GAS PLASMA IRRADIATION OF RICE

III. Influence on Brown Rice and Rice Bran[1]

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ABSTRACT

Rice bran and brown rice were treated with gas plasma irradiation to determine its effects on oil stability and on certain other physical properties of the petroleum ether solubles.

The rate of free fatty acid development in the lipids of stored brown rice and in the stored bran separated from rice kernels was much slower in gas plasma-irradiated samples than in nonirradiated controls. Gas plasma irradiation profoundly changed the chemical and physical characteristics of rice oil from both stored brown rice and stored separated rice bran. The average molecular weight of the oil extracted from irradiated rice bran had increased. In addition, the oil was less saturated than that of the nonirradiated controls. The investigation demonstrated that these changes are effected specifically by the gas plasma irradiation rather than by the coincidental heat-vacuum effect of irradiation.

The lipids in brown rice and in bran separated from rice kernels undergo a rapid hydrolysis with formation of free fatty acids (3). This is a disadvantage in the production of a commercial edible oil and necessitates the immediate treatment of the bran, either by extraction, drying, steaming, or chemical treatment, to prevent this free fatty acid formation (9,10). It has been found that decreasing storage temperature of bran tends to retard free fatty acid formation (8). Also, if the bran is sufficiently dried and maintained at a low moisture content, the increase of free fatty acid content is retarded (7,8).

It has been reported that the use of a glow discharge irradiation treatment was effective in modifying various oils (17) and in altering the properties of cotton fiber wax (15). Recent investigations in this laboratory (5,11) have shown that the marked changes in the hydration characteristics and appearance of milled rice subjected to similar irradiation treatments were due primarily to the coincidental heat vacuum treatment.

The present study was undertaken to determine if gas plasma irradiation exerted any influence on the stability of the oil in rice bran or brown rice and to ascertain if the petroleum ether-extractable

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lipids from irradiated bran or brown rice differed from that extracted from nonirradiated controls.

Materials and Methods

Brown Rice. Bluebonnet 50 variety rice, 1959 crop of foundation seed, was obtained near Crowley, Louisiana. Immediately after harvesting, the rice was dried under ambient conditions and stored at 15°C. It was dehulled as required and the whole-grain brown rice was separated in accordance with standard small-scale shelling and grading methods (12,14).

Bran. Rice bran was obtained by milling in accordance with standard laboratory milling procedures (12,13). It was then passed through a 20-mesh sieve, and the bran collected in a container held in dry ice. Portions of this material, which were not immediately required, were transferred to a freezer at about −22°C. These precautions were successful in retarding the development of free fatty acids in the bran.

Apparatus. A schematic diagram and description of the irradiation apparatus were given in the previous papers of this series (5,11). It is illustrated in Fig. 1. For certain experiments, temperature control of the sample under treatment was attained by water-jacketing the irradi-

