during storage are shown in Fig. 2. "L" values decreased only slightly with time. This change cannot be interpreted as

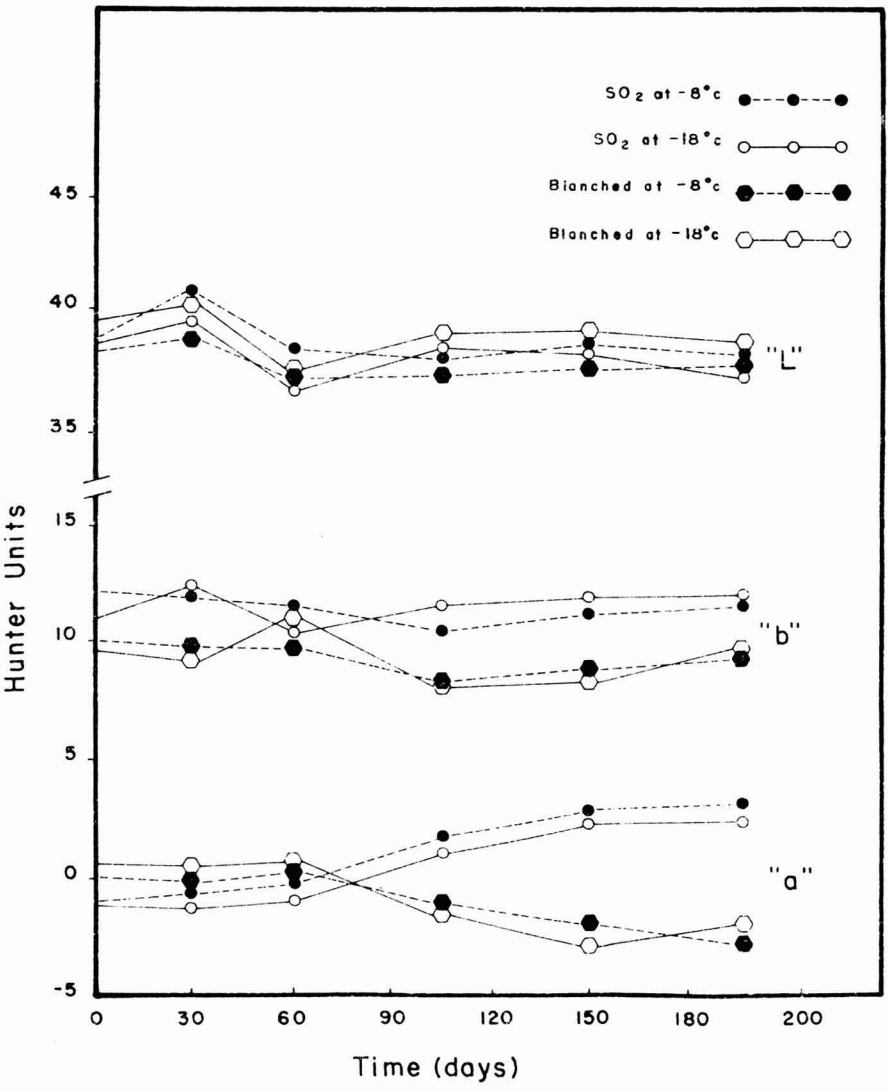

FIG. 2. HUNTER COLOR VALUES OF APPLE SLICES DURING STORAGE

a tendency, but as experimental error due to variation in samples. Hunter "b" values did not change during storage, but "a" values showed a tendency toward green for the thermally blanched samples, while values for gas treated samples rose on this scale. This is in agreement with the subjective sensory test (which will be discussed later) in which thermal blanched samples appeared to be greener and gas treated ones yellower. This difference may be explained by the light scattering of the blanched product, in which water filled the intratissue voids, whereas, as compared to that of the gas treated samples the structure was more porous.

Browning of a clarified extract, as measured by absorbance at 420 nm, showed no significant changes at either temperature during the whole storage period which was 195 days. These results concur with Hunter "L" values.

pH results for the difference samples are shown in Table 1. pH of the thermally treated apples rose from 3.65 (original raw material) to an average of 3.83, while in the gas treated samples it decreased to an average of 3.39. The increase in pH can be explained by dilution during blanching. In the gas treated samples the dissolution of SO_2 in the tissues led to an increase in the acidity.

Table 1. pH values of apple slices during storage

Storage Time (Days)	pH Before Baking	After Baking	pH Before Baking	After Baking
	TB 8		S 8	
0	3.75	3.90	3.28	3.78
30	3.88	3.78	3.43	3.75
60	3.85	3.78	3.24	3.80
105	3.80	3.81	3.35	3.73
150	3.75	3.94	3.48	3.75
195	3.90	3.85	3.50	3.70
	TB 18		S 18	
0	3.78	3.84	3.25	3.73
30	3.95	3.70	3.45	3.71
60	3.80	3.85	3.29	3.70
105	3.83	3.84	3.41	3.80
150	3.97	3.83	3.51	3.76
195	3.80	3.80	3.50	3.75

TB 8 - Thermally blanched and stored at −8°C
TB 18 - Thermally blanched and stored at −18°C
S 8 - SO_2 treated and stored at −8°C
S 18 - SO_2 treated and stored at −18°C

Baked samples from both treatments reached almost the same pH values (average of 3.78). The removal of SO_2 in gas treated samples was the cause for this increase.

Soluble solids results are presented in Fig. 3. It was observed that the soluble solids contents of gas treated samples were always higher than those of the thermally treated ones, indicating the loss of soluble solids during blanching.

