This paper gives the results of analysis of a kind of Chinese preserved eggs called pidan. The Chinese and other Oriental peoples preserve eggs, not necessarily to keep them unchanged, but to make various new substances—a process analogous to the production of cheese from milk. The products have been little studied and the literature on the subject is therefore limited. Hanzawa\(^1\) describes a number of Chinese methods of preservation and gives the results of a bacteriological study of pidan. The descriptive part of his article and also a portion of one by Gibbs\(^2\) referred to below, are given in almost literal translation by Long\(^3\). Earlier work is that of Svoboda\(^4\) on Oriental preservation in wood ashes, extensively quoted by König\(^5\) and by Kossowicz\(^6\). In 1908 a paper appeared by Vosseler\(^7\) on egg preservation in the tropics. Gibbs and his coworkers\(^2\) describe a process of preparing eggs used in the Philippines and give analyses of these and fresh ducks' eggs. The United States Department of Agriculture makes brief mention of Oriental eggs in one of its Farmers' Bulletins.\(^8\) A recent number of the National Geographic

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Magazine\textsuperscript{9} gives pictures which are probably of the kind of eggs that we have studied.

\textit{Preparation and Physical Properties of Pidan.}

Pidan is made from ducks' eggs and is a factory product. The following description of its preparation was obtained from the manager of a factory. It is similar to the method given by Hanzawa, but more detailed. To an infusion of $1\frac{1}{2}$ pounds of strong black tea are stirred in successively 9 pounds of lime, $4\frac{1}{2}$ pounds of common salt, and about 1 bushel of freshly burned wood ashes. This pasty mixture is put away to cool over night. Next day 1,000 ducks' eggs of the best quality are cleaned and one by one carefully and evenly covered with the mixture, and stored away for 5 months. Then they are covered further with rice hulls, and so with a coating fully $\frac{1}{2}$ inch thick are ready for the market. They improve on further keeping, however, for at first they have a strong taste of lime which gradually disappears. Eggs preserved in lime-water and salt are also said to have a lime-like taste.\textsuperscript{8} The eggs are eaten without cooking.

They are very different from fresh eggs. The somewhat darkened shell has numerous dark green dots on the inner membrane. Both the white and yolk are coagulated; the white is brown, more or less like coffee jelly, and the yolk greenish gray with concentric rings of different shades of gray. The yolk gradually loses its peculiar color on exposure. Numerous tyrosine-shaped crystals are found on the side of the white next to the yolk, apparently formed on the vitellin membrane. The taste of the eggs is characteristic and the odor markedly ammoniacal. It may also be noted here that the eggs have no odor of hydrogen sulfide and that no blackening of lead acetate paper could be detected during 15 minutes' treatment of the finely divided yolk and white with acid in closed weighing bottles.

The appearance of the eggs, however, is not wholly unique, considering the alkalinity of the materials used for preservation. Evéquoz and Haussler\textsuperscript{10} observed that when water-glass contains too much alkali, the latter diffuses into the egg, making the white into a yellow transparent mass and solidifying the yolk. König quotes Svoboda to the same effect, and states that Oriental eggs kept in wood ashes become stiffened and look like hard-boiled eggs. The changes in pidan formation are


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doubtless also bacteriological. Hanzawa isolated five kinds of bacteria from them, inoculated fresh eggs with these bacteria, and then placed them in water-glass for several months. The resulting substance was similar to pidan in color and hardness.

It is interesting to compare pidan with various published descriptions of decomposed eggs. Kossowicz in the first part of his monograph reviews the literature of the subject, chiefly from the bacteriological point of view, but with numerous descriptions of the spoiled eggs. Especially noteworthy are Gayon's observations\(^\text{11}\) that while most of his eggs gave off hydrogen sulfide on spoiling, some which decomposed in the absence of air had an odor of phosphine and ammonia. This is the only reference that we have found to the presence of free ammonia in eggs, or at least in sufficient quantity to give a noticeable odor. Numerous descriptions are also given of eggs darkened in color and of pasty or jelly-like consistency, but most of these dark solid eggs smelled of hydrogen sulfide. The formation of greenish spots of mould or bacteria on the inside of the shell is often noted, both in early work and in Kossowicz's, and tyrosine-shaped crystals have been observed\(^\text{13}\) on the vitellin membrane. Poppe\(^\text{13}\) adopted Schrank's classification of spoiled eggs as mouldy eggs, eggs smelling of hydrogen sulfide (the typical rotten eggs), and eggs recognized by putrid decomposition and a cadaver-like smell—none of which describes pidan. Thus in spite of numerous points of similarity between these variously described decomposed eggs, none of them resemble pidan closely. Comparisons with cold storage eggs are made below.

Methods of Analysis.

Determinations were made of total solids, ether extract, acidity of ether extract, alkalinity of ash, nitrogen as total nitrogen, coagulable, non-coagulable, volatile, and amino nitrogen, and lecithin phosphorus and total phosphorus. The methods used were chiefly those of the Association of Official Agricultural Chemists.\(^\text{14}\)

The egg was first weighed whole, the yolk and white were separated and weighed, chopped into small pieces, and dried in air at 45°C.\(^\text{15}\) All but a few tenths of 1 per cent of the water or volatile matter of the yolk and a little less of the white was lost during the process. The total water

\(^{11}\) 1873. Quoted by Kossowicz.\(^\text{6}\)


\(^{13}\) Poppe, K., Arb. k. Gesundhamsie, 1910, xxxiv, 186. Schrank, 1894.


\(^{15}\) Leach, A. E., Food Inspection and Analysis, New York, 3rd edition, 1914.
content was determined by further drying in hydrogen at 100°C. after pulverizing the partially dried substance. The ash and the alkalinity of ash were determined on the residue after total drying, as was also the ether extract of the yolk, the extraction being continued for 20 hours in some cases and 8 in others. In the first ether extract determination petroleum ether was used, but as the result was unexpectedly low, anhydrous ether was substituted thereafter, although it gave only slightly higher results. Several eggs were used in duplicating the moisture and fat determinations. For the nitrogen determinations portions of white and yolk, about 3 gm. each, were weighed in closed weighing bottles containing dilute acid, for it had been noted that the egg when opened gave off ammonia or some volatile ammoniacal substance in sufficient quantity to give a marked odor and promptly to turn a piece of red litmus held over it decidedly blue.

The coagulable, non-coagulable, and volatile nitrogen were determined upon the same portion of the egg. This portion was first ground with hydrochloric acid, neutralized with sodium hydroxide, reacidified with acetic acid to a faint but distinct acidity, and then heated to boiling for 3 minutes. If the acidity was too faint, the solution remained milky after heating, and was hard to filter. The clear filtrate was made up to 150 cc. The residue was used for