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CEREAL STORAGE EFFECTS

Deteriorative Changes in the Oil Fraction Of Stored Parboiled Rice

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Changes in the oil fraction of stored parboiled rice have been followed as criteria of loss in quality. Storage of parboiled rice in the dark at several temperatures permitted a study of rancidification and of nonenzymatic changes in the oil as measured by peroxides, monocarbonyl compounds, and free acids. In open-container storage, values for peroxides, monocarbonyls, and free acids remain low during an induction period, then rise markedly at or just before the time rancid odors appear. Peroxides and monocarbonyls again decrease to low residual values and rancidity disappears. Free acid values remain at the higher level. Original moisture contents of 11.4 to 12.5% fall to about 10% at 77° F., 6% at 100° F., and 3% at 140° F. Storage lives of two parboiled rices show the same relative order at 77°, 100°, and 140° F. Monocarbonyl maxima occurring at about 1 year at 77° F. are found after about 1 month at 140° F. and 1 week at 180° F. This observation may serve as a basis for accelerated testing of storage life. In closed storage at 77° and 100° F. peroxide and monocarbonyl changes are similar to those for open storage, though induction periods are longer. At 140° F. no rise is shown. Free acidity increases linearly for considerable periods at all three temperatures. The rancidifying effect of light on fat-containing foods was confirmed for parboiled rice during storage at 77° F.

PARBOILED RICE offers some unique advantages in studying the complex processes of deterioration in cereal grains, especially those occurring in the oil fraction. This fraction may be present as less than 1% of the grain, yet have marked effects on acceptability because of rancidity development. Both hydrolytic and oxidative rancidity may occur (*1*); hydrolytic action is favored by high moisture content and oxidative action by low moisture. The importance of biological factors in deterioration of damp grain has been summarized by Milner (*17*). The role of native cereal enzymes and of mold lipases has been discussed by Geddes (*11*), who points out that more research is necessary to evaluate their respective parts in rancidification processes.

Enzymes have been inactivated in parboiled rice. It is prepared by soaking, steaming under pressure, drying while still in the husk, and then milling in the usual manner for white rice. Besides inactivating enzymes, this wet-heat processing enriches the endosperm in solubles such as sugars, minerals, and vitamins, at least partially gelatinizes the starch, and probably destroys some of the native antioxidants. Behavior of the oil fraction of parboiled rice in storage must reflect the absence of native enzymes, as well as of fungal enzymes under conditions that do not support fungal growth.

This report presents the changes in several characteristics of the oil fraction of parboiled rice over a range of storage conditions, and provides information useful for comparison with changes in the oil of rice containing active enzymes. The trends shown offer a basis for a possible accelerated test for storage life of moist heat-processed rices such as parboiled and quick-cooking rice.

Materials

The main rice supply comprised two 100-pound lots from the 1952 harvest which had been commercially parboiled and milled. The 100 pounds of Pearl (short-grain, Pearl 1) had been prepared by a continuous process which involves the usual steeping, steaming, and drying. The Century Patna (long-grain) had been prepared by a batch process which involves subjecting the rice to a vacuum prior to addition of the steeping water. The rice was received directly after milling and was held at room temperature about 2 weeks before storage tests were started.

Another 50-pound supply of Pearl was

Component, %	Rice Stock: Pearl 1	Pearl 2	Century Patna
Moisture (5)	12.8	12.2	11.5
Ether extractable (7)	0.92	1.24	0.39
Crude fiber (8)	0.41	0.38	0.27
Ash (6)	1.09	0.92	0.72
Total nitrogen (2)[a]	0.98	0.99	1.20
Amino nitrogen[b]	0.066	..	0.065
Total sulfur (20)	0.09	..	0.10
Sulfur dioxide[c]	0.023	0.026	0
Nitrogen-free extract	78.6	79.1	79.6
Total sugars (as glucose) (3, 4, 10)[d]	1.04	1.01	0.66
Reducing sugars (as glucose) (3, 10)	0.14	0.09	0.19

Table I. Analytical Data on Parboiled Rice Supplies

[a] Kjeldahl-Wilfarth-Gunning method.
[b] Van Slyke manometric method.
[c] Adaptation of Monier-Williams method (9).
[d] Micro-Somogyi method.

obtained as rough parboiled rice, and milled in the laboratory with a McGill huller and miller. The milled rice was sieved, aspirated, and finally rubbed in a huck towel in small portions to remove adhering dust. This provided an undermilled parboiled rice (Pearl 2), which was stored at 0° F. (−18° C.) until used.