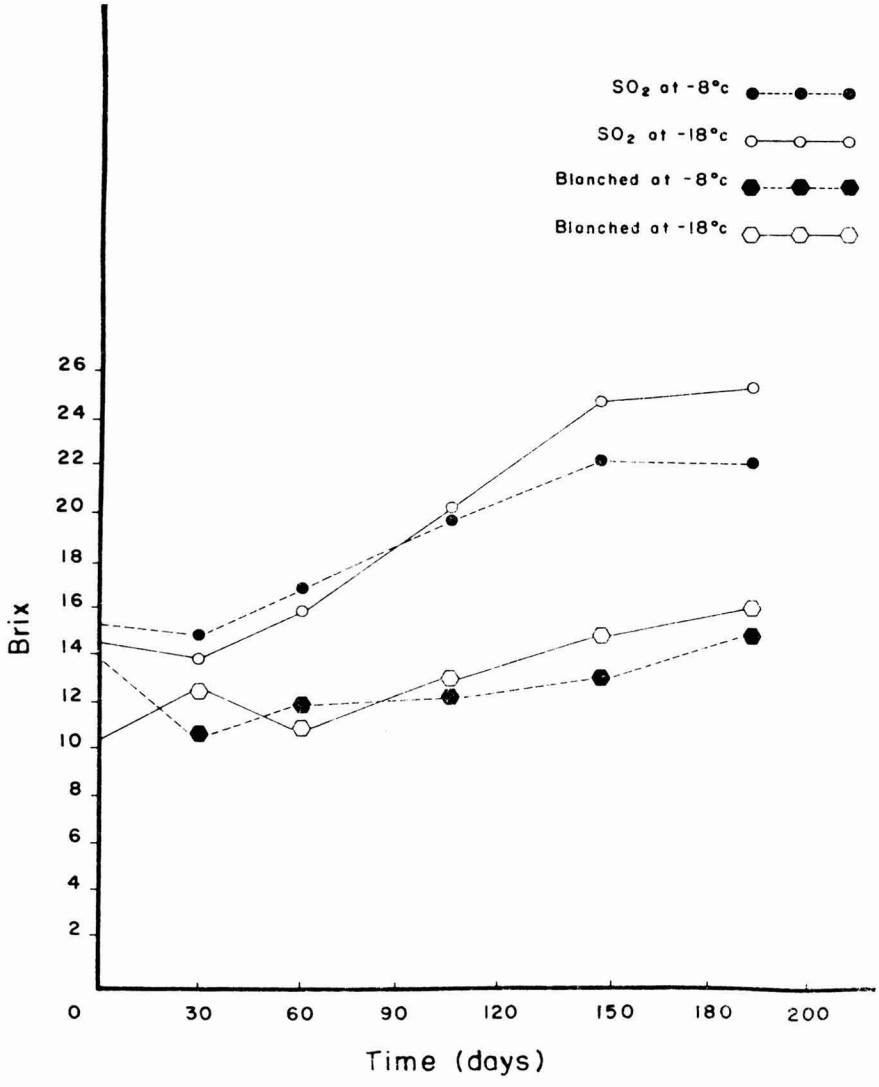

FIG. 3. SOLUBLE SOLIDS IN APPLE SLICES (AFTER BAKING) DURING STORAGE

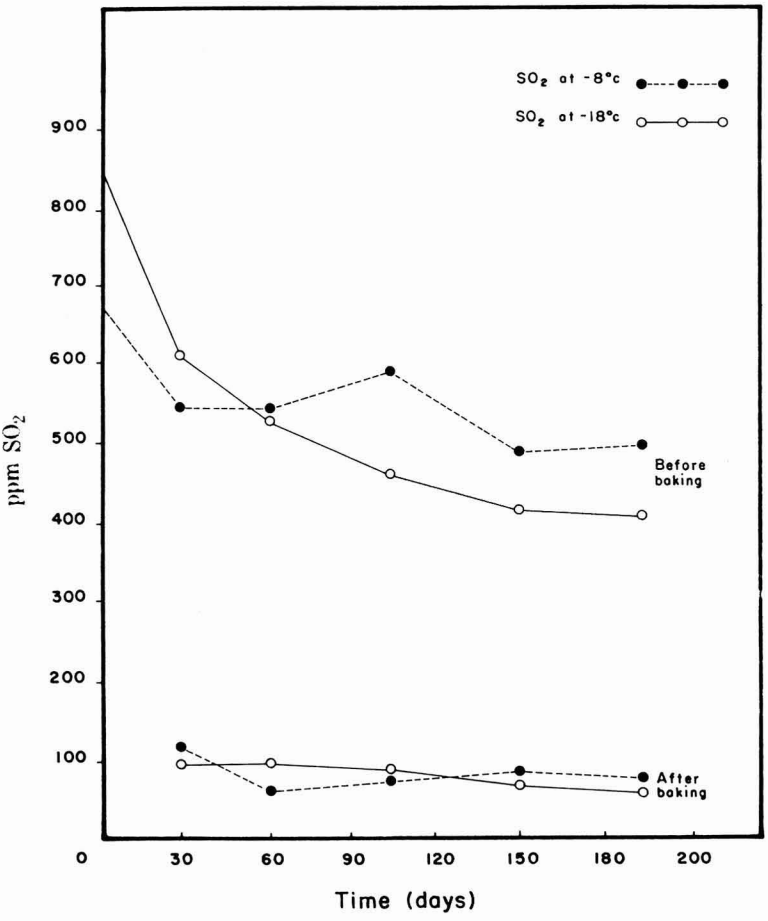

FIG. 4. RESIDUAL SO_2 IN APPLE SLICES DURING STORAGE

An increase in soluble solids from the original level of 14°Bx was noted for the stored samples from both treatments. This might be due to some loss of vapor through the package. Higher moisture barrier materials can be used to prevent this phenomenon.

Residual Sulphur Dioxide

Figure 4 gives values for residual SO_2 in samples before and after baking. SO_2 concentration decreased with storage time and after baking, SO_2 levels were close to the sensory acceptable levels as well as permissible levels.

In general, concentrations of SO_2 below 100 ppm are considered to be permissible. Berk (1976) mentioned that at concentrations over 30 to 50 ppm the odor and taste of SO_2 becomes objectionable. Many countries limit its use to specific applications.

Enzyme Activity

The adequacy of gas treatments was determined by enzymatic assays of catalase and polyphenol oxidase. Quantitative enzymatic assays were made on fresh apples in order to obtain the initial activity (100%).

The activity of these two enzymes was inhibited by SO_2 gas treatment and thermal blanching and there was practically no regeneration during storage as is shown in Table 2.

Since an undesirable SO_2 odor and taste remained in the samples, SO_2 was diluted with N_2, and the effect of various gas mixtures on the inactivation of both enzymes was evaluated.

Samples were submitted to gas treatments of 15 s with gas mixtures of 75, 50, and 25% SO_2. Enzymatic assays were performed after 10 days

Table 2. Residual enzyme activity in apple slices during storage

Storage Time (Days)	Enzyme Activity (%)			
	CAT	PPO	CAT	PPO
	TB 8		S 8	
0	0.0	1.25	0.0	0.00
30	0.0	1.95	12.5	0.00
60	6.5	0.00	1.9	1.39
105	0.0	0.00	0.0	1.60
150	3.1	0.90	0.0	2.20
195	0.0	0.00	0.0	0.00
	TB 18		S 18	
0	0.0	0.13	0.0	0.80
30	0.0	0.35	17.0	0.70
60	1.9	0.00	0.0	0.00
105	0.0	0.60	0.0	0.00
150	0.0	1.27	0.0	0.62
195	0.0	0.00	0.0	0.00

CAT - catalase
PPO - polyphenol oxidase
TB 8 - thermally blanched and stored at −8°C
TB 18 - thermally blanched and stored at −18°C
S 8 - SO_2 treated and stored at −8°C
S 18 - SO_2 treated and stored at −18°C

of storage at −18°C and showed 100% inactivation. Residual SO_2 was 36-72 ppm as shown in Table 3.

When samples, treated with an atmosphere containing 25% SO_2, were submitted to vacuum (29 in) for a period of 4 h, residual SO_2 dropped to non-detectable levels and no regeneration of either enzyme could be observed.

Sensory Evaluation

Results of the sensory evaluation are presented in Table 4. The comparisons were done on samples from the same storage period, in two replicates. The numbers represent the average sensory score of the baked apple samples, where 1 is the highest score and 4 is the lowest. The samples from both treatments and both storage temperatures were equally liked, and the SO_2 treatment did not have an adverse effect either on taste or on texture.

It is worth noting that some panelists preferred even the SO_2 treated samples, due to color or solid content, but this preference was nullified by the averaging procedure.

Table 3. Enzyme activity and residual SO_2 of samples treated with different gas mixtures after 10 days of storage

SO_2 in N_2 (% vol)	Enzyme Activity CAT (%)	Enzyme Activity PPO (%)	Residual SO_2 (ppm)
75	0	0	72
50	0	0	—
25	0	0	36

Table 4. Average values for sensory evaluation of apple slices during storage

	Treatment							
Storage	TB 8		TB 18		S 8		S 18	
Time (Days)	Texture	Taste	Texture	Taste	Texture	Taste	Texture	Taste
0	2.85	2.85	2.85	2.85	2.38	2.54	2.58	2.38
30	3.41	3.45	3.04	3.18	2.41	2.36	2.45	2.23
60	2.45	2.86	2.63	3.05	3.05	2.55	2.68	2.27
105	2.40	2.70	2.10	2.60	2.50	2.00	2.50	1.80
150	2.50	2.40	2.25	2.40	2.25	2.20	2.25	2.55
195	2.61	3.08	2.65	2.96	2.54	2.35	2.54	2.38

TB 8 - Thermally blanched and stored at −8°C
TB 18 - Thermally blanched and stored at −18°C
S 8 - SO_2 treated and stored at −8°C
S 18 - SO_2 treated and stored at −18°C

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ON MELANOIDIN FORMATION WITH FURFURAL PARTICIPATION: SYNTHESIS OF MELANOIDINS FROM FURFURAL AND GLYCINE

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Received for Publication January 3, 1983
Accepted for Publication July 12, 1983

ABSTRACT

A method for synthesis of model melanoidins at high yields from furfural and glycine is proposed. It was found that for the melanoidin the elemental composition, and the IR, UV and mass spectra did not change considerably during the course of the reaction. An empirical formula for the constitutional repeating unit—$C_{21}H_{17}NO_6$—is proposed on the basis of elemental analysis. The evolution of carbon dioxide during the reaction is proved.

INTRODUCTION

The present concepts about melanoidin formation in the course of the Maillard reaction are based on the assumption that the interaction between the initial amino acid and the carbohydrate results in a great number of highly reactive compounds. Subsequently color products with a higher molecular weight are formed.

The first step of the reaction—the formation of low molecular weight intermediates—has been studied in detail. It is interesting to note that the interaction between a simple amino acid and a simple carbohydrate, e.g. glycine and D-glucose, leads to a great number of low molecular products with various structures and properties (Olsson *et al.* 1978).

The second step—the formation of color products with higher molecular weights—has not been studied precisely and systematically. Not

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much is known about their molecular weight, polydispersity, chemical structure and homogenity, content and structure of chromophore groups, etc.

Furfural is one of the products of interest derived from pentoses destruction in the Maillard reaction. Since furfural is a reactive compound it may be expected to take an active part in the formation of colored high molecular weight products—melanoidins. The first proposals connected with this were made by Schiff (1887). The formation of furan aldehydes by heating a solution of carbohydrates and amino acids was shown by Wolform *et al.* (1949). The role of furfural and glycine in melanoidin formation was studied by Tan *et al.* (1950). The similarity between the products formed to the products obtained from D-xylose and glycine has been shown by elemental analysis, UV, and IR spectroscopy. Based on the similarity between reductones and the products of the Stenhouse reaction, Nomura (1965) has discussed the interaction between furfural and aniline as a model of nonenzymic browning. Haas *et al.* (1948) have found that furfural is formed in a concentrate of dried apricots. The removal of furfural by continuous extraction with ethylacetate sharply decreases the rate of browning and vice versa—addition of furfural increases the rate.

