Storage Changes in Parboiled Rice

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Color changes during storage of Pearl (Caloro) and Century Patna parboiled rice were shown to be negligible for about one year at room temperature, 77° F. (25° C.) in either open or sealed containers. At 100° F. (37.8° C.) and 140° F. (60° C.) the changes appeared after 3 to 4 months, due to nonenzymatic browning, accompanied by losses of reducing sugars, amino nitrogen, and free amino acids. Analyses were too insensitive to follow browning during storage. Sulfur dioxide added to the Pearl rice during parboiling inhibited browning, and gradually disappeared during storage, but did not delay rancidification. Varietal and process effects were evaluated by accelerated storage tests at 140° F. Moisture contents decreased from about 11 to 3.5% during 28 days of storage. Varietal differences had a minor effect on rancidification, but process differences greatly changed the keeping quality of a single variety.

The unique value of using parboiled rice in studies of the complex processes of deterioration in cereal grains has been pointed out (*7*) in connection with an investigation of the contained oil. The lack of complication by native cereal enzymes, which are destroyed during parboiling, applies also to changes in grain constituents other than the oil. Observations on some of these changes, made concurrently with the oil studies, are reported herein.

Parboiled rice of domestic manufacture has a light to medium amber color and is richer than white rice in such solubles as vitamins, minerals, and sugars (*12*). Color development varies with processing conditions (*17*) and has been attributed to the Maillard or "nonenzymatic browning" reaction. This reaction, involving reducing sugars and amino-nitrogen compounds, has recently been reviewed by Hodge (*6*). The color of parboiled rice deepens during storage at elevated temperatures. Observation of this deepening of color and measurement of changes in related constituents indicate that this is a further stage of nonenzymatic browning.

Properties of parboiled rice are affected to some extent by the processing conditions used in its manufacture. Varietal differences may also be reflected in the product. Kik (*11, 13, 14*) has made extensive investigations of the effects of various parboiling conditions on milling quality and vitamin contents of the milled product. Roberts and coworkers (*17*) recently found that physical properties of parboiled rice vary with severity of processing conditions. Rao and coworkers (*16*) have shown that parboiled rice rancidifies more rapidly than white rice.

Storage studies from this laboratory (*7*) demonstrated that stability differences occur between different parboiled rices, that these can be objectively recognized and evaluated, and that elevated-temperature storage gives comparable results in reduced time.

This report presents data which allow partial evaluation of the separate influences of variety and processing on the stability of the resulting parboiled rice.

Color Increases and Compositional Changes during Storage

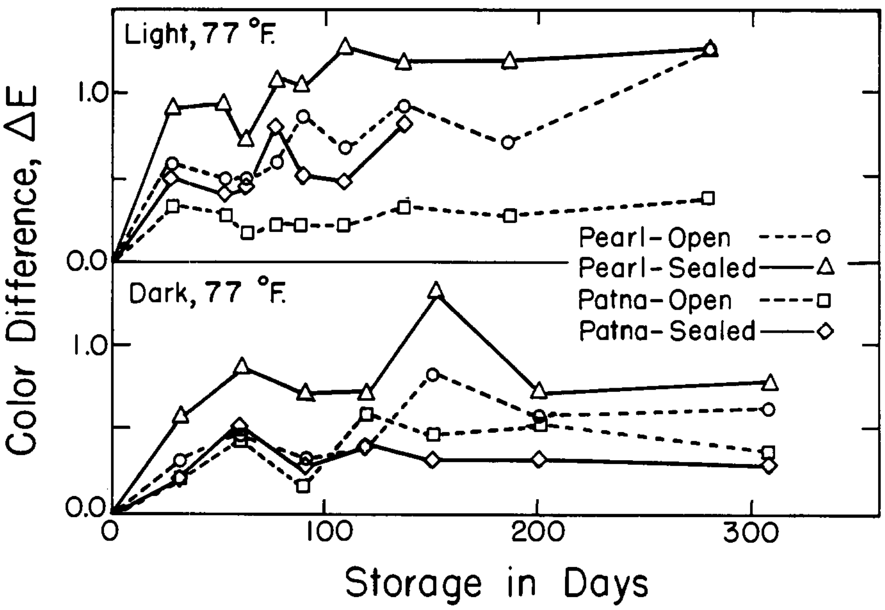
Materials and Methods. The measurements reported here were made on the same samples of rice from two 100-pound lots of commercially parboiled and milled Pearl and Century Patna that were used in observing changes in the oil fraction (*7*). The Pearl rice is the short-grain, rather opaque variety typical of California-grown rice. Century Patna is a flinty, semitranslucent, long-grain variety grown in the southern states. Sulfur dioxide had been used in parboiling the Pearl rice but not the Patna. Table I reports analytical data on the original supplies.