Analytical data for the three rices are given in Table I.

Methods

Storage was performed with 200-gram portions of rice either in 400-ml. beakers covered by watch glasses (open containers) or in sealed 500-ml. flat-bottomed boiling flasks (sealed containers). Samples were held at room temperature (77° ± 4° F.), 100°, and 140° F. in the main series of tests, and at 160° and 180° F. in supplementary tests. Thermostatically controlled rooms or ovens were used to maintain all elevated temperatures. One series of samples was kept under the normal diffuse daylight and artificial light of a north-exposure laboratory for testing effects of light.

The 100° F. temperature is that used by the Quartermaster Food and Container Institute in evaluating storage life of foods for military purposes. That of 140° F. approximates the temperature of the widely used Schaal oven test (19) and is also above the range in which fungi generally grow.

Peroxides were determined by Smith's (21) modification of the colorimetric ferric thiocyanate procedure of Hills and Thiel (12). Values obtained are about twice as large as those given by the iodometric method, but the procedure requires much less material and shows excellent reproducibility (16). It is well suited for comparative use in a series of measurements. As used, conveniently sized portions of rice (ground to pass 20-mesh) were shaken with benzene for 20 minutes, filtered, and washed with benzene. The filtrate was made up to 50 ml., and aliquots were added to 3 ml. of methanol. The solution was made to 10 ml. with benzene and measured as directed by Smith (21) by means of a Klett-Summerson photoelectric colorimeter with a No. 52 filter. Total oil was determined on other aliquots of the 50-ml. benzene extract. Results are given in microequivalents of oxygen per gram of oil.

Monocarbonyl compounds (essentially aldehydes) were determined according to the method of Pool and Klose (18). One- to 3-gram samples of the rice, ground to pass 20-mesh, were soaked 1 hour in 4 to 5 ml. of benzene. Solid and liquid were both transferred to the reaction column with several small portions of benzene, and the regular procedure for fats and oils was followed. Developed color in the eluates was measured on a Klett-Summerson photoelectric colorimeter fitted with a No. 42 filter. Results, reproducible to about 2%, are given in micromoles per gram of oil.

Free acidity in the oil of the stored rice was determined by the modified Ames and Licata titration (14). Reported values, averages of duplicate titrations, are in microequivalents per gram of oil.

Moisture contents were determined by heating 10-gram portions of the ground rice in a forced-draft oven at 220° F. (105° C.) for 16 hours (14).

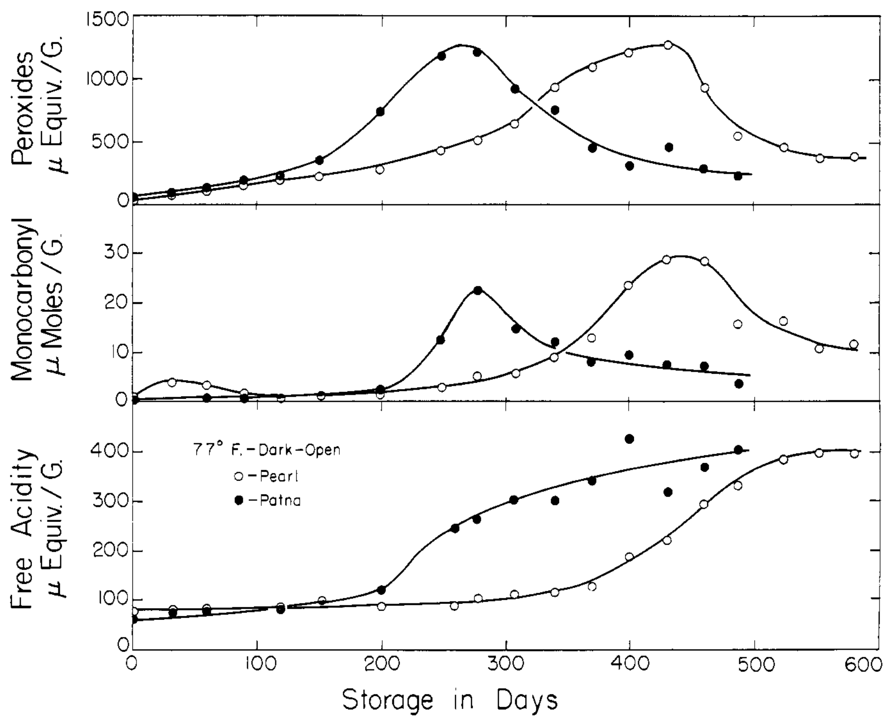
Odors of all samples were evaluated, usually by two or more persons, on removal of samples from storage.