Other authors, however, doubt the participitation of furfural and 5-hydroxymethylfurfural in nonenzymic browning. Anet (1959) has investigated the interaction between glycine and different intermediate products of the Maillard reaction, including 5-hydroxymethylfurfural at a pH of 5.5. The data showed that 5-hydroxymethylfurfural takes a minor part in the melanoidin formation. Kamada and Sakurai (1959) have investigated the browning of soya-products, pentoses, hexoses and furfural in the presence of amino acids at 38°C. It has been shown that furfural does not take part in this process.

It is accepted in other studies that the carbonyl derivatives of furan do not take a substantial part in the nonenzymic browning. However, only a few of the authors have tried to isolate and to characterize the colored products of the interaction between furfural and glycine.

The object of the present work is to propose a convenient method of synthesis of furfural melanoidins at high yields. The main physical and spectral characteristics of the products isolated are discussed.

MATERIALS AND METHODS

Materials

Furfural was distilled prior to use. Glycine (Reanal–Hungary) was used as received.

Methods

Melanoidins were synthesized at the following molar ratio—furfural : glycine : water = 4 : 1 : 5. Furfural (38.4 g, 0.4 mol), glycine (7.5 g, 0.1 mol) and water (9 g, 0.5 mol) were heated at stirring in a water bath at 95°C without correcting for acidity. After a certain reaction time (3 to 100 h) the polymers obtained were isolated by precipitation in 96% ethanol (200 cc). The solid product was repeatedly washed with a total 1.3 cm^3 of 96% ethanol for complete removal of the unreacted furfural and the other low molecular products. The reaction product was controlled by a ninhydrin test for the presence of unreacted glycine.

Analyses

IR spectra (KBr pellets) were recorded on a UR-20 Carl Zeiss Spectrometer. UV spectra were recorded on a Specord UV/VIS–Carl Zeiss spectrometer (solvent—dimethylformamide). The extinction coefficient ϵ ($l \cdot mol^{-1} \cdot cm^{-1}$) was calculated for the constitutional repeating unit ($C_{21}H_{17}NO_6$) of the polymer.

RESULTS AND DISCUSSION

The interaction between furfural and glycine is accompanied by an intensive browning of the reaction mixture. As shown in Table 1 the yield of polymer rapidly increases up to 20 h reaction time. At reaction times over 50 h the increased viscosity of the reaction mixture impedes the proper stirring. The reaction products obtained respectively for 3, 7, 20 and 50 h are soluble in dimethylformamide, dimethylsulfoxide, pyridine and glacial acetic acid. At a reaction time of over 50 h (e.g. 80 or 100 h) the products are partially insoluble. Probably a partial cross-linking of the reaction products proceeds in this case. The polymers obtained at reaction times of from 3 to 100 h are not soluble at room temperature in water, 10% potassium hydroxide, 10% hydrochloric acid, methanol, ethanol and diethylether. They are partially soluble in chloroform, dioxane and tetrahydrofuran. The data show that the most appropriate duration for preparative work is from 10 to 20 h reaction time.

The elemental analysis data (Table 1) shows that the content of carbon, hydrogen and nitrogen does not change considerably with reaction times of from 3 to 100 h.

As mentioned above Tan *et al.* (1950) have isolated polymers resulting from the interaction between furfural and glycine (molar ratio 1:10 and 1:1). The products slightly differ in their elemental content

Table 1. Yield, elemental composition and extinction coefficients of the products obtained

Run No.	Time (H)	Yield (g)	Yield (%)	Elemental Composition[a] (%) C	H	N	Extinction Coefficients[c] $\epsilon(1 \cdot mol^{-1} \cdot cm^{-1})$ 280nm	340nm
1	3	4.6	10	68.57	5.12	4.11	9.33	6.42
2	7	10.6	23	65.54	4.51	3.49	9.74	6.78
3	20	18.2	40	65.20	4.51	3.56	10.40	7.18
4	50	21.6	47	67.40	4.76	3.33	10.54	7.46
5	80	24.6	54	68.06	3.91	3.71	b	b
6	100	25.2	55	69.53	4.90	3.95	b	b

[a]Calculated for constitutional repeating unit $C_{21}H_{17}NO_6$: C – 66.49, H – 4.49, N – 3.69(%)
[b]The product is partially soluble in dimethylformamide
[c]Calculated for constitutional repeating unit $C_{21}H_{17}NO_6$

depending on the reaction time, temperature and method of isolating (found: C-59-67%, H-4-5, N-3-4 %). These results are in coincidence with ours although our experiments have been performed at a ratio 4:1.

The empirical formula $C_{21}H_{17}NO_6$ was determined for the polymer. We have accepted it for the constitutional repeating unit of the high molecular products obtained. It corresponds to the following reaction:

$$C_2H_5NO_2 + 4(C_5H_4O_2) - CO_2 - 2(H_2O) \rightarrow C_{21}H_{17}NO_6$$

1 mol	4 mol	1 mol	2 mol	
glycine	furfural	carbon dioxide	water	polymer

The evolution of carbon dioxide was shown by reaction with barium hydroxide solution. The CO_2 evolution is evidence that Strecker degradation of glycine takes place. From the equation it is seen that the proper molar ratio between furfural and glycine for synthesis of polymers is 4:1 as chosen in the present work. That is why higher yields are obtained in the present work as compared to those obtained by Tan *et al.* (1950). The scheme proposed is in accordance with Carson and Olcott's results (1954). These authors have studied the products of interaction between acetaldehyde and ethylamine and on the basis of the elemental analysis have drawn the following scheme:

$$C_2H_5N + 4(C_2H_4O) - 2(H_2O) \rightarrow C_{10}H_{19}NO_2$$

1 mol	4 mol	2 mol	
ethylamine	acetaldehyde	water	polymer

The IR spectra of the melanoidins obtained in the present investigation show intensive bands in the range 700-1720 cm^{-1} (Fig. 1). There are no marked maxima over 2500 cm^{-1}. The wide plateau at 2800-3600 cm^{-1} is due to O-H and N-H groups which take part in hydrogen bonds. The band at 1600-1720 cm^{-1} may be due to C=C, C=N or C=O bonds. The absorption at 1610 and 1390 cm^{-1} probably is due to COO^- ion. The maxima at 1160, 1080, 1010, 810 and 740 cm^{-1} are characteristic for the furan ring and give an evidence of the presence of furan groups in the polymer.

An absorption maximum at 280 nm and a shoulder at about 340 nm are observed in the UV-spectra of the melanoidins obtained (Fig. 2). The type of the absorption spectra of the reaction products is one and the same for various reaction times of from 3 to 50 h. The absorption maxima do not shift in the course of the reaction. The extinction