Table I. Analytical Data on Parboiled Rice Supplies

Component, %	Rice Stock: Pearl	Rice Stock: Century Patna
Moisture	12.8	11.5
Ether extractable	0.92	0.39
Crude fiber	0.41	0.27
Ash	1.09	0.72
Total nitrogen	0.98	1.20
Amino nitrogen	0.066	0.065
Total sulfur	0.09	0.10
Sulfur dioxide	0.023	0
Nitrogen-free extract	78.6	79.6
Total sugars (as glucose)	1.05	0.67
Reducing sugars (as glucose)	0.14	0.20

Rice was stored as 200-gram samples either in 400-ml. beakers covered with watch glasses (open storage) or in sealed 500-ml. flat-bottomed boiling flasks (sealed storage). Samples were held in the dark at room temperature (77° ± 4°), 100°, and 140° F. (25°, 37.8°, and 60° C.). One series of samples was also kept under the normal diffuse daylight and artificial light of a northern exposure laboratory to test effects of light.

The color of the dry whole-grain par-



Fignre 1. Color changes of parboiled rice

Table II. Moisture Changes in Parboiled Rice Stored in Open Containers

77° F.						100° F.			140° F.		
Light			Dark								
	H₂O, %			H₂O, %			H₂O, %			H₂O, %	
Days	Pearl	Century Patna	Days	Pearl	Century Patna	Days	Pearl	Century Patna	Days	Pearl	Century Patna
0	12.5	11.4	0	12.5	11.4	0	12.5	11.4	0	12.5	11.4
28	11.3	10.7	32	11.7	11.0	10	10.7	8.9	5	7.5	6.2
53	11.0	10.6	60	11.2	10.7	21	7.5	7.4	9	5.6	5.7
63	10.5	10.6	90	11.0	10.6	32	7.1	6.6	14	4.5	4.6
77	10.6	10.5	151	10.1	10.0	46	7.3	6.7	19	4.0	3.8
89	10.6	10.4	200	10.3	10.0	63	6.5	6.4	26	2.7	2.6
109	10.1	9.8	249	10.4	10.2	73	6.8	6.6	37	3.1	3.0
137	9.8	9.7	308	10.6	10.5	90	6.5	6.3	48	2.6	3.1
186	9.7	9.7	340	10.6	10.5	111	6.1	6.2			
252	10.1	10.0				132	5.9	6.0			
365	9.9	9.8				181	6.1	6.2			
						290	6.5	6.8			

Table III. Sulfur Dioxide Content of Pearl Rice

(In parts per million)[a]

Storage, Days	Open 77° F. light	Open 77° F. dark	Open 100° F. dark	Closed 77° F. light	Closed 77° F. dark	Closed 100° F. dark
0	231	231	231	231	231	231
77	89	...	...	83	...	...
90	...[b]	...	115	...	...	108
150	...	209	186	...	158	56
161	64	...	...	0	...	...
175	...	...	206	...	...	...
280	84	92	...	...	106	...
290	...	...	181	. ...	...	77

[a] 140° F. samples had zero sulfite content when first tested after 90 days' storage.
[b] Indicates no test.

boiled rice was measured on the Hunter color and color-difference meter (*10*), as in a previous study by Roberts and coworkers (*17*). Color differences, ΔE, were calculated from the measurements, with color values of the original rice samples as standards. In general a ΔE value of one unit is about the limit of perceptibility.