Results and Discussion

The data may conveniently be divided for purposes of discussion into three main categories: (1) storage in open containers in the dark, (2) storage in sealed containers in the dark, and (3) storage in the light. Results are chiefly presented graphically to show the trends observed.

Open Storage In Dark The general march of events showed an induction period followed by marked increases, in rapid sequence, in the rates of formation of peroxides, monocarbonyl compounds (or aldehydes), and free acids, and then a subse-

Figure 1. Changes in oil during open storage in the dark at 77° F.



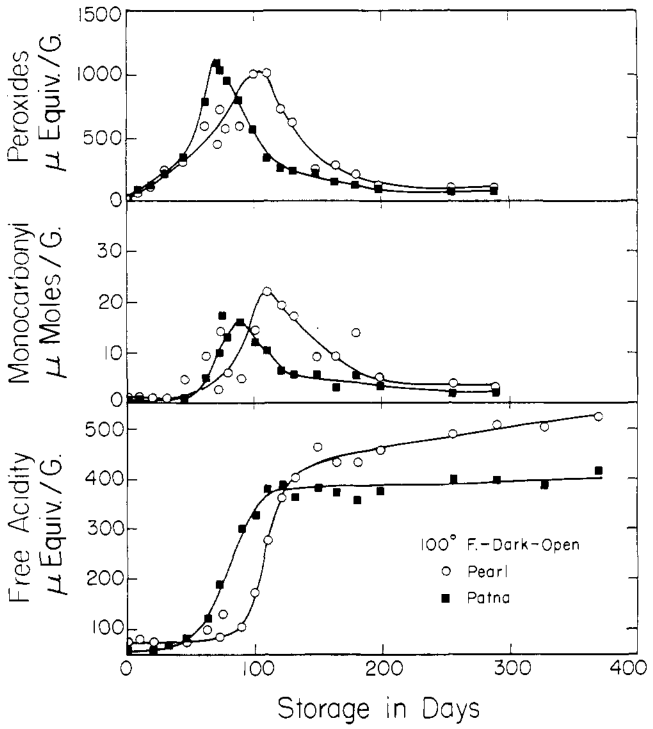


Figure 2. Changes in oil during open storage in the dark at 100° F.

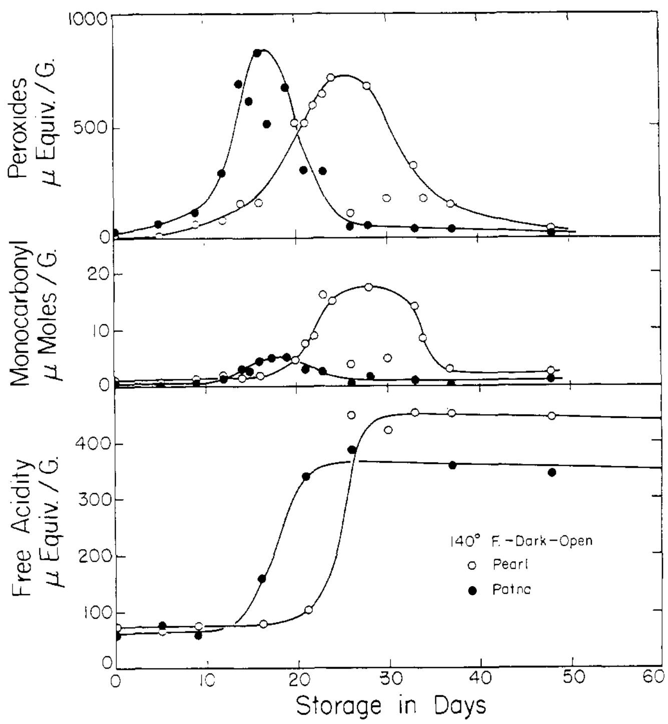


Figure 3. Changes in oil during open storage in the dark at 140° F.

quent decrease in the peroxide and monocarbonyl content of the oil. Free acidity remained at a high level or continued to increase slowly. Rancidity was detectable at or shortly after the end of the induction period. Rancid odor disappeared when peroxide and monocarbonyl values had fallen to low levels, though stale or perfumy odors sometimes remained.

