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STUDIES ON THE DETERIORATION OF DRY SEASONED NOODLE DURING THE STORAGE

By

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Introduction

Dry seasoned noodle (D. S. N.) is one of dehydrated food products which are popular with the public, and its consumption in Japan has increased year by year. D. S. N. is fried with edible fats in order to dehydrate and to raise its flavor, with the result that the fats are considerably absoved in it. It is supposed, therefore, that the fats contained in D. S. N. are autoxidized and become indigestible by the effects of air, sunlight and some other factors during the storage in markets or at home.

Although the rancidification of edible fats has been studied by several groups of workers in recent years, little attention has been paid to the changes of fats contained in D. S. N. While the food poisoning which was given rise to by the deterioration of D. S. N. has been reported by Miura *et al.* (1) and reviewed by Yanagisawa (2). And it was found that the rancidification of fats was the cause of the food poisoning, accordingly it seems that the characteristic changes of fats are related to the nutritive value of D. S. N.

In general, D. S. N. is kept for a long period of time before they are served on table. It seems reasonable to assume, therefore, that the deterioration of D. S. N. is influenced by the various conditions under which it is kept in storage in markets or at home.

In view of the above reasons, it appeared to be of interest to investigate the deterioration of D. S. N. The present investigation was undertaken to obtain the information about the changes of nutritive value of D. S N. under various conditions under which it is kept in storage by determining the chemical properties of fats, polymerization of fatty acids and the digestion coefficient of proteins.

Experimentals

Materials

There are many kinds of D. S. N. on the market, but the one having the highest fat-contents among them was obtained commercially and submitted to analysis, for the purpose of the present investigation was mainly to see the characteristic changes of fats.

Procedures

Samples were assigned to 4 groups and stored for about six months as follows: Group I−in a dark place at 3° ; Group II−in a dark place at room temperature (from 20 to 30°) ; Group III−in a light place exposed to the sunshine at room temperature

(from 20 to 30°) ; Group IV—in an incubator at 37°.

A portion of samples in each group was taken at the interval of about ten days, and powdered with electric crusher. Then the fats were extracted with ethyl ether from the powdered samples by Soxhlet method. After exception ethyl ether, the extracted fats from all noodles were submitted to analysis the chemical properties such as acid value, saponification value, ester value, iodine value, peroxide value and T. B. A. value. Moreover, partition column chromatography on silica gel about the mixtures of fatty acids isolated from fats was undertaken to see the contents of dimers, trimers and the secondary products derived from the fatty acids.

The residua except the fats were tested for the digestion coefficient of proteins.

Analytical methods

Acid value (A. V.) ; this was determined by the usual titration method with 0.1 N potassium hydroxide-ethyl alcohol solution.

Saponification value (S. V.) ; this was determined by the usual titration method with 0.5 N hydrochloric acid solution after saponification with 0.5 N potassium hydroxide-ethyl alcohol solution.

Ester value (E. V.) ; this was calculated as follows :

$$E.\,V. = S.\,V. - A.\,V.$$

Iodine value (I. V.) ; this was determined by Wijs method.

Peroxide value (P. V.) ; this was determined by the method of Wheeler (3).

T. B. A. *value* ; this was determined by the method of Turner *et al.* (4) with measuring the optical density at 532 mμ.

The isolation of fatty acids ; after the fats were saponified with 0.5 N potassium hydroxide-ethyl alcohol solution for 3 hours, ethyl alcohol was evaporated under reduced pressure and the residue dissolved in warm water, then the solution was acidified in excess with dilute sulfric acid, and the fatty acids of upper layer were extracted with ethyl ether in a separatory funnel. The extracted solution was dehydrated with sodium sulfates after washing with the distilled water and then ethyl ether was evaporated under reduced pressure.