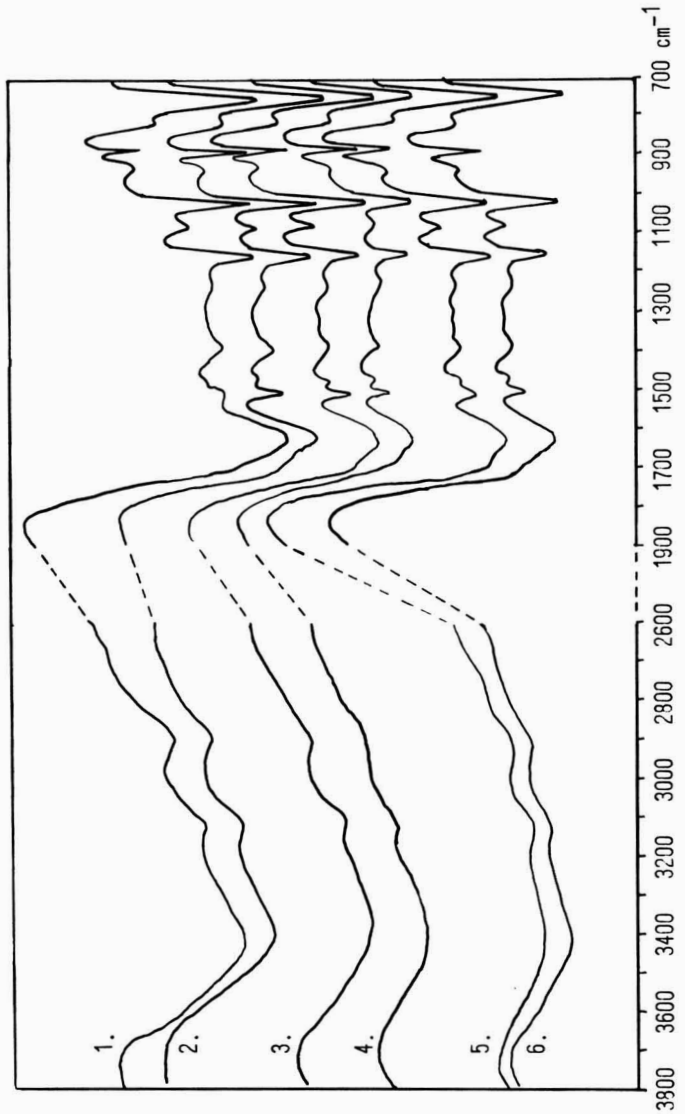

FIG. 1. IR SPECTRA OF FURFURAL MELANOIDINS ACCORDING TO TABLE 1

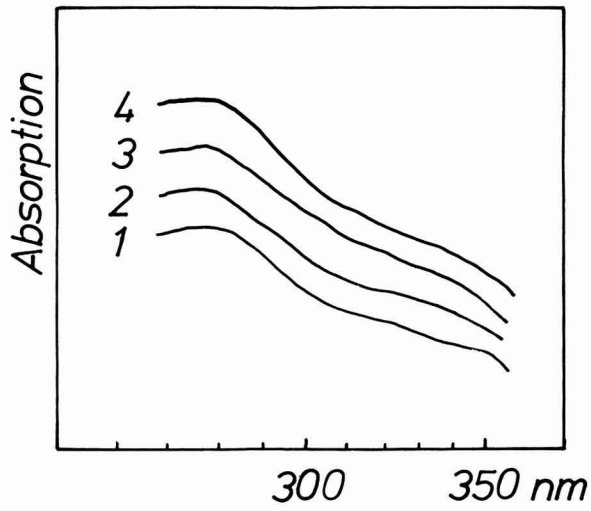

FIG. 2. UV SPECTRA OF FURFURAL MELANOIDINS ACCORDING TO TABLE 1

coefficients ϵ_{280} and ϵ_{340} slightly increase during the reaction and at the fiftieth hour they are 11% higher than those at the third hour. This difference is close to the precision of the method so it is not correct to interpret it. At that the ratio $\epsilon_{280}/\epsilon_{340}$ is constant for all products investigated and it is equal to 1.43 ± 0.02. The identity of the UV and IR spectra of the compounds obtained at different reaction times shows that not only the elemental composition but also the type and the ratio of the functional groups monitored by spectral methods remain constant in the course of the reaction.

The mass spectra of the furfural melanoidins obtained at different reaction times are too similar (Fig. 3). The fragments with m/e = 96, 95, 44 and 39 are with the highest intensity.

No doubt, the method of recording the mass spectra at temperatures above 270°C causes a thermal destruction of melanoidins. An intensive thermal destruction is observed at heating of melanoidins under nitrogen at 270-300°C. It is accompanied by carbon dioxide evolution which is proved by reaction with barium hydroxide solution. Presence of furfural in the pyrolyzate is established by thin-layer chromatography. The peak m/e = 44 is probably due to carbon dioxide. Peaks m/e = 96, 95, 67, 39 are characteristic for furfural and its fragments (Fig. 3).

The results obtained show that furfural takes part in melanoidin formation.

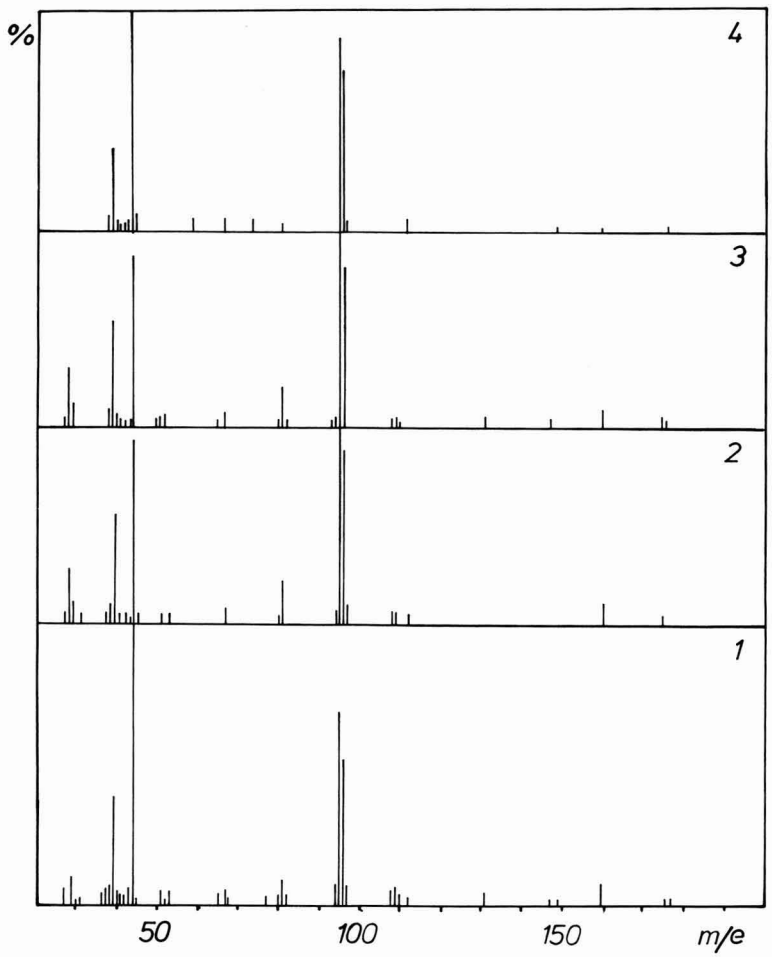

FIG. 3. MASS SPECTRA OF FURFURAL MELANOIDINS ACCORDING TO TABLE 1

ACKNOWLEDGMENTS

The authors thank Dr. Kováčik—Higher Institute of Chemical Technology—Bratislava, ČSSR for recording mass spectra of the compounds

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ON MELANOIDIN FORMATION WITH FURFURAL PARTICIPATION: INITIAL STEP OF THE REACTION OF FURFURAL WITH GLYCINE ESTERS

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Received for Publication January 3, 1983
Accepted for Publication July 12, 1983

ABSTRACT

The interaction between furfural and methyl or ethyl esters of glycine in the presence of triethylamine was studied as a model of furfural participation in melanoidin formation. The reaction has been stopped at its initial step. N-furylidene-β-(2-furyl)serine, methyl, respectively ethyl ester was isolated as a main product. It was shown that in chloroform the compounds cyclotautomerize resulting in the corresponding oxazolidines. The erythro configuration of N-furylidene-β-(2-furyl)serine, methyl ester is verified by comparison with a sample prepared by an alternative route. The corresponding N-acetyloxazolidines are derived by acylation of the compounds obtained.

INTRODUCTION

Depending on the reaction conditions, the interaction between furfural and glycine may result in various products—low molecular furfural pigments. The isolation of the low molecular reaction products of furfural and glycine or glycine esters is of particular interest but it is of a considerable experimental difficulty. Probably these compounds form furfural polymers in the subsequent steps of the reaction.

The interest in these compounds has grown up since it has been found that they are intermediates in the synthesis of bioactive compounds.

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Hayes and Gever (1951) have isolated N-furylidene-β-(2-furyl)serine, potassium salt, obtained from glycine and furfural. The attempts to isolate the free acid have failed due to decomposition of the compounds into β-(2-furyl)serine and furfural. Bergmann *et al.* (1951) have investigated the condensation of aromatic aldehydes with glycine esters. They have isolated the corresponding esters of N-arylidene-β-arylserine. When the aromatic aldehyde is furfural, the attempts to perform the same reaction have failed. Under the conditions studied—heating of the amino ester and furfural in methanol—the reaction does not stop at its initial step but it proceeds until a polymer is formed. The formation of the low molecular product is possible after the furan substitution with nitrogroup at the 5 position. This indicates that the furan group takes an important part in the subsequent reactions of the low molecular weight products. It is known that furfural is an important precursor of melanoidins obtained by interaction between amino acids and pentoses (Tan *et al.* 1950; Nomura 1955). Thus to estimate the furfural role in the melanoidin formation, the chemistry of the interaction between furfural and glycine or glycine esters has to be studied in detail.

In the present work the low molecular products of the interaction between furfural and glycine esters are studied. The composition and the structure of the compounds isolated are determined.

MATERIALS AND METHODS

Materials

Furfural was distilled prior to use. Glycine (Reanal–Hungary) was used as received. The solvents (ethanol, chloroform, diethyl ether, acetone, glacial acetic acid) and the other chemicals were p.a. grade. DC-Alufolien Kieselgel 60-(Merck–Germany)-plates were used for thin layer chromatography (TLC).

Methods of Synthesis and Analytical Data

Glycine, methyl and ethyl esters, hydrochlorides were prepared as described by Curtius and Goebel (1888). Erythro-β-(2-furyl)serine (I) and threo-β-(2-furyl)serine (II) were synthesized according to Inui *et al.* (1968).