Total and reducing sugars were determined as glucose by the micro-Somogyi method (*1*, *2*, *4*), and sulfur dioxide was measured by an adaptation of the Monier-Williams procedure (*3*). Moisture was determined by heating 10-gram portions of rice (ground to pass 20-mesh) in a forced-draft oven at 220° F. (105° C.) for 16 hours (*9*).

Results and Discussion

Moisture contents of the two varieties in open storage (Table II) soon became closely similar under each exposure condition. The samples lost moisture faster and to a greater extent as the storage temperature was higher, and hence their moisture contents became increasingly different from those of corresponding samples in closed storage. Because moisture has an important influence on certain compositional changes in biological materials, this variation should be considered in interpreting the present results. Further experiments to define the effect of different moisture contents would be desirable.

Color. Color development at room temperature (77° F.) was marked by a slight initial increase followed by little or no change over a period of 10 to 11 months (Figure 1). Samples exposed to light darkened slightly more than those in the dark, and Pearl tended to brown more than Patna. However, all increases were near or below the visually detectable limit, and the minor differences are without practical significance.

At 100° F. color differences again showed an initial rise (Figure 2), after which little change occurred until about four months had elapsed. Then progressive darkening began and continued throughout the experiment. During this phase rice in sealed containers became browner than that in open storage, and Patna darkened more than Pearl. The more pronounced change of open-stored Patna during early stages of storage is not understood.

At 140° F., as shown in Figure 3, the distinction between open and closed storage became marked. Open-storage samples soon dried down to about 3% moisture content and showed a moderate, gradually decreasing rate of browning. Patna again changed somewhat more than Pearl. Closed-storage rice with original moisture contents continued to darken, and finally became a deep mahogany brown. Initially, Patna darkened more rapidly than Pearl, but after about 3 months the Pearl became the darker of the two. This may be a reflection of the higher moisture content of the Pearl rice. The lag in color increase of the Pearl for the first 50 days seems due to its original 230 p.p.m. of sulfur dioxide. This had disappeared when tested after 90 days of storage.

Sulfur Dioxide. The presence of sulfur dioxide appears responsible for the generally lighter color of Pearl rice during storage than that of Patna. Color development in Pearl rice at 100° and 140° F. was less than that in Patna in all instances where sulfite remained detectable. Table III illustrates changes in sulfite content during various storage regimes. Its disappearance was generally hastened as additional energy was supplied, whether from temperature increase or from light, though erratic values prevent firm conclusions. More rapid disappearance in closed than in open containers illustrates a nonevaporative fate. Reaction of the sulfite with carbonyl-containing intermediates of the Maillard reaction would adequately account for the present results. McDonald and Milner (*15*), in related studies on browning of wheat germ, postulated that the inhibition of browning they found when bisulfite was present was due to complexation of the carbonyl intermediates. This is in accord with Hodge's (*6*) proposal that bisulfites are among the best inhibitors of browning because, in addition to being carbonyl reagents, they are reducing agents which would keep reductones in the inactive reduced form.

Reducing Sugars. Losses of reducing sugars should occur during storage if the accompanying browning is of the Maillard type. Table IV shows that losses in sugar content did develop, and that they were confined to the reducing sugars. Illumination effects were not evident, and losses at 77° and 100° F. were about the same. Only at 140° F. were increased losses of appreciable magnitude observed. Pearl rice showed consistently greater losses than did Patna. That this was not directly reflected in color increases is undoubtedly due to the presence of sulfite. Where differences were evident, reducing-sugar decreases were greater in closed than in open containers. This is consistent with color development.

Amino Nitrogen. Reductions in available amino nitrogen should occur along with sugar losses in nonenzymatic browning. The low original free amino nitrogen percentages of the rice (0.065 and 0.066 for Pearl and Patna, respectively) precluded accurate observation of small progressive changes, but analysis of both rices after 370-day closed storage at 140° F. showed only 0.03% amino nitrogen remaining. Additionally, appreciable reductions were found (*8*) in the content of free alanine, asparagine, cystine, glutamic acid, and methionine in a related experiment on Patna aged 28 days at 180° F. (82° C).