Partition column chromatography on silica gel ; silica gel was suspended in 20 per cent methyl alcohol-benzen mixtures, and poured into a glass tube 15 mm. in diameter and 30 cm. long. Fifty ml. of the solvent mixture were then passed through the silica gel in order to pack the column and, when the level of the solvent mixture had dropped to that of silica gel, 50 per cent petroleum benzin-benzen mixtures containing the fatty acids as prepared above was added. When the level had again reached that of the silica gel, petroleum benzin introduced followed in turn 2 per cent methyl alcohol-benzen mixtures and ethyl ether. All eluates were collected in 10 ml. fractions with a mechanical fraction collector. Each fraction was then titrated with 0.05 N sodium hydrox ide-ethyl alcohol solution and phenolphthalein as the indicator.

Digestion coefficient ; this was determined by modification the method of Melnick *et al.* (5). Twenty g. of the residue except the fats were suspended in 100 ml. of distilled water and 30 ml. of 0.074 M phosphate buffer solution were added and then the solution was adjusted to pH 8.4. After 20 ml. of 1 per cent pancreatin solution were mixed, the solution was filled up to 180 ml. with distilled water, and 10 ml. of toluen were added to the solution.

The mixed solution was kept at 37° in an incubator for 24, 48 and 72 hours, respectively. After that hte digestion coefficients were determined by usual formol titration method.

Results and Discussion

The changes of the chemical properties of fats extracted from D. S. N. under various conditions under whch it is kept in storage are shown in Figs. 1-4 and Table 1.

It was found that A. V. generally increased as days go by and especially showed higher values in both groups of higher-temperature and sunshine-exposure than those in the other groups, as shown in Fig. 1.

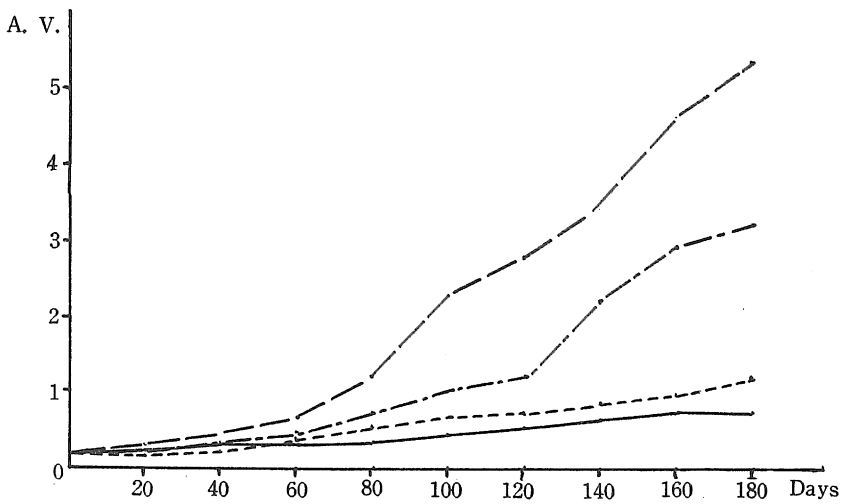

Fig. 1. The changes of A. V. in D. S. N.

Group-I Group-II Group-III Group-IV

These tendencies were remarkable after about one hundredth day. In view of the above facts, it seems most reasonable to conclude that the increasing of free fatty acids in fats of D. S. N. may have relation to both factors of temperature and sunlight.

Table 1. The change of S. V. and E. V. in D. S. N.

Days		20	40	60	80	100	120	140	160	180
Group-I	S. V.	182.3	183.0	182.7	183.5	183.0	184.1	183.0	183.4	182.9
	E. V.	181.0	182.7	182.4	183.1	182.6	183.6	182.1	182.7	182.2
Group-II	S. V.	183.0	182.5	183.3	183.6	182.8	184.0	183.7	183.2	183.1
	E. V.	182.8	182.2	182.9	183.1	182.1	183.2	182.8	182.2	181.9
Group-III	S. V.	182.9	182.7	184.0	183.8	183.2	182.7	183.3	183.5	183.1
	E. V.	182.6	182.2	183.3	181.6	180.9	179.9	179.9	178.9	177.7
Group-IV	S. V.	182.5	183.0	182.9	184.3	183.7	183.5	183.1	183.7	182.9
	E. V.	182.3	182.6	182.5	183.6	182.6	182.3	179.9	180.7	178.3

Kajimoto (6) found that A. V. of fats had increased by heating the fats or leaving them in air, and Inoue *et al.* (7) demonstrated essentially identical tendencies, too, and moreover that the rancidity of fats was most significantly recognized in case of sunshine exposure. The present author has confirmed these findings.