ERYTHRO-N-FURYLIDENE-β-(2-FURYL)SERINE, METHYL ESTER (III)

Ethereal solution of diazomethane was added to a suspension of 0.670 g (0.00254 mol) of the dioxane adduct of (I) in 60 cm^3 of methanol, until a persistent yellow color was obtained and the gas evolution stopped. The solvent was removed under reduced pressure and 9 cm^3 of chloroform, 0.6 cm^3 (0.0072 mol) of furfural and 1.2 g of anhydrous calcium sulfate were added to the residue. The mixture was allowed to stand at 20°C for 30 min and was kept overnight at −20°C. The solution was filtered, the chloroform was removed under reduced pressure and 15 cm^3 of diethyl ether were added. Yield: 0.301 g (37%) of erythro-N-furylidene-β-(2-furyl)serine, methyl ester; mp 111-113°C after recrystalization from acetone.

Anal. Calcd for $C_{13}H_{13}NO_5$: C-59.30, H-4.94, N-5.32
Found: C-58.75, H-5.34, N-5.26 %

TLC	R_f = 0.66, eluent–chloroform: ethanol = 10:1 v/v
UV	$\epsilon_{277\ nm} = 2.01 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
	$\epsilon_{219\ nm} = 1.42 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
IR	3250 (O-H, hydrogen bonds), 3140 (C-H in the furan ring), 1745 (C=O), 1640 (C=N), cm^{-1}
MS	167 (20), 152 (18), 109 (9), 108 (82), 97 (8), 96 (100), 95 (88), 81 (47), 74 (13), 67 (15), 53 (19), 52 (9), 51 (13), 50 (6), 44 (25), 43 (10), 42 (9), 41 (8), 39 (55), 38 (16), 37 (10) m/e (%).

THREO-N-FURYLIDENE-β-(2-FURYL)SERINE, METHYL ESTER (IV)

An ethereal solution of diazomethane was added to 3.6 g (0.21 mol) of (II) suspended in 150 cm^3 of methanol until a persistent yellow color appeared and the gas evolution stopped. The solvent was removed under reduced pressure and 30 cm^3 of chloroform, 5 cm^3 (0.06 mol) of furfural and 10 g of anhydrous calcium sulfate were added to the residue. The mixture was allowed to stand at 20°C for 30 min and was kept overnight at −20°C. The solution was filtered, the chloroform was removed under reduced pressure and 50 cm^3 of diethyl ether were added to the residue. Yield: 1.2 g (22%) of threo-N-furylidene-β-(2-furyl)serine, methyl ester; mp 97-99°C after recrystalization from acetone.

Anal. Calcd for $C_{13}H_{13}NO_5$: C-59.30, H-4.94, N-5.32
Found: C-58.58, H-5.16, N-5.34 %.
TLC $R_f = 0.79$; eluent-chloroform: ethanol = 10:1 v/v
UV $\epsilon_{276\ nm} = 2.15 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
$\epsilon_{216\ nm} = 1.34 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
IR 3240 (O-H, hydrogen bonds), 3140 (C-H in the furan ring), 1740 (C=O), 1635 (C=N), cm^{-1}. The IR spectrum differs from the IR spectrum of (III) below 1350 cm^{-1}.
MS 167 (19), 152 (15), 109 (7), 108 (63), 97 (8), 96 (100), 95 (90), 81 (36), 74 (9), 67 (15), 53 (15), 52 (7), 51 (11), 50 (8), 44 (18), 43 (7), 42 (9), 41 (8), 40 (8), 39 (53), 38 (17), 37 (10), m/e (%).

N-FURYLIDENE-β-(2-FURYL)SERINE, METHYL ESTER (V)

A mixture of 18.8 g (0.15 mol) of glycine, methyl ester, hydrochloride, 200 cm^3 of chloroform, 40 cm^3 (0.285 mol) of triethylamine, 24.8 cm^3 (0.30 mol) of furfural and 20 g (0.17 mol) of anhydrous magnesium sulfate was stirred at room temperature for 2 h. The reaction mixture was kept overnight at room temperature. The solid phase was separated by filtration. The filtrate was washed with water ($3 \times 50\ cm^3$) and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. Diethyl ether (50 cm^3) was added to the oily residue and the mixture was kept overnight at −20°C. Yield of crude product: 20.6 g (52%); yield of product after repeated recrystalizations from acetone: 20%, mp 111-113°C, mixed mp of (III) and (V)-111-113°C.

Anal. Calcd for $C_{13}H_{13}NO_5$: C-59.30, H-4.94, N-5.32
Found: C-60.08, H-4.86, N-5.01, %
TLC $R_f = 0.66$; eluent-chloroform: ethanol = 10:1 v/v
UV $\epsilon_{277\ nm} = 2.03 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
$\epsilon_{219\ nm} = 1.32 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$
IR 3250 (O-H, hydrogen bonds), 3140 (C-H in the furan ring), 1745 (C=O), 1640 (C=N), cm^{-1}
^1H NMR $\delta = 7.93$ (singlet, 1H, −CH=N−), 7.50-6.25 (two multiplets, $2 \times 2 \times 3H$, furan protons in the linear and the cyclic isomer), 6.60 (doublet, 1H, -O-CH-N- in the cyclic isomer), 3.82 (singlet, 3H, $-OCH_3$ in the linear isomer), 3.58 (singlet, 3H, $-OCH_3$ in the cyclic isomer), 3.37 (singlet, 1H, -OH in the linear isomer), ppm.

MS 167 (20), 152 (18), 109 (9), 108 (82), 97 (8), 96 (100), 95 (90), 81 (45), 74 (13), 67 (16), 53 (19), 52 (9), 51 (12), 50 (6), 44 (33), 43 (9), 42 (10), 41 (7), 40 (8), 39 (51), 38 (15), 37 (10), m/e (%).

N-FURYLIDENE-β-(2-FURYL)SERINE, ETHYL ESTER (VI)

(VI) was synthesized by a method analogous to the latter by the use of 20.6 g (0.147 mol) of glycine, ethyl ester, hydrochloride, 200 cm^3 of chloroform, 40 cm^3 (0.285 mol) of triethylamine, 20 g (0.17 mol) of anhydrous magnesium sulfate and 24.8 cm^3 (0.30 mol) of furfural. Yield of crude product: 21.9 g (54%); yield of product after several recrystalizations from acetone: 24%; mp 106-108°C.

Anal. Cal l for $C_{14}H_{15}NO_5$: C-60.60, H-5.41, N-5.05
Found: C-60.79, H-5.50, N-5.13, %.

TLC R_f = 0.72, eluent-chloroform: ethanol = 10:1 v/v

UV $\epsilon_{277\ nm} = 2.23 \times 10^4\ 1 \cdot mol^{-1} cm^{-1}$
$\epsilon_{219\ nm} = 1.51 \times 10^4\ 1 \cdot mol^{-1} cm^{-1}$

IR 3290 (O-H, hydrogen bonds), 3120 (C-H in the furan ring), 1748 (C=O), 1642 (C=N), cm^{-1}

^1H NMR δ: 7.94 (singlet, 1H, -CHN), 7.50-6.25 (two multiplets, 2 × 2 × 3H, furan protons in the linear and the cyclic isomers), 6.59 (doublet, 1H, -O-CH-N= in the cyclic isomer), 4.28 (multiplet, 2H, $-OC\underline{H}_2CH_3$ in the linear isomer), 4.00 (multiplet, 2H, $-OC\underline{H}_2CH_3$ in the cyclic isomer), 3.62 (triplet, 1H, CH-N$\underline{H}$=CH in the cyclic isomer), 3.43 (singlet, 1H, O-H in the linear isomer), 1.28 (triplet, 3H, $-OCH_2CH_3$ in the linear isomer), 1.10 (triplet, 3H, $-OCH_2C\underline{H}_3$ in the cyclic isomer), ppm.

MS 181 (19), 152 (25), 109 (12), 108 (100), 97 (9), 96 (96), 95 (87), 88 (12), 81 (46), 80 (5), 67 (15), 53 (19), 52 (9), 51 (11), 50 (5), 44 (35), 43 (5), 42 (9), 41 (6), 40 (8), 39 (50), 38 (16), 37 (9), m/e (%).

3-ACETYL-2,5-DI(2-FURYL)-4-OXAZOLIDINECARBOXYLIC ACID, METHYL ESTER (VII A,B)

1.5 g (0.0057 mol) of (V) were dissolved at intensive stirring in 3 cm^3 of acetic anhydride at room temperature. The mixture was kept overnight and after that 20 cm^3 of water were added. The mixture was

neutralized by addition of 10 cm^3 of 30% potassium hydroxide. The oily product obtained was extracted with chloroform (3 × 10 cm^3) and the combined extracts were dried over anhydrous sodium sulfate. The reaction mixture was chromatographed through a silica gel column with chloroform as the eluent. A mixture (1.63 g, 93%) of two isomers of 3-acetyl-2,5-di(2-furyl)-4-oxazolidinecarboxylic acid, methyl ester was obtained. The mixture was separated by TLC (adsorbent-silica gel, eluent-chloroform: acetone = glacial acetic acid = 100:10:1). The following compounds were isolated:

a) 3-acetyl-2,5-di(2-furyl)-4-oxazolidinecarboxylic acid, methyl ester (VII a), mp 70.5-72.5°C

Anal. Calcd for $C_{15}H_{15}NO_6$: C-59.02, H-4.92, N-4.59
Found: C-59.17, H-4.94, N-4.44, %

TLC R_f = 0.80, eluent-chloroform: acetone: glacial acetic acid = 100:10:1, v/v

UV $\epsilon_{220\ nm} = 2.45 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$

IR 3120 (C-H in the furan ring), 1755 (C=O, ester), 1670 (C=O, amide), cm^{-1}

^1H NMR δ: 7.50-6.25 (multiplet, 2 × 3H, furan protons), 6.94 (doublet, 1H, -O-CH-N), 5.31 and 4.93 (two doublets, 2 × 1H, >N-CH-CH-O-, J = 7 Hz), 3.79 (singlet, 3H, -OCH_3), 2.06 (singlet, 3H, -N-C(O)-CH_3), ppm.