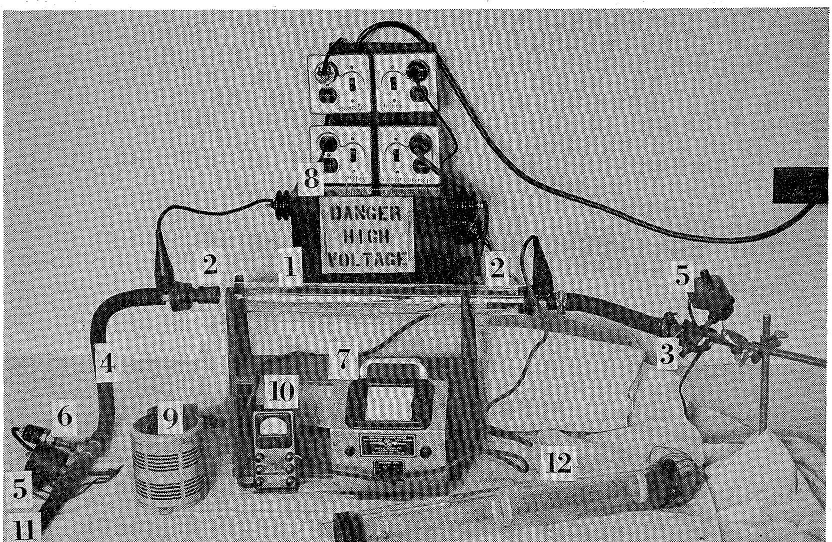

Fig. 1. Gas plasma irradiation apparatus: 1, glass tube; 2, black iron couplings (electrodes) mounted in rubber stoppers by means of short nipples; 3, needle valve; 4, rubber pressure tubing; 5, two-way solenoid valve; 6, pressure-sensing element; 7, absolute pressure indicator; 8, luminous-tube transformer; 9, variable transformer; 10, milliammeter; 11, vacuum-pump attachment; 12, jacketed glass tube.

ation chamber and controlling the temperature of the water (5).

Brown Rice Treatment. Freshly hulled brown rice, 30 g., was irradiated for 15 min. at 50 ma. intensity and at 2 mm. of mercury. A great many batches were treated and consolidated into one lot, which was mixed for 5 min. in a Twin shell dry blender[5] to assure sample uniformity. The irradiated brown rice and two controls (an untreated brown rice and a vacuum-treated nonirradiated brown rice treated for 15 min. at 2 mm. of mercury) were placed in kraft paper bags and stored at ambient conditions (approximately 23°C. and 50% r.h.). Periodically samples were withdrawn and milled in a McGill Miller (13), and the bran was collected as described in the following paragraph on bran treatment. Free fatty acids were determined on the petroleum ether-soluble material (1) of the brans, and moisture contents (16) were obtained on representative samples of the unmilled brown rice.

Bran Treatment. Bran, which had been stored in a freezer or with dry ice since its removal from the rice, was dried to about 2% moisture content in a forced-draft oven for about 3 hr. at 85°C. It was subjected to irradiation (7 min., 2 mm. mercury, 50 ma.) in 10-g. quantities. Approximately 125 g. were treated, mixed, and held at about −22°C. in sealed containers. About 8 months later the bran was placed in a desiccator containing saturated monobasic ammonium phosphate and held at a temperature of about 23°C. Relative humidity within the desiccator was approximately 92%. Prior to this and periodically thereafter samples were withdrawn for determinations of free fatty acids (1) and moisture (16). Controls consisting of an untreated bran and a nonirradiated vacuum-treated sample were handled in a similar manner.

A variation of the above study was run to evaluate the effects of different storage and treatment variables, establish more definitive experimental control, and to avoid any possible effects of the long period of cold storage prior to irradiation and vacuum treatments. The irradiation treatment (5 min., 2 mm. of mercury, 100 ma.) of freshly obtained bran was initiated 5 min. after the vacuum was first applied; thus for a 5-min. treatment the sample was held for 5 min. at 0 ma., and 5 min. at 100 ma. The corresponding nonirradiated control was held for 10 min. in vacuum at 0 ma. This was done to compensate for the variable amount of time required to evacuate the system to 2 mm. of mercury pressure. Four experimental controls were used. These consisted of an untreated sample, a nonirradiated vacuum-treated sample, an un-

[5] It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

treated bran that had been dried, and a nonirradiated vacuum-treated sample prepared in a 40°C. water-jacketed tube (5). The irradiated sample had a final moisture content of about 3%. All of the others, except the untreated sample, were dried at 85°C. to about this same moisture level. Preparation of these samples took approximately 5 days. As each sample was prepared, it was placed in a freezer (−22°C.) until all of the processing was completed. They were then transferred to sealed desiccators containing saturated sodium chloride to obtain a relative humidity of 75% and held at a room temperature of about 23°C. Samples were withdrawn at intervals for determinations of free fatty acids and moisture (1,16).