S. V. of fats shown in Table 1 as the mean values were almost identical and independent of the various conditions under which D. S. N. was kept in storage.

Matsuo (8) observed that S. V. of fats heated at 250° for 10 hours had decreased compaired with those of fresh fats. In no case were any decreased values on this experiment, but it seems that a better understanding of the posibility of decreasing might be reached if D. S. N. were stored for a longer period of time. It is not possible, therefore, on present evidence to decide whether S. V. level of fats increase or not during the storage. These questions can be answered only by further experimental work. As a matter of course, E. V. calculated by subtracting A. V. from S. V. decreased slightly according as A. V. increased.

It is supposed that the double bonds in the unsaturated fatty acids are tightly related to the rancidity of fats, therefore, I. V. indicating the degree of unsaturation in fats was determined. The results are given in Fig. 2.

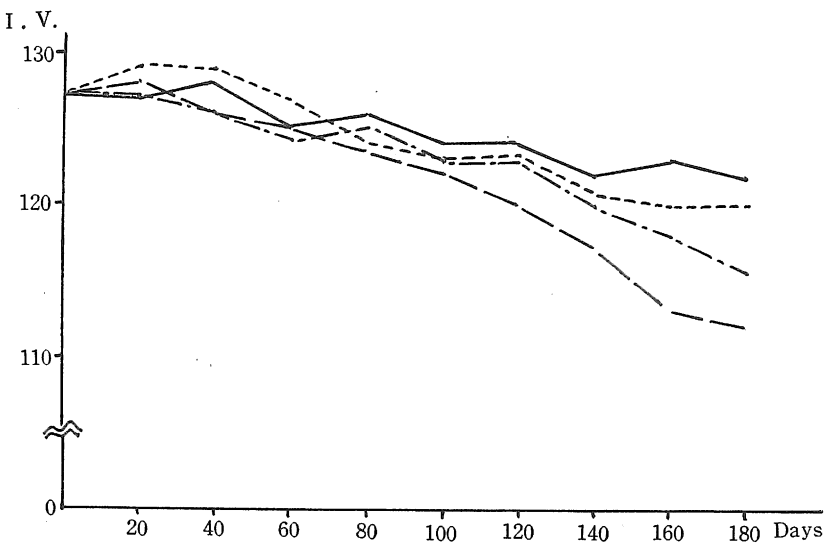

Fig. 2. The changes of I. V. in D. S. N.

It was evident from these data that I. V. levels in all groups decreased more or less during the storage. These tendencies were remarkable in Group III and Group IV; that is, the changes of I. V. were dependent upon both factors of sunlight and temperature, as in the case of A. V. And the fact that the effect of sunlight was greater than that of temperiature was in good agreement with the observation of Inoue *et al.* (7). It may be concluded from these results that the decreasing of double bonds in the unsaturated fatty acids was especially accelerated by exposing to the sunshine during the storage. The decreasing of I. V. in the thermally heated or autoxidized fats was reported by Kajimoto *et al.* (9), Akitani *et al.* (10) and Matsumoto (11).

The decrease of double bonds in unsaturated fatty acids may be expected to influence the producing peroxide. From this view, P. V. estimated and the results were summarized in Fig. 3.