Table IV. Sugar Content of Rices

Storage, Days	Reducing[a]				Nonreducing[a]			
	Century Patna		Pearl		Century Patna		Pearl	
	Open	Closed	Open	Closed	Open	Closed	Open	Closed
				140° F. Dark				
0	0.20	0.20	0.14	0.14	0.47	0.47	0.91	0.91
33	0.12	...[b]	...	...	0.50	...	...	...
70	0.15	0.08	0.11	0.10	0.47	0.40	0.90	0.82
150	0.08	0	0.05	0	0.48	0.49	0.89	0.89
271	...	Tr	...	Tr	...	0.50	...	0.86
				100° F. Dark				
0	0.20	0.20	0.14	0.14	0.47	0.47	0.91	0.91
150	0.11	0.10	0.07	0.07	0.49	0.49	0.81	0.96
328	0.15	0.14	0.11	0.11	(0.63)[c]	(0.62)	1.09	1.09
424	0.16	0.15	0.13	0.11	0.49	0.46	1.02	1.03
				77° F. Dark				
0	0.20	0.20	0.14	0.14	0.47	0.47	0.91	0.91
151	0.12	0.12	0.07	0.08	0.50	0.50	0.94	0.96
				77° F. Light				
0	0.20	0.20	0.14	0.14	0.47	0.47	0.91	0.91
161	0.13	0.12	0.08	0.07	0.50	0.49	0.97	0.98

[a] Percentages on dry basis.
[b] Indicates no test.
[c] Values in parentheses appear to be in error.

Conclusions

The original destruction of enzymes, the storage losses of reducing sugars and amino nitrogen, the increase in browning rate with increased moisture or temperature, the lack of oxygen requirement, and the marked inhibition of color by sulfur dioxide confirm that the browning is of the Maillard type.

Measurements of the small percentages of reducing sugars and amino nitrogen present in rice lack the sensitivity necessary for evaluation of small differences in color development.