These events are illustrated in Figures 1 to 3 for 77°, 100°, and 140° F. Under these test conditions the two rices maintained the same stability relative to each other. The Patna rice reached the end of the induction period slightly ahead of the Pearl at all three temperatures. This empirical relation held regardless of rate or extent of moisture loss (Table II), which was naturally greater as the storage temperature was raised.

Moisture contents of Pearl and Patna rices were strictly comparable under each exposure condition. As the moisture content of all samples was progressively—and more rapidly—lowered as temperature was raised, both drying and heating forces contributed to more rapid rancidification. This double force would also operate in commercial storage. No study of the relative importance of the two factors has been made.

The increased speed of rancidification with increase in temperature is well known, as are the accumulation and subsequent destruction of peroxides. Monocarbonyls also build up and disappear, and rancidity is evident during the time they are present. The general sequence of events fits the picture of oxidative rancidification wherein peroxides are formed and decomposed to aldehydes, which in turn are oxidized to acids. The aldehydes appear to be the most transient, and are one or two orders of magnitude less than peroxides at all times.

The ratio of peroxides to monocarbonyls is not a constant, as may be seen from Figure 3, but passes through a maximum and decreases by the time rancidity becomes evident. This accords with the observation of Pool and

Table II. Moisture Changes in Parboiled Rice During Dark Storage

77° F.			100° F.			140° F.			160° F.		180° F.	
	H_2O, %			H_2O, %			H_2O, %		Pearl 2			
Days	Pearl 1	Patna	Days	Pearl 1	Patna	Days	Pearl 1	Patna	Days	H_2O, %	Days	H_2O, %
0	12.5	11.4	0	12.5	11.4	0	12.5	11.4	0	12.2	0	12.1
32	11.7	11.0	10	10.7	8.9	5	7.5	6.2	4	6.0	3	4.9
60	11.2	10.7	21	7.5	7.4	9	5.6	5.7	7	4.1	6	3.1
90	11.0	10.6	32	7.1	6.6	14	4.5	4.6	9	3.9	7	2.4
151	10.1	10.0	46	7.3	6.7	19	4.0	3.8	11	3.6	8	2.2
200	10.3	10.0	63	6.5	6.4	26	2.7	2.6	13	3.2	9	1.8
249	10.4	10.2	73	6.8	6.6	37	3.1	3.0	15	2.6	10	1.7
308	10.6	10.5	90	6.5	6.3	48	2.6	3.1	18	2.6	13	1.8
340	10.6	10.5	111	6.1	6.2				20	2.3		
400	10.3	10.4	132	5.9	6.0				25	2.2		
431	10.0	10.0	181	6.1	6.2							
461	10.1	9.9	290	6.5	6.8							
523	9.8	...										
580	9.9	...										

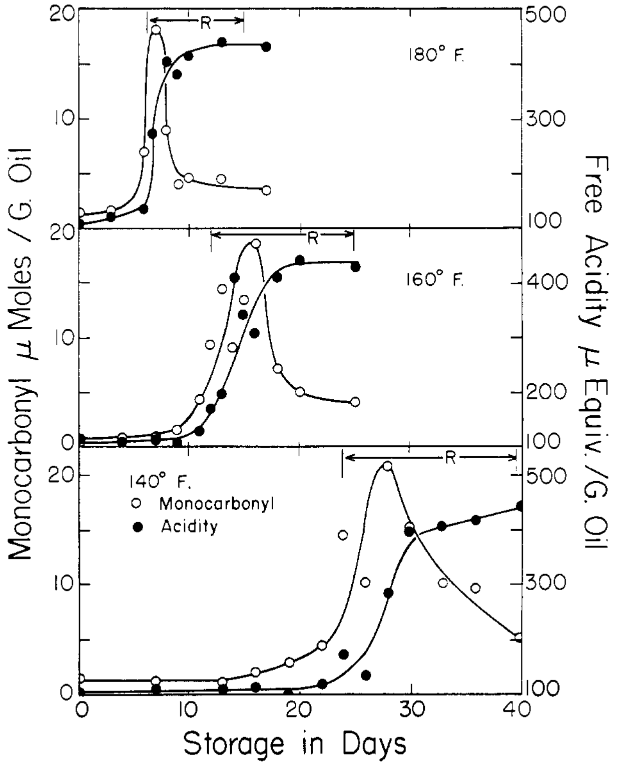


Figure 4. Changes in oil during open storage in the dark at 140° to 180° F.