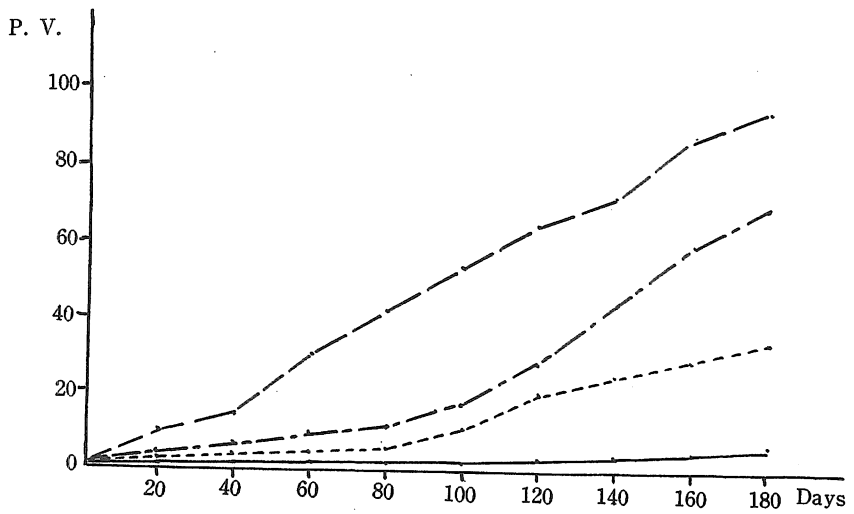

Fig. 3. The changes of P. V. in D. S. N.

The results showed that the P. V. levels of D. S. N. in all groups rised during the storage and these tendencies were remarkablly found under the condition of sunshine-exposure. Kajimoto *et al.* (6) (9) demonstrated that the rise of P. V. was recognized by heating the fats or leaving them in air, and it was found by Matsumoto (11) that the P. V. in the fats decreased by heating in excess or by storage for a long time. Under various conditions undertaken in this experiment, however, P. V. continued to increase day by day.

On the other hand, besides such chemical properties as mentioned above, the optical

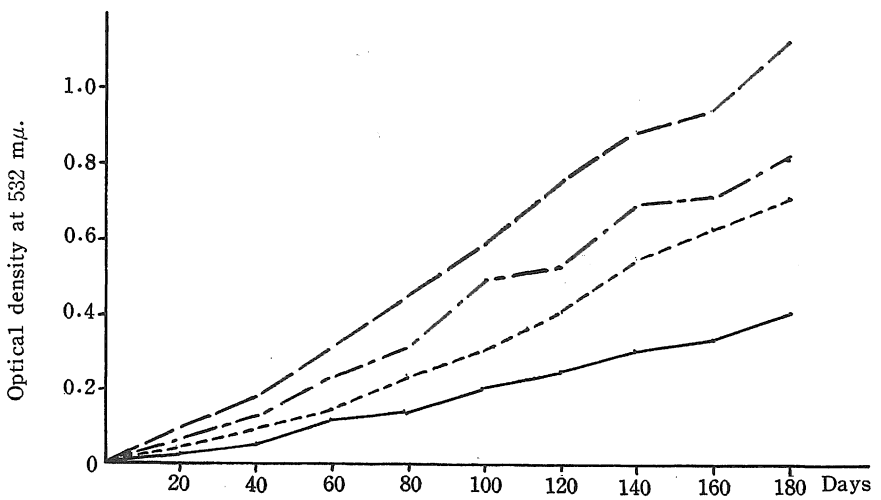

Fig 4. The changes of T. B. A. value in D. S. N.

density at 532 mμ per 1 g. of fats was measured by 2-thiobarbituric acid method to see the degree of the rancidity of fats. The data are shown in Fig. 4.

It was recognized from the nature of the curves that T. B. A. values had more sharply increased in proportion to the degree of fats rancidity than any other chemical properties. These results were almost identical with the facts which had been reported by Turner *et al.* (4) and Goldwell *et al.* (12). It may be concluded, therefore, that T. B. A. value is most suitable index in order to see the rancidity of fats. The results that T. B. A. values under both conditions of higher-temperature and sunshine-exposure more increased than those under the other conditions were essentially the same as those in the discussion about A. V. and P. V. The relatively greater rise in sunshine exposed group than any other group suggests that the ultra violet ray has the greatest relation to the rancidity of fats, and the same results have been reported by Inoue *et al.* (13).