MS 305 (2), 209 (5), 178 (7), 168 (5), 167 (8), 153 (11), 152 (100), 150 (10), 138 (17), 136 (6), 135 (15), 122 (5), 120 (17), 109 (31), 108 (19), 107 (21), 96 (19), 95 (19), 81 (17), 80 (16), 78 (12), 59 (10), 53 (7), 52 (12), 51 (5), 44 (31), 43 (35), 42 (6), 40 (7), 39 (14), m/e (%).

b) 3-acetyl-2,5-di(2-furyl)-4-oxazolidinecarboxylic acid, methyl ester (VII b), mp 92-94°C.

Anal. Calcd for $C_{15}H_{15}NO_6$: C-59.02, H-4.92, N-4.59
Found: C-59.41, H-4.96, N-4.51, %

TLC R_f = 0.57, eluent-chloroform: acetone: glacial acetic acid = 100:10:1, v/v

UV $\epsilon_{219\ nm} = 2.37 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$

IR 3120 (C-H in the furan ring), 1755 (C=O, ester), 1670 (C=O, amide), cm^{-1}

^1H NMR δ: 7.50-6.25 (multiplet, 2 × 3H, furan protons), 7.05 (doublet, 1H, C-CH-N), 5.41 and 4.93 (two doublets, 2 × 1H, >N-CH-CH-O-, J = 7 Hz), 3.35 (singlet, 3H, -OCH_3), 1.80 (singlet, 3H, >N-C(O)-CH_3), ppm

MS 305 (5), 209 (3), 178 (6), 168 (5), 167 (22), 153 (13), 152 (100), 150 (6), 138 (3), 136 (6), 135 (25), 122 (6), 121 (15), 109 (23), 108 (17), 107 (9), 96 (22), 95 (35), 81 (22), 80 (16), 78 (10), 60 (11), 59 (13), 57 (22), 56 (8), 55 (23), 53 (5), 52 (8), 51 (12), 45 (24), 44 (29), 43 (82), 42 (12), 40 (5), 39 (18), m/e (%).

3-ACETYL-2,5-DI(2-FURYL)-4-OXAZOLIDINECARBOXYLIC ACID, ETHYL ESTER (VIII)

2.0 g (0.0072 mol) of (VI) were dissolved at intensive stirring in 4 cm^3 of acetic anhydride at room temperature. The mixture was kept overnight. Water (20 cm^3) was added and the mixture was neutralized by 20% potassium hydroxide (20 cm^3). Yield: 1.76 g (76%) of 3-acetyl-2,5-di(2-furyl)-4-oxazolidinecarboxylic acid, ethyl ester; mp 115-118°C after purification by column chromatography (adsorbent-silica gel, eluent-chloroform: acetone: glacial acetic acid = 100:10:1).

Anal. Calcd for $C_{16}H_{17}NO_6$: C-60.19, H-5.33, N-4.39
Found: C-59.99, H-5.30, N-4.41, %

TLC R_f = 0.64, eluent-chloroform: acetone: glacial acetic acid = 100:10:1, v/v

UV $\epsilon_{221\ nm} = 2.05 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$

IR 3140 (C-H in the furan ring), 1750 (C=O, ester), 1670 (C=O, amide), cm^{-1}

NMR δ: 7.50-6.25 (multiplet, 2 × 3H, furan protons), 7.09 (doublet, 1H, -O-CH-N), 5.43 and 4.96 (two doublets, 2 × 1H, >N-CH-CH-O-, J = 7 Hz), 4.02 (multiplet, 2 H, -O-CH_2CH_3), 1.86 (singlet, 3H, >N-C(O)-CH_3 1.1) (triplet, 3H, -O-CH_2CH_3), ppm

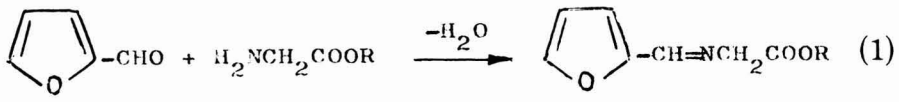
MS 319 (6), 276 (2), 230 (2), 203 (2), 181 (26), 178 (8), 167 (13), 166 (100), 150 (7), 149 (5), 147 (9), 138 (28), 136 (5), 135 (28), 122 (5), 121 (9), 109 (28), 108 (15), 107 (32), 96 (11), 95 (23), 94 (22), 81 (21), 80 (20), 53 (8), 52 (11), 51 (6), 44 (27), 43 (40), 42 (6), 41 (7), 40 (8), 39 (14), m/e (%).

The UV spectra were recorded on a Specord UV/VIS, Carl Zeiss Spectrometer (solvent: anhydrous methanol). The IR spectra were recorded on a Pye Unicam spectrometer (KBr pellets). The ^1H NMR analyses were performed in chloroform-d on a Cameca-350 MHz apparatus. The mass spectra are obtained on a MS 902S mass spectrometer at ionization chamber temperature 60°C, ionizing voltage of 70 eV and emission 100 μA.

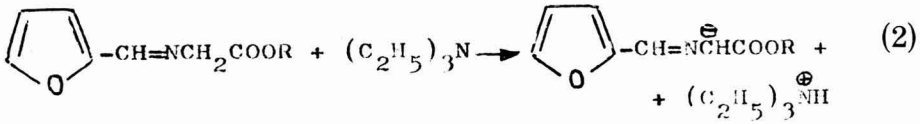
RESULTS AND DISCUSSION

It is known that the interaction between furfural and glycine results in the formation of a Schiff base which is stable only in alkaline medium. For that reason it may be isolated only as a salt. Because of the instability and the high reactivity of the products, glycine esters are used in the present study as a model of the initial step of furfural participation in melanoidin formation. In foodstuffs the Maillard reaction takes place mainly as an interaction between reducing sugars and the amino groups of amino acids. The carboxyl groups in proteins are converted into amide groups. Thus the protection of the glycine carboxyl group is proper because it resembles the melanoidin formation in nature.

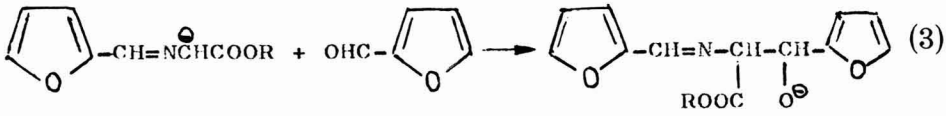
N-furylidene-β-(2-furyl)serine, methyl and ethyl esters instead of the expected esters of the Schiff base are obtained by the interaction between furfural and glycine esters with triethylamine as the catalyst. The compounds obtained are products of condensation of the ester of the Schiff base with one more molecule of furfural. A carbanion is formed by the interaction between triethylamine and the acid hydrogen atoms of the intermediate Schiff base (reaction 2). It may be assumed that the reaction proceeds as follows:



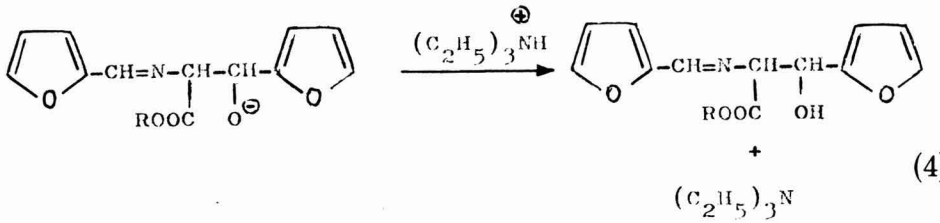
(1)



(2)



(3)



(4)

R= $-CH_3$ (V) ; R = $-C_2H_5$ (VI)

Obviously, the mild reaction conditions used—low temperature and a weak base as a catalyst—allow the stopping of the reaction at its initial step and the isolation of the products at good yields. N-furylidene-β-(2-furyl)serine, methyl and ethyl esters have not been described in the literature up to now. The structure of these compounds are confirmed by elemental analyses data, IR, NMR and mass spectra. The mass spectra of (V) and (VI) show all fragments of the structures proposed. Figures 1 and 2 may be proposed for the fragmentation of (V) and (VI).