Klose (*18*) on fat-containing vegetable foods, but contrasts with the excellent correlation found by Klose and others (*15*) in the fat of stored poultry.

The regular appearance of rancid odors at or just following the times at which monocarbonyl values begin to show a rapid increase indicates that measurement of monocarbonyl content should prove a valuable objective test for the onset of rancidification.

Supplementary storage tests, using the Pearl 2 sample and measuring monocarbonyl and acidity values, were made at 140°, 160°, and 180° F. The results, presented in Figure 4, show the same course of reaction as at the lower temperatures, and the same mechanism apparently holds over the range 77° to 180° F. If the times required to reach maximum monocarbonyl content are plotted against temperature (Figure 5), the points fall on a smooth, apparently hyperbolic curve. These facts suggest that microorganisms did not play a significant part in the reactions under consideration. If they had, an expected increased metabolism at optimal growth temperatures (around 100° F.) would have been reflected in an irregularity in the curve.

The foregoing discussion indicates that open storage of parboiled rice in the dark at elevated temperatures forms the basis of an accelerated storage test. For instance, a sample which showed maximum monocarbonyl content after some 450 days at room temperatures reached a corresponding maximum at 7 days at 180° F. Further development would, of course, be necessary to establish the general validity of such a test.

Sealed Storage In Dark At room temperature (Figure 6) the occurrences of rancid odors, peroxides, monocarbonyls, and free acids in rice in sealed containers are qualitatively very similar to the same phenomena in open containers, except that induction periods are somewhat longer. There is also a general development of a slightly sour odor, suggesting fermentation. During the induction period, free acidity increases slowly at a linear rate. These samples, unlike those stored in open containers, retain their original moisture content.

Reactions at 100° F. show slight differences (Figure 7). Peroxide and monocarbonyl values remain smaller than those for the rice stored at room temperature. Moreover, the breaks in the curves for free acidity are less abrupt than in previously discussed tests.

At 140° F. (Figure 8) the reaction picture is decidedly different. There is no increase whatever in eproxide or monocarbonyl values, and free acidity shows a linear increase for at least 70 days. There is little, if any, development of rancid odors. Fermentative odors (including that of butanol) become strong and are accompanied by those of protein degradation. A considerable change in over-all reaction mechanisms has occurred, and no useful accelerated test is evident. Supplementary tests run on Pearl 2 in sealed containers at five temperatures between 77° and 180° F. gave linear acidity increases with time in all cases. When the rates of these increases are plotted against temperature, the points fall on a parabolic curve (Figure 9). This shows a linear relation on log-log paper, and the curve may be expressed by an equation of the type,

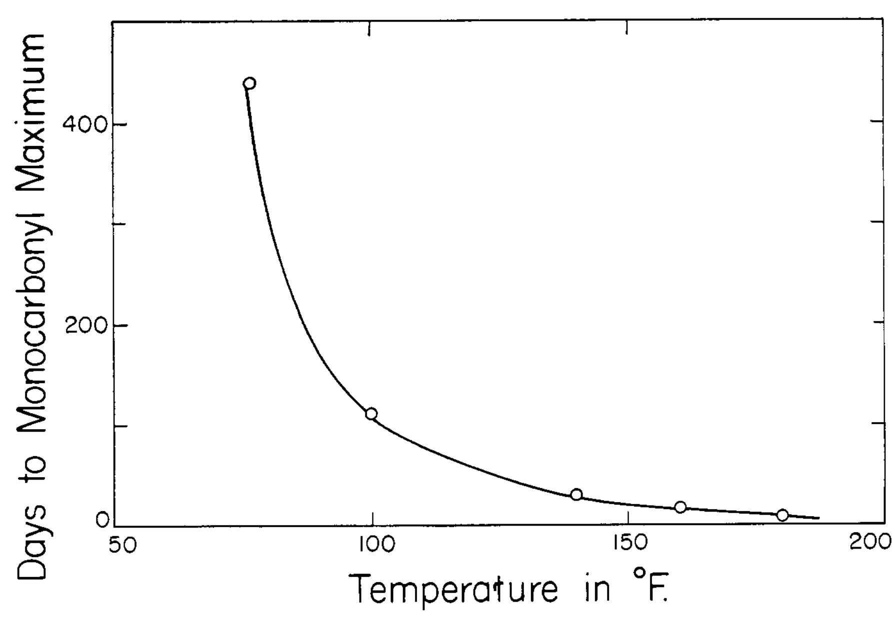
$$R = at^x$$

where R is the rate of acidity increase, t is temperature, and a and x are constants. The numerical values would, of course, vary with the moisture content and other characteristics of the rice, as well as with the processing it has received.