Silieca gel column chromatography was undertaken to see the polymerization of fatty

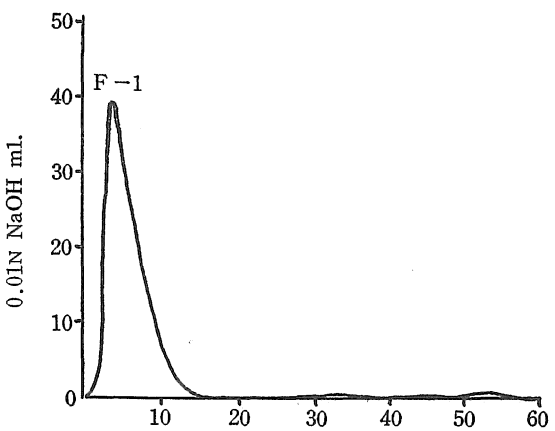

Fig. 5. The chromatogram of the fresh D. S. N.

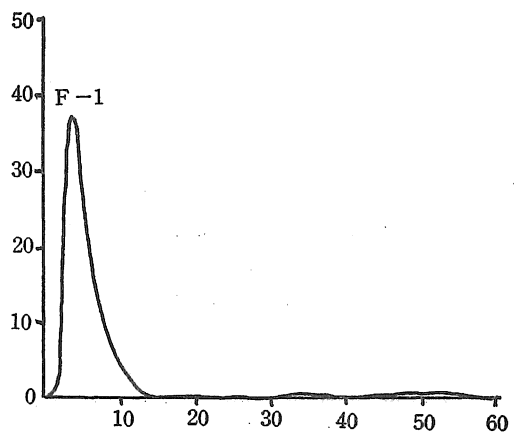

Fig. 6. The chromatogram of Group-I.

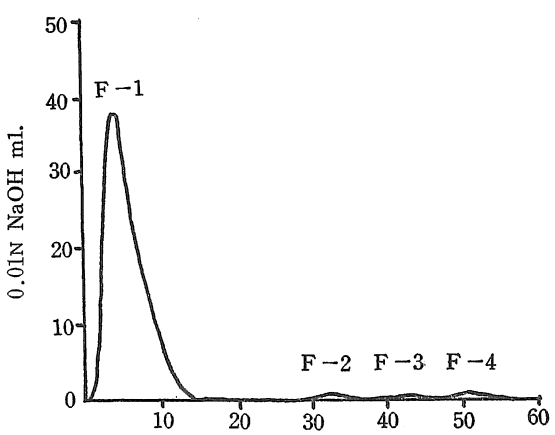

Fig. 7. The chromatogram of Group-II.

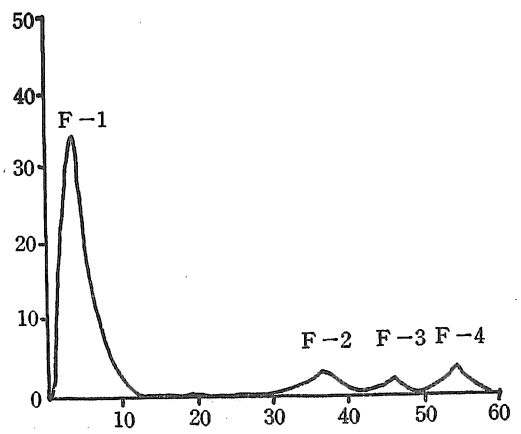

Fig. 8. The chromatogram of Group-III.

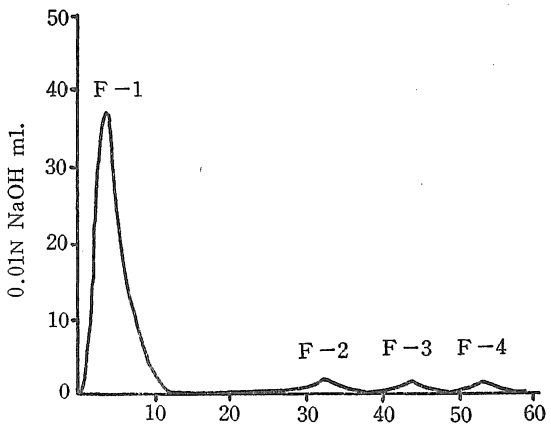

Fig. 9. The chromatogram of Group-IV.

acids which were isolated from D. S. N. stored under various conditions for about six months. The chromatograms are shown in Figs. 5-9.