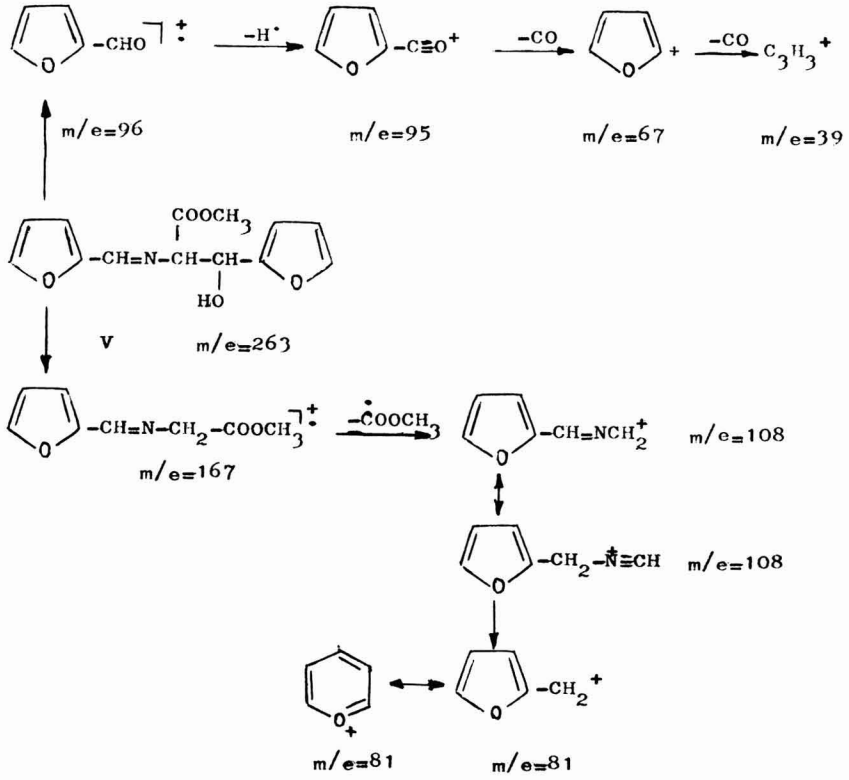


FIG. 1. HYPOTHETICAL MASS SPECTRAL FRAGMENTATION OF N-FURYLIDENE-β-(2-FURYL)SERINE, METHYL ESTER (V)

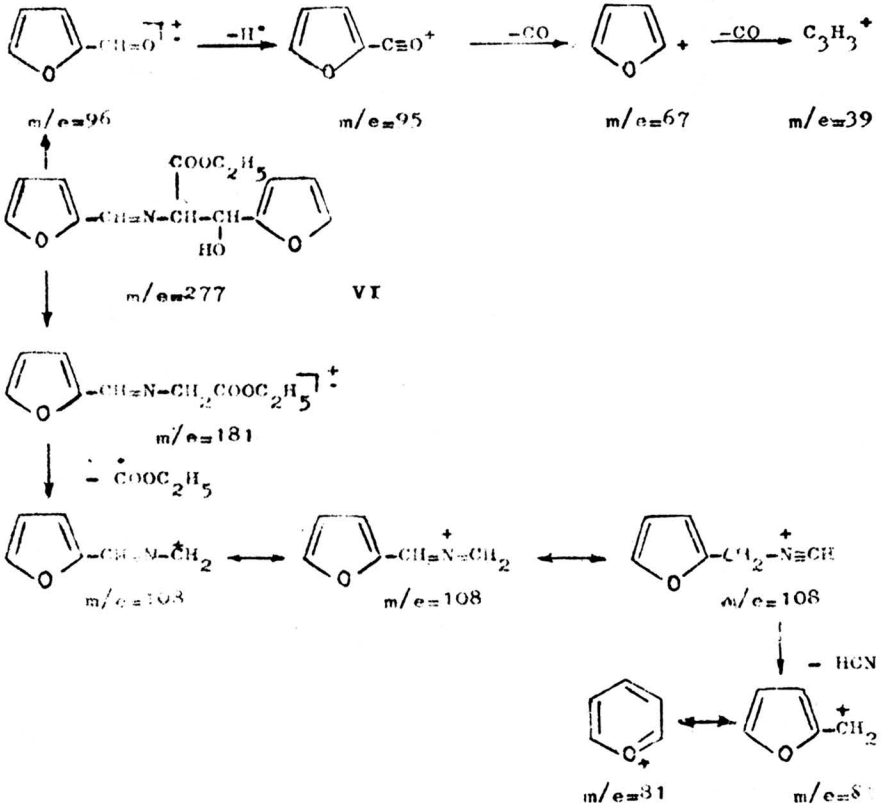
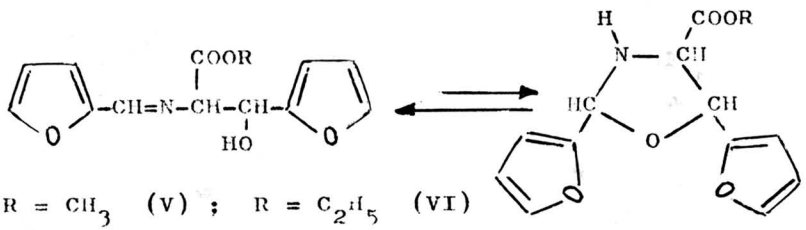


FIG. 2. HYPOTHETICAL MASS SPECTRAL FRAGMENTATION OF N-FURYLIDENE-β-(2-FURYL)SERINE, ETHYL ESTER (VI)

The structure of (V) is proved also by comparison with independently synthesized samples. As seen from Fig. 3 the compounds (III) and (V) are identical. This proves the erythro configuration of (V).

The ^{1}H NMR spectra of solutions of (V) and (VI) show that probably a part of N-furylidene-β-(2-furyl)serine, methyl and ethyl esters cyclotautomerize in solution resulting in the corresponding oxazolidines (reaction 5):



R = CH_3 (V) ; R = C_2H_5 (VI) (5)

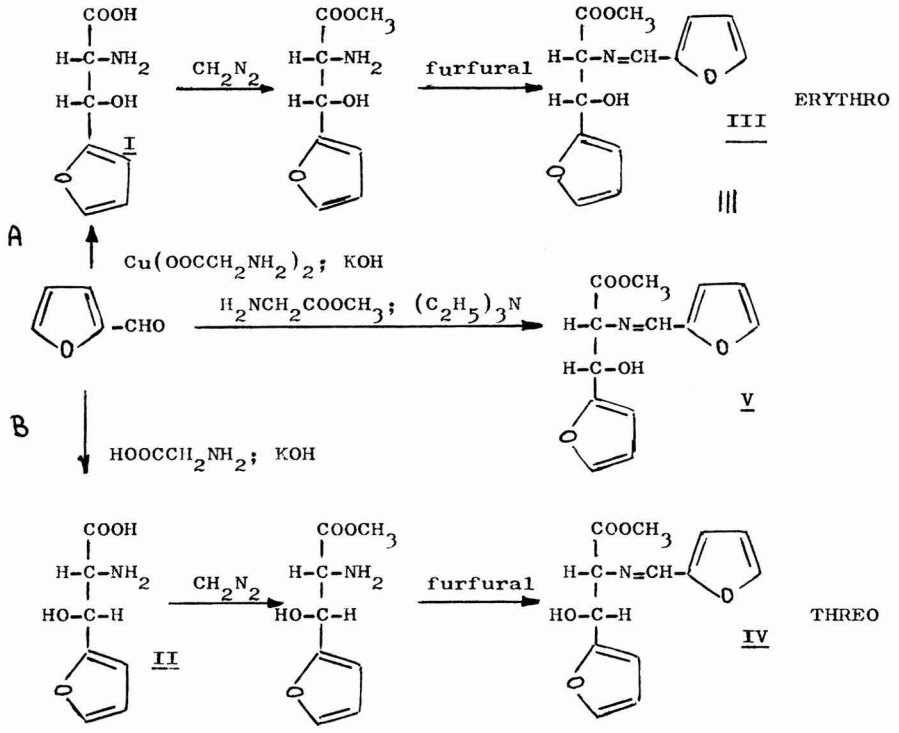
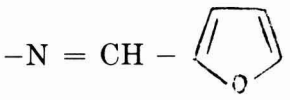


FIG. 3. VERIFICATION OF THE STRUCTURE OF THE COMPOUND (V) BY THE INDEPENDENT SYNTHESES A AND B OF ERYTHRO- AND THREO-N-FURYLIDENE-β-(2-FURYL)SERINE, METHYL ESTER

The possibility of such cyclotautomerization at acylation of esters of N-arylidene-β-arylserine is shown by Bergmann *et al.* (1951). In order to investigate the cyclotautomerization, acylation of (V) and (VI) has been carried out in the present study. The N-acetyloxazolidine derivatives of (V)-(VIIa) and (VIIb) have been obtained. The products probably are isomers. Only the N-acetyl derivative (VIII) and traces of a product with $R_f = 0.85$ which has not been isolated have been formed from (VI) by acylation.