Enzymes and microflora appear not to be causative agents in this acidity development, for enzymes have been inactivated during the processing, and the change in rates of acid formation continues smoothly into temperature ranges above those ordinarily permitting growth of microflora.

Storage In Light Light has, as expected, a considerable effect in reducing the storage life of parboiled rice maintained at room temperature. The time to reach rancidity in open storage (Table III) as judged by odor was reduced from 250 to 160 days for Patna, and from 400 to 75 for Pearl

Figure 5. Time to reach maximum aldehyde content *vs.* temperature for open storage in the dark



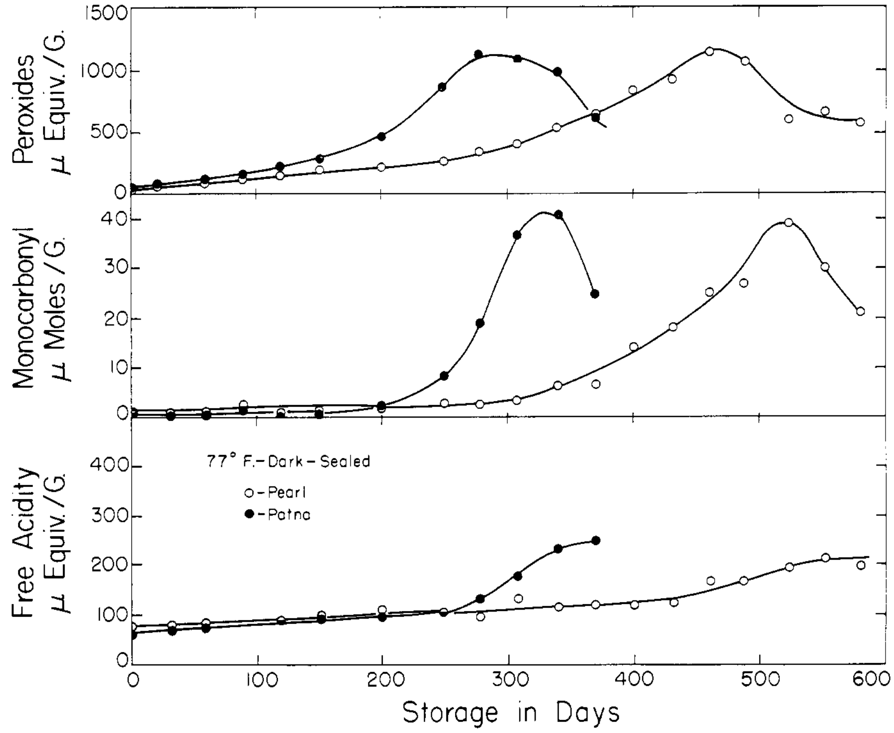


Figure 6. Changes in oil during sealed storage in the dark at 77° F.

rice. The markedly greater effect on Pearl rice may be connected with the presence of sulfur dioxide in the grain, and experiments have been designed to test this point.

Little, if any, induction period precedes changes in the measured oil characteristics during open storage in the light for either type of rice. Moreover, differences between samples in open and in closed storage (Table III) are appreciably less than were found during storage in the dark. The considerable irregularity of data for Pearl rice may reflect in part some unevenness of illumination. This is not the only cause, however, for the Patna rice stored under the same conditions is much more regular. The additional effect in the Pearl is attributed to a greater variation in characteristics among individual grains within the test samples than occurs in the Patna rice.

General Finally, an advantage of studying parboiled rice is its difference from raw rice. Information is still too meager to permit any extensive comparison between the two types, though investigations now planned or under way will permit increased evaluation of the differences. Development of acidity follows separate courses in raw and in parboiled rice. This difference corresponds to that found (*13*) for acids developing in the dark at 77° F. for raw brown rice and for brown rice from steamed and dried paddy. This latter material corresponds to parboiled rice in its behavior. The rapid early increase of acids in raw brown rice has been attributed to the effect of enzymes.