These reported results have the prac-

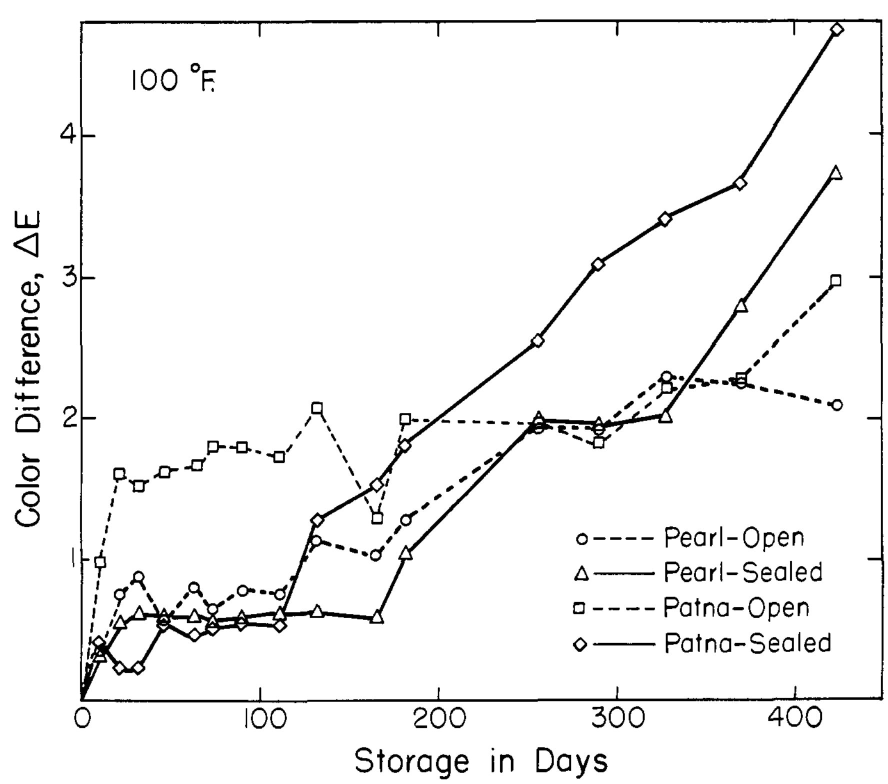


Figure 2. Color changes of parboiled rice held at 100° F. in the dark

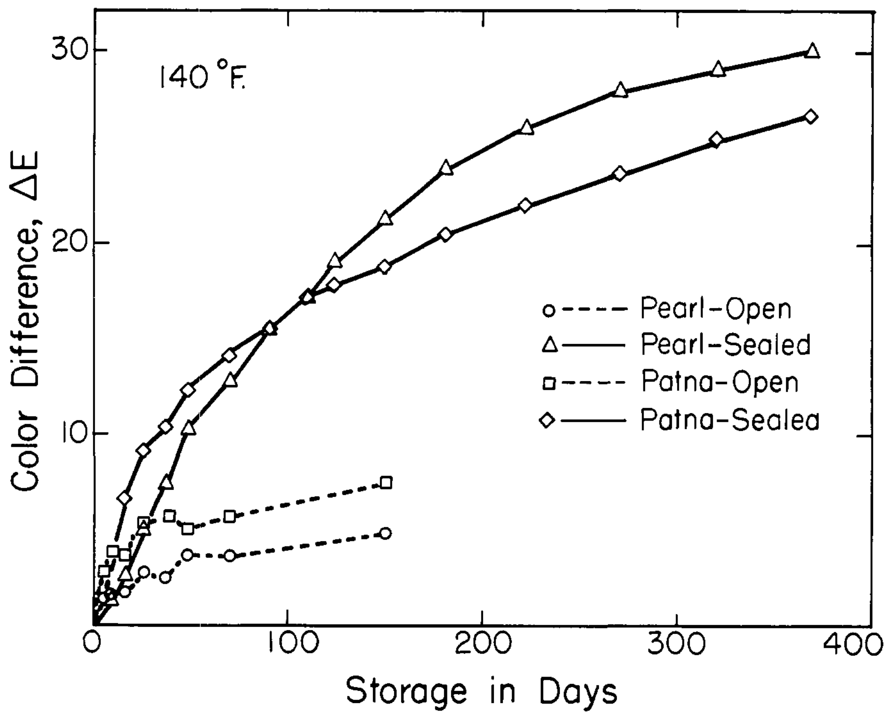


Figure 3. Color changes of parboiled rice held at 140° F. in the dark

Table V. Analytical Data on Rice Samples

Components	Patna 1	Pearl 1	Pearl 2	Pearl 2 + SO_2
	Rice Stock and Treatment			
	Components, %			
Moisture	10.8	9.9	11.0	11.1
Ether extractable	0.38	0.49	0.47	0.32
Crude fiber	0.23	0.28	0.23	0.19
Ash	0.78	0.81	0.85	0.74
Total nitrogen	1.18	0.98	0.94	0.91
Amino nitrogen	0.04	0.05	0.05	0.05
Total sugars (as glucose)	0.82	0.86	1.02	1.02
Reducing sugars (as glucose)	0.18	0.22	0.11	0.11
Sulfur dioxide	...	...	...	0.023

Table VI. Moisture Percentages in Stored Parboiled Rice

Storage, Days	Patna 1	Pearl 1	Pearl 2	Pearl 2 + SO_2
	Rice Stock and Stored Parboiled Rice			
	Moisture, %			
0	10.8	9.9	11.0	11.1
8	6.7	6.0	6.4	6.7
13	3.8	4.5	4.6	4.5
18	4.2	3.7	4.3	3.5
25	3.8	3.7	3.6	3.5

Table VII. Sugars and Amino Nitrogen in Parboiled Rice Stored 28 Days at 60° C.