The cyclic structure of (VIIa), (VIIb) and (VIII) is confirmed by spectral data. No spectral evidence for the chromophore



is present in the UV spectra. -N=CH groups are not detected by IR and NMR spectroscopy. The mass spectra of the compounds substantially differ from the mass spectra of (V) and (VI). The fragmentation

of the oxazolidine cycle complicates the spectra by increasing the number of fragments and decreasing their percentage.

The formation of N-acetyl derivatives of their cyclic forms at acylation of (V) and (VI) proves the possibility of proceeding of the cyclotautomerization (5) in solutions.

ACKNOWLEDGMENTS

The authors kindly acknowledge Dr. Q.T. Pham—CNRS, Laboratoire des Matériaux Organiques et Service Central d'Analyses, Vernaison, France for recording the NMR spectra.

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BOOK REVIEWS

CRC Handbook of Lethality Guides for Low Acid Canned Foods. C.R. Stumbo, K.S. Purohit, T.V. Ramalerishnan, D.A. Evans and F.J. Francis. CRC Press, 2000 N.W. 24th Street, Boca Raton, Florida 33431. 1983. Volume I Convection Heating $74.50, Volume II Convection Heating $74.50 ($85 Outside U.S.)

The two volumes represent many thousands of hours of calculations of process times for low acid canned foods (LACF). Volume I gives a brief introduction to process time calculations for LACF using both the Ball Formula and Stumbo Method. Consideration is given to calculations for food safety (12D reduction for *C. botulinum* with a D_{250} of 0.2 min) as well as for commercial sterility (4D reduction for *C. sporogenes* with a D_{250} of 1.5 min). The introduction to Volume I contains tables of calculated process times for both safety and sterility based on input data of Z value (12 to 24), f_H values, can size, retort temperature, and product initial temperature. The tables cover almost 500 pages and are based on the actual ranges of the above parameters experienced in industry. Thus one could use the table to simply establish a process time by only measuring the f_H value for the particular product and then assuming the organism has the lowest Z value possible and that the initial temperature is low. Volume II after a brief introduction has the calculated values for convection heated foods. These two books, although expensive, are extremely valuable for anyone doing thermal processing in industry.

Dr. Theodore P. Labuza

The Role of Food Product Development in Implementing Dietary Guidelines. Edited by G.E. Livingston, R.J. Moshy, and C.M. Chang. Food and Nutrition Press, Inc., Westport, Connecticut, 06880. 121 pp. 1980. $34.00.

The 14 chapters of this book resulted from a conference sponsored by the American Health Foundation Food and Nutrition Committee in April, 1979. The purpose of the conference was to consider the implication of the dietary guideline for agriculture and the food industry.

The authors of each chapter are extremely qualified and often considered top experts in their field. Unfortunately, as with any symposia, it is difficult to see the continuity between the chapters and some authors do not relate or have difficulty in relating their area of expertise to the topic at hand.

Journal of Food Processing and Preservation 7 (1983) 127-129.

The most refreshing chapter is the one by Donald Sullivan from Botsford Ketchin who delivered suggestions on motivating the consumer to follow the "dietary guidelines."

The text is easy to read and concepts and summaries are clearly stated. It contains much useful information. Many excellent points are made regarding the government's interaction in the area of dietary guidelines.

For those professionals interested in developing and selling products related to the dietary guidelines, it is the only book of its kind which even addresses the problems and issues in the area.

Dr. M.K. Schmidl

Review of Meat Microbiology. Edited by M.H. Brown, Applied Science Publishers, London.

This book is a collection of chapters written by specialists on specific commodities and on quality assurance aspects of meat microbiology. The contributors work in the United Kingdom, New Zealand, Northern Ireland, or France. Consequently, many of the references to specifics are framed for the processing industries of those countries.

The chapter on microbiology of carcass meats by Nottingham begins at the elementary level and proceeds through recent concerns over specific microorganisms of significance such as *Aeromonas putrifaciens.* Mead uses a similar treatment on poultry and game birds with special sections on the hung game bird and the uneviscerated bird for specific markets. Chapters on fresh meat processing by Sutherland and Varnum, on bacon and ham by Gardner, and on by-products by Swingler cover specific commodity aspects; whereas, the chapter on microbial interactions with meat by Gill considers meat composition, attachment, growth, and microbial degradation from a fundamental point of view. This chapter coupled with the one on chilling, freezing, and thawing by Rosset form a matrix with the earlier chapter on commodities.

Roberts has constructed a comprehensive chapter on bacteria of public health significance in meats that blend well with the earlier commodity chapters. The chapter on sampling schemes and limits by Kelsby is useful in reviewing and understanding the general approach to statistically significant measurement of microorganisms. Finally, Brown and Baird-Parker comment on microbiological examination of meats and describe a variety of specifications and interpretations. This chapter is especially useful if the methodology and the interpretation are consistent with the locale in which the microbiology is being conducted. Obviously this book has considerable value in the UK or Europe and should be useful to any organization that intends to

manufacture or distribute product in those regions. Also, with appropriate interpretation or from a fundamental information standpoint, this book has materials that are valuable for anyone working in the area of meat microbiology.

F.F. Busta

Food Engineering and Dairy Technology, by H.G. Kessler. Verlag A. Kessler, P.O. Box 1721, D-8050 Freising (F.R. Germany).

This is the English edition of the book, published in 1976 in the German language. The first two chapters deal with principles of fluid mechanics and heat transfer. Mechanical separation, ultrafiltration, reverse osmosis and electrodialysis processes with applications in the milk industry are described in the next couple of chapters. A large part of the book deals with thermal processes which include one chapter on pasteurization and sterilization. This is followed by a discussion on concentration by evaporation and freeze drying. Principles of psychrometry, absorption and desorption, and drying of food products are described next. One chapter is devoted to packaging. A major part of rest of the book deals with applications of basic engineering principles to the following processes: buttermaking, cheese manufacture, fluid milk processing, ice cream manufacture and whey processing. The last section of the book deals with pumps, stirrers, mixers, cleaning and effluent treatment. Thermophysical data on dairy and a few other food products is given at the end of the book followed by 374, mainly German, references.

Given the nature of the subject, the author has done a remarkable job in organizing and presenting information in a fashion which can be easily followed by the reader with rudimentary knowledge of engineering principles. This book is highly recommended for engineers and food technologists working in the food industry. The book is not intended as a textbook for engineering students. For food science students this book presents potential problems, for example: (1) the symbols used in the book are different than what most of the students are used to, (2) most of the references are in German which are difficult to trace by an average student, and (3) there are no worked example problems or practice problem sets.

There are no references cited for the tables on the physical data. It seems the author intended to have these included but they were missed during printing. This is indicated by the empty parentheses on pages 584, 585, 589 and 591. This book is an excellent reference material and is a must for all Food Science libraries.

A. Bakshi

F
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P

JOURNALS AND BOOKS IN FOOD SCIENCE AND NUTRITION

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GUIDE FOR AUTHORS

Typewritten manuscripts in triplicate should be submitted to the editorial office. The typing should be double-spaced throughout with one-inch margins on all sides.

Page one should contain: the title, which should be concise and informative; the complete name(s) of the author(s); affiliation of the author(s); a running title of 40 characters or less; and the name and mail address to whom correspondence should be sent.

Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

The main text should begin on page three and will ordinarily have the following arrangement:

Introduction: This should be brief and state the reason for the work in relation to the field. It should indicate what new contribution is made by the work described.

Materials and Methods: Enough information should be provided to allow other investigators to repeat the work. Avoid repeating the details of procedures which have already been published elsewhere.

Results: The results should be presented as concisely as possible. Do not use tables *and* figures for presentation of the same data.

Discussion: The discussion section should be used for the interpretation of results. The results should not be repeated.

In some cases it might be desirable to combine results and discussion sections.

References: References should be given in the text by the surname of the authors and the year. *Et al.* should be used in the text when there are more than two authors. All authors should be given in the References section. In the Reference section the references should be listed alphabetically. See below for style to be used.

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HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57*, 142–147.

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Table 1. Activity of potato acyl-hydrolases on neutral lipids, galactolipids, and phospholipids

Description of experimental work or explanation of symbols should go below the table proper.

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Short notes will be published where the information is deemed sufficiently important to warrant rapid publication. The format for short papers may be similar to that for regular papers but more concisely written. Short notes may be of a less general nature and written principally for specialists in the particular area with which the manuscript is dealing. Manuscripts which do not meet the requirement of importance and necessity for rapid publication will, after notification of the author(s), be treated as regular papers. Regular papers may be very short.

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JOURNAL OF FOOD PROCESSING AND PRESERVATION VOL. 7, NO. 2

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