In addition to extending the present study to a comparison with the behavior of the oil fraction in raw white rice, other topics of importance are suggested, such as the effect of moisture differences on changes not caused by microflora and the relationship of changes in the oil fraction to those occurring in other constituents of the rice kernel, particularly the starch and protein.

Acknowledgment

The authors wish to thank Arthur Bevenue, Marion C. Long, Earl F. Potter, and Henry Wright for determination of the analytical data on the rice supplies, and N. Floy Bracelin for preparing the illustrations.

The Pearl rice was supplied through

Figure 7. Changes in oil during sealed storage in the dark at 100° F.

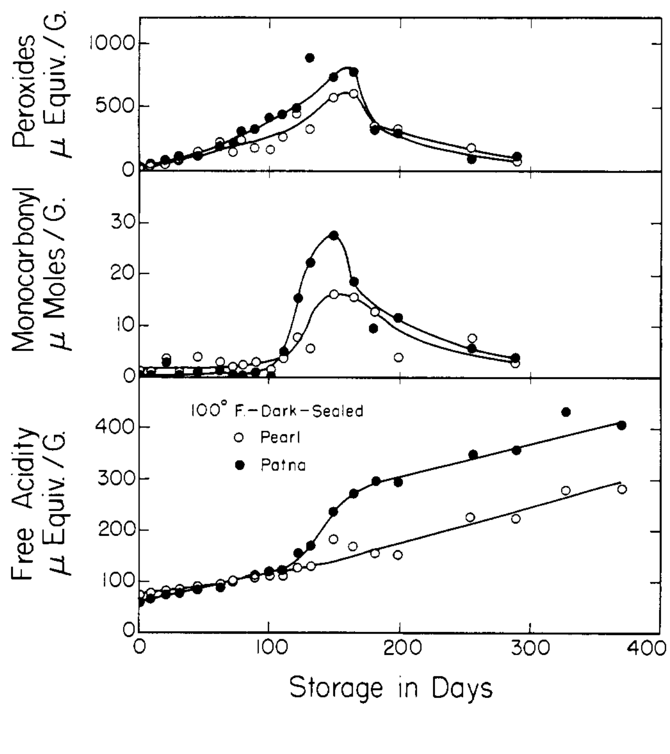


Figure 8. Changes in oil during sealed storage in the dark at 140° F.