Sample	Sugars, %[a] Total Original[b]	Total Final	Reducing Original[b]	Reducing Final	Amino Nitrogen[a], % (Van Slyke) Original[b]	Final
Patna 1	0.93	0.75	0.21	0.18	0.05	0.07
Pearl 1	0.96	0.83	0.24	0.21	0.06	0.08
Pearl 2	1.15	1.16	0.12	0.11	0.06	0.08
Pearl 2 + SO_2	1.15	1.16	0.12	0.14	0.06	0.06

[a] On moisture-free basis.
[b] Data from Table I converted to moisture-free basis.

tical connotation that prolonged storage at elevated temperatures will yield a product which has an undesirable color, as well as the previously noted (7) undesirable flavors.

Influence of Varietal and Processing Differences on Storage Properties

Materials and Methods Pearl rice (Caloro) and Century Patna were again chosen as widely different varieties for investigation.

The two parboiling treatments were also appreciably different. These were special operations, performed on particular lots of rice, and do not necessarily reflect commercial processing. Treatment 1, applied to both Patna and Pearl, was a batch process. Patna was soaked 4 hours and Pearl 6 hours at 135° F. (57° C.), followed by 5-minute pressure steaming and by drying. These different soaking times were required to give closely comparable products because of differences in physical characteristics of the grain. Treatment 2, applied to another portion of the same lot of Pearl rice used in Treatment 1, was a contimous operation comprising 20-minute steeping at 190° F. (88° C.), 20-minute pressure steaming, and subsequent drying. Sulfur dioxide was introduced with the steam during a portion of the experiment to supply sulfited Pearl rice.

The stocks of rice were milled to corresponding degrees in laboratory milling equipment and adjusted to similar moisture contents by air-drying. Table V presents analytical data on the material before storage, obtained by previously reported methods (7).

Storage of 200-gram portions of the rice in 400-ml. beakers covered with watch glasses was performed for 28 days in a thermostatically controlled gravity-convection oven at 140° F. (60° C.). Individual portions were removed at intervals, observed for color and rancid odor, and analyzed for moisture (wet basis), free acidity (9), and monocarbonyl content (7). Final measurements of sugars and amino nitrogen were also made (7).

Results and Discussion Starting materials exhibited only two significant differences. Patna showed a higher total nitrogen content than did Pearl, though amino nitrogen contents were strictly comparable. Rices subjected to Treatment 1 contained less total sugar, but more reducing sugar, than those from Treatment 2. This is evidently a processing effect.

Moisture contents of the four samples (Table VI) remained comparable throughout the storage period despite the fall from 11 to 3.5%. This lowering of moisture content contributed toward more rapid rancidification than would have occurred at the original moisture levels. It is recognized that rancidification of fat in cereal products is generally hastened by drying, whereas lipolysis and free acidity formation are more rapid at higher moisture levels. The interplay of these factors, recently ably summarized by Cuendet and coworkers for wheat products (*5*), seems generally similar in all cereal products.

Color development was observed visually only. Final colors were: Pearl 2, medium brown; Pearl 1, deep amber; Patna 1, medium amber; and Pearl 2 plus sulfur dioxide, light amber. The protective action of sulfite on color was clearly evident.

Changes in reducing sugars and in amino nitrogen were so small, as shown in Table VII, that no appreciable significance can be assigned them. Total differences in reducing sugars are within the variations previously found (Table IV) during storage of parboiled rice samples. Apparent slight increases in amino nitrogen were found after 28 days, as compared with corresponding slight losses after 370 days, at 140° F. (60° C.). It appears that these measurements are too insensitive at the existing low values of the components for correlation with color development. Decreases in total sugars for rices from Treatment 1 remain unexplained.

The possible role of monocarbonyl compounds from oxidation of oil in modifying the part played by reducing sugars in the browning reaction can only be minor. Maximum monocarbonyl values amount to approximately 3% of reducing sugars, and to 1% of amino nitrogen, on an equivalence basis.