Bran Analyses. Samples, prepared in the same manner as those above but without the drying step, were used to determine total oil yield and the chemical and physical properties of the extractable oil. Total lipids were determined by a 5-hr. petroleum ether extraction in a Soxhlet apparatus. The solvent-free extract was used for the determination of Wijs iodine value (1) and molecular weight by freezing-point depression in benzene (4). The infrared spectra of the oil samples were determined in carbon tetrachloride with the Perkin-Elmer Infracord, Model 137 (see footnote 5).

Results and Discussion

The rate of free fatty acid development in irradiated brown rice was slower than in either the nonirradiated vacuum-treated control or the untreated rice (Table I). Untreated dried rice bran stored at 92% r.h. developed fatty acids (Table II) at a very rapid rate. At about

TABLE I

FREE FATTY ACID DEVELOPMENT IN BROWN RICE STORED AT 23°C. AND 50% RELATIVE HUMIDITY

Storage Time	Untreated		Nonirradiated[b]		Irradiated[c]	
	FFA[a]	Moisture	FFA	Moisture	FFA	Moisture
weeks	%	%	%	%	%	%
0	3.7	. . .	4.2	. . .	3.1	. .
3	8.7	13.5	7.5	13.2	4.8	13.0
6	10.4	13.2	9.6	13.1	6.3	12.8

[a] FFA = free fatty acids.
[b] Vacuum treatment; 15 min., 2 mm.
[c] Vacuum treatment; 15 min., 2 mm.; 50 ma. irradiation.

the seventh day, this sample had become matted, that is, it no longer had a particulate character, but was covered by very fine moldlike filaments. The moisture content of the bran at that time exceeded the hygroscopic equilibrium (18%) for these conditions. Free fatty acid

TABLE II

FREE FATTY ACID DEVELOPMENT IN BRAN[a] STORED AT 23°C. AND 92% RELATIVE HUMIDITY

STORAGE TIME	UNTREATED		NONIRRADIATED[c]		IRRADIATED[d]	
	FFA[b]	Moisture	FFA	Moisture	FFA	Moisture
days	%	%	%	%	%	%
0	1.5	3.8	1.7	4.0	1.8	4.4
3	20.7	16.9	15.8	13.7	11.9	14.8
7	46.5	20.2	35.8	17.4	26.3	17.7
10	81.9	22.3	48.2	19.1	40.7	19.2

[a] Held at —22°C. for 8 months prior to test.
[b] FFA = free fatty acids.
[c] Vacuum treatment; 7 min., 2 mm.
[d] Vacuum treatment; 7 min., 2 mm.; 50 ma. irradiation.

development increased almost twofold in the 3 days following matting of the bran by mold. Both of the treated samples were slower in developing free fatty acids and had molded less than the untreated bran. The irradiated sample was the most stable.

The four differently treated samples of freshly milled bran, which had been dried to approximately 3% moisture immediately after treatment and stored at about 75% r.h., developed free fatty acids at rates dependent upon their treatments. Free fatty acids developed most rapidly in untreated bran and most slowly in the irradiated sample (Table III). The other samples showed very little difference in their

TABLE III

FATTY ACID DEVELOPMENT IN BRAN[a] STORED AT 23°C. AND 75% RELATIVE HUMIDITY

STORAGE TIME	UNTREATED		UNTREATED AND DRIED		NON-IRRADIATED[b]		NONIRRADIATED-HEATED[c]		IRRADIATED[d]	
	FFA[e]	Moisture	FFA	Moisture	FFA	Moisture	FFA	Moisture	FFA	Moisture
days	%	%	%	%	%	%	%	%	%	%
0	2.4	13.1	2.5	2.5	2.7	3.6	2.7	3.5	...	3.3
2	9.4	13.5	5.2	9.1	4.7	9.1	5.3	9.3	4.7	10.2
5	17.7	13.4	8.7	10.9	13.5	11.2	13.9	11.0	10.7	11.5
9	26.3	14.0	23.5	12.1	23.5	12.4	23.8	12.1	15.9	12.5
16	34.4	14.4	33.8	13.5	32.0	13.3	32.5	13.4	24.1	13.3
27	52.0	14.4	53.6	13.0	54.4	13.5	53.4	13.1	32.1	12.8