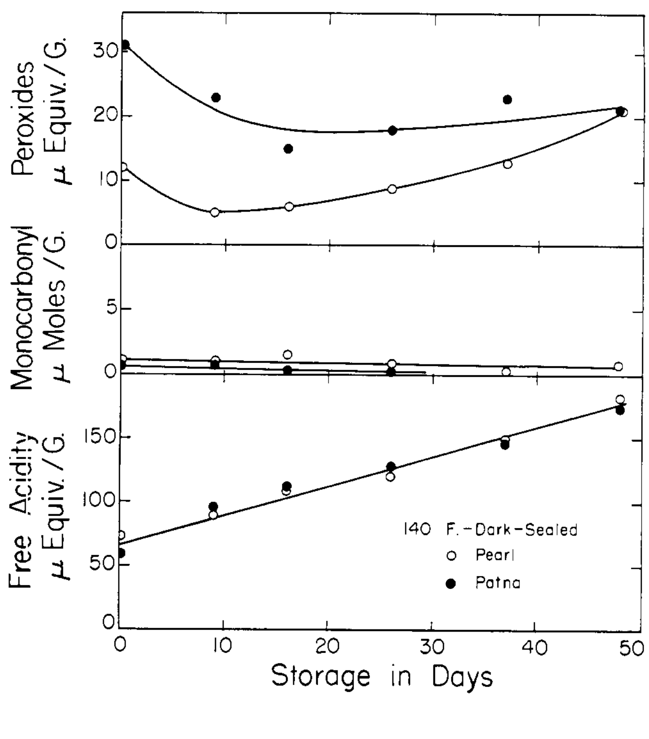


Table III. Storage of Parboiled Rice at Room Temperature (77° F.) in Light

Storage, Days	Open Containers								Sealed Containers					
	Pearl 1				Patna				Pearl 1			Patna		
	H_2O, %	CO[a]	PV[b]	FA[c]	H_2O, %	CO	PV	FA	CO	PV	FA	CO	PV	FA
0	12.5	1.1	12	73	11.4	0.8	31	58	1.1	12	73	0.8	31	58
28	11.3	3.9	421	74	10.7	1.5	227	66	4.7	409	77	0.5	175	70
39	...	8.2	746	77	...	2.3	408	...	8.5	676	86	1.0	314	...
53	11.0	9.8	564	85	10.6	3.0	404	75	7.3	486	82	3.6	381	71
63	10.5	15.1	829	89	10.6	1.5	278	86	24.6	1200	90	2.8	404	85
70	...	18.6	1103	...	...	...	...	...	12.2	756	...	...	...	...
77	10.6	8.4	647	88	10.5	3.0	361	87	10.3	515	91	2.6	379	81
89	10.6	17.6	1220	105	10.4	0.7	577	92	16.0	946	100	6.2	894	87
98	...	22.3	1104	116	...	9.9	984	108	24.5	1158	110	6.2	653	94
109	10.0	19.2	1046	136	9.8	6.6	881	121	30.2	1162	118	9.0	891	107
123	...	31.6	1393	168	...	12.6	1288	227	24.5	1165	112	11.5	859	100
137	9.8	32.7	1265	197	9.7	11.1	1183	155	42.6	1411	140	17.7	938	127
161	...	24.8	1005	150	...	20.4	1277	143	42.6	1296	171	26.7	1160	151
186	9.7	40.9	964	213	9.7	20.4	1295	222	42.2	1001	165	...	...	...
209	...	34.6	878	249	...	22.2	1058	216	50.2	989	191	51.3	1230	181
252	10.1	18.7	756	350	10.0	14.6	738	303	31.5	854	203	30.3	887	234
280	...	20.6	766	413	...	11.6	672	345	27.5	520	213	...	...	...
320	...	12.1	524	390	...	3.8	473	345	17.4	469	229	...	...	...
365	9.9	8.0	276	436	9.8	5.0	141	352	17.2	316	218	...	...	...

[a] Monocarbonyl values, micromoles per gram of oil.
[b] Peroxide values, microequivalents of oxygen per gram of oil.
[c] Free acidity, microequivalents per gram of oil.

the courtesy of R. R. Mickus, Rice Growers' Association of California, Sacramento, Calif. The Century Patna rice was supplied through the courtesy of K. K. Keneaster, Converted Rice, Inc., Houston, Tex.

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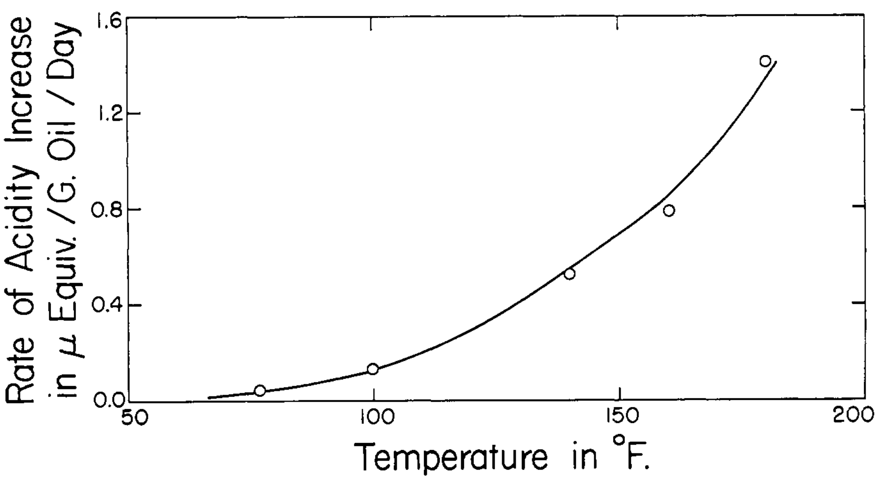
Figure 9. Relation of temperature to rates of acidity increase for sealed storage in the dark



Taste and Odor — Correction

In the article on "Taste and Odor. Study of Tastes and Odors Produced by Chloridation of Simple Nitrogenous Compounds" [Ingols, R. S., Hodgden, H. W., and Hildebrand, J. C., J. Agr. Food Chem., **2**, 1068 (1954)] the third column of page 1068, the fifth line should read "excess hypochlorous acid." In the second paragraph, the sixth from the last line should read "amino acid derivative was detected." In the last line "studies" should be "studied." On page 1069, first column, the second line above Table I should read "hypochlorous acid." In the Literature Cited, (5), the third line should read "Fincher, E." In Table I the heading in the right-hand column should read "P.P.B."