The pattern of development of free acids and monocarbonyl compounds (Figure 4) for each rice was in complete agreement with results of previous studies (*7*) wherein changes at 140° F. were found directly comparable with those at room temperature. Monocarbonyls remained low during an induction period. Then, at or just before the time rancid odors appeared, monocarbonyls increased rapidly. After a short period of maximum value, they declined to low values again. Rancidity disappeared at this time. Free acidity increased rapidly from initial low levels just after the rise in monocarbonyls occurred and remained high when monocarbonyls decreased.

It is clearly evident from Figure 4 that Pearl and Patna rices subjected to the same processing develop rancidity in approximately the same time. Conversely, the same Pearl rice exhibits distinctly different degrees of stability after differing treatments. Presence of sulfur dioxide appears not to delay rancidification, but does inhibit color development. A similar inhibition of browning in wheat germ by bisulfite is recorded by McDonald and Milner (*15*).

Conclusion The present results show, in the light of recent data (*7*) on effects of storage at normal and elevated temperatures, that the maximum shelf-life of parboiled rice is dependent not on variety but on processing conditions. Hence it would be possible to modify the keeping quality as well as the appearance of the commercial product by variations in the manufacturing process.

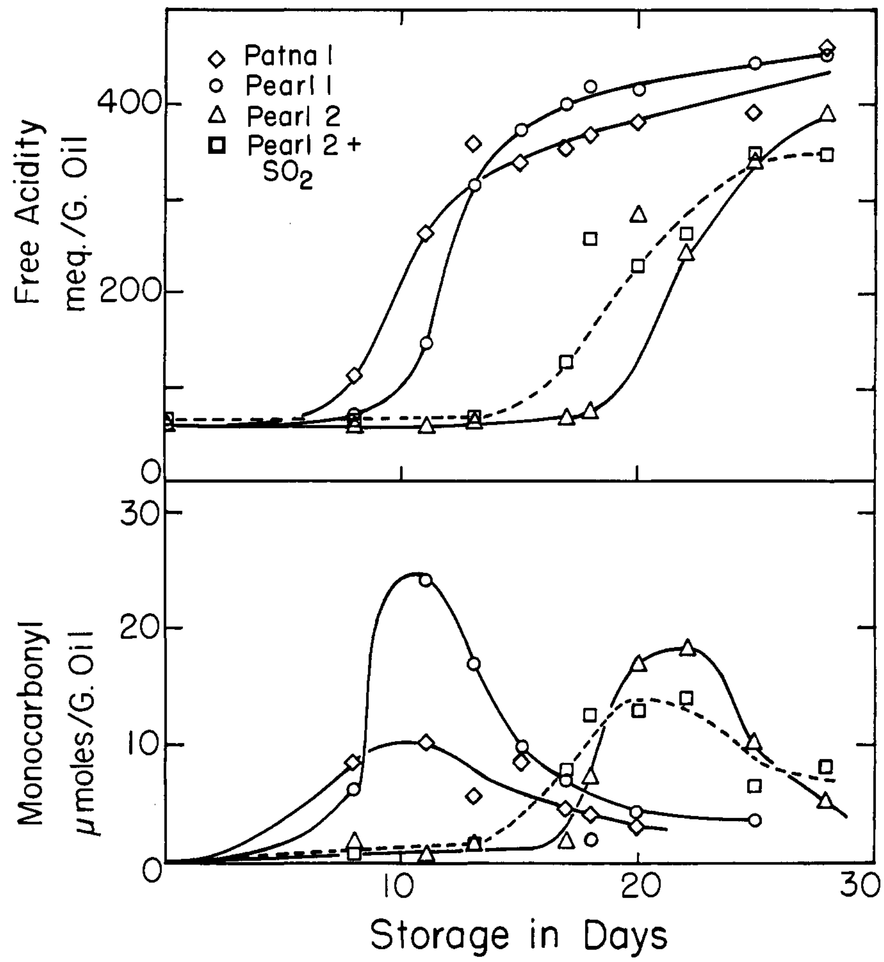


Figure 4. Changes in monocarbonyls and free acids in the oil of parboiled rice during storage in open containers in the dark at 140° F.

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