It seems that 4 peaks shown as F-1, F-2, F-3 and F-4 indicate the monomers, dimers, trimers and the secondary products of dimers, respectively; a similar investigation has been already demonstrated by Kajimoto *et al.* (14).

It was found that there were some differences among 4 groups. That is, the contents of dimers, trimers and the secondary products of dimers in D. S. N. stored under the both conditions of higher-temperature and sunshine-exposure increased compared with those in fresh ones. Hashimoto and Mori (15) (16) have recognized the same results in the investigation on D. S. N. stored at 30° for 70 days, and moreover, demonstrated that thermally oxidized fats were more indigestible than the fresh ones.

The tendencies as mentioned above were most significantly recognized in the case of sunshine-exposure, as shown in Fig. 8, and next in the case of higher-temperature, as shown in Fig. 9. On the other hand, such tendencies were not recognized in the other 2 groups. It may be concluded, thefefore, that the polymerization of the fatty acids in D. S. N. is influenced by sunlight and temperature, especially by the former, and consequently D. S. N. become indigestible during the storage for a long period.

It was supposed that the denaturation of proteins in D. S. N. might be caused by the storage for a long period, in addition to the rancidification of fats. The digestion coefficients of them, therefore, were estimated and the results are shown in Table 2.

Table 2. The changes of the digestion coefficients of proteins in D. S. N. (%)

Days	20	40	60	80	100	120	140	160	180
Group-I	47.3	47.5	48.0	47.3	48.3	49.0	49.0	48.9	50.2
Group-II	46.2	47.3	47.6	48.2	49.6	50.3	50.4	51.2	52.2
Group-III	46.8	48.2	50.2	51.3	51.2	53.6	58.4	58.5	60.3
Group-IV	47.4	48.9	49.9	49.1	50.3	51.2	50.5	53.2	57.2

In all groups the rises of the digestion coefficients were recognized around one hundredth day. And it was found that these tendencies were greater in Group III than in any other group. On the other hand, the period until the time when the digestion coefficients began to rise—the lag period—was longer in Group I than in any other group. It seems, therefore, that the denaturation of proteins may be influenced by the same factors of storage conditions as in the case of the rancidification of fats. In view of the results of the studies on the deterioration of D. S. N, it may be concluded that the changes of the fats and proteins contained in D. S. N. stored for a long

period of time are influenced by temperature and sunlight, and remarkably by the latter. In this connection, it would be interesting to study the aspects of the fatty acids composition in D. S. N.

Summary

The presen investigation deals with the deterioration of the dry seasoned noodle—a kind of the convenient foods—under the various environmental conditions during the long period of storage.

Some chemical properties of the noodle fats and the digestion coefficients of the noodle proteins were determined to observe the degree of the deterioration. The following results were obtained.

It was recognized, in general, that acid values, peroxide values and T. B. A. values increased during the storage, and that iodine values, on the contrary, decreased. These tendencies depended upon the environmental conditions under which it is kept in storage ; that is, it seemed that the both factors of sunlight and temperature influenced the rancidification of fats, and the chemical properties changed in proportion as the fats acidify. Among the chemical properties of fats, T. B. A. value was the most suitable index in order to observe the fats rancidity.

The polymerization of the fatty acids was affected by sunlight and temperature, and remarkably by the former, showing the same results as in the case of the other chemical properties ; that is, the formation of dimers or trimers of the fatty acids was recognized most clearly in the cae of sunshine-exposure.

The rises of the digestion coefficients of the proteins were recognized, more or less, in all groups, but here again the rise in the sunshine exposed group showed the greatest change.

In vies of the above facts, the most reasonable conclusion to be drawn from the available data is that, in order to prevent the deterioration of D. S. N., it is the most suitable method to preserve it in the dark place at a temperature as low as possible.

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