[a] Held at —22°C. for less than 5 days prior to test.
[b] Vacuum treatment; 5 min., 2 mm.
[c] Vacuum treatment; 5 min., 2 mm.; heated at 40°C.
[d] Vacuum treatment; 5 min., 2 mm.; 100 ma. irradiation.
[e] FFA = free fatty acids.

rate of acid development. These data indicate that irradiation at 100 ma. for 5 min. at a pressure of 2 mm. of mercury had a definite stabilizing effect on the oil in the bran. The other conditions necessary for glow discharge, i.e. vacuum and heat, did not materially affect the rate of free fatty acid formation. A comparison of the data in Tables II and III for the untreated controls at zero days shows little change in free fatty acids in 8 months' storage at −22°C.

During these studies it was noted that there was approximately 40% less oil extractable (Table IV) by petroleum ether from the irradiated bran than from the other samples. The extracted oil from irradiated bran was plastic and almost solid at room temperature, whereas the oils from nonirradiated brans were liquid.

TABLE IV
IODINE NUMBER, MOLECULAR WEIGHT, AND YIELD OF PETROLEUM ETHER-EXTRACTABLES FROM TREATED RICE BRANS

Sample	Moisture after Treatment	Petroleum Ether-Extractables		
		Yield	Iodine Number [a]	Average Molecular Weight
	%	%		
Untreated	13.5	27.1	101	765
Nonirradiated [b]	7.8	25.9	101	...
Nonirradiated-heated [c]	5.9	24.9	101	761
Irradiated [d]	3.6	15.3	70	1243

[a] Iodine absorbed, g. per 100 g. extracted material.
[b] Vacuum treatment; 5 min., 2 mm.
[c] Vacuum treatment; 5 min., 2 mm.; heated at 40°C.
[d] Vacuum treatment; 5 min., 2 mm.; 100 ma. irradiation.

The total petroleum ether-extractables, iodine number, and molecular weight of the oil from freshly treated bran samples were determined. There was less unsaturation, as shown by the smaller iodine number. A significant amount of polymerization resulted from irradiation as indicated by the higher molecular weight. The vacuum control, which had been prepared at 40°C. to simulate the estimated highest temperature attained during a 5-min. irradiation at 100 ma., showed no difference in its properties from those of the oil from the untreated bran. The infrared spectra of all samples were identical. These results are comparable to those reported by Stone (15), who observed a decrease in the amount of wax recovered from irradiated cotton fiber.

Boelhouwer *et al.* (2), using the glow discharge but under somewhat different conditions, reported that linseed oil was polymerized. Their results were obtained by treating oil in hydrogen at a pressure of 80 mm. of mercury, 70°C., 24 ma. with an applied frequency of 500 Hertz in an apparatus rotated at 10 r.p.m. A sample treated for about 18 hr. under these conditions exhibited a molecular weight increase of about 67% and a decrease of about 22% in iodine number.

In contrast to this finding, only 5 min. of irradiation were required for a similar change in molecular weight and iodine value of rice bran oil for a treatment at 100 ma. and 2 mm. of mercury. The values reported in Table IV for the irradiated sample were obtained for the petroleum ether-extractable oil, which represented only about 57% of the initial total lipids content of the bran.

It is concluded from this study that gas-plasma irradiation, rather than heat and/or vacuum, profoundly changed the chemical and physical characteristics of rice oil from both stored brown rice and stored separated rice bran. The properties of the oil extracted by petroleum ether from irradiated rice bran indicated that polymerization had increased the average molecular weight, and that it was less saturated than the oil of the controls. The physical changes in the characteristics of the oil brought about by irradiation may be of significance in the technological uses of this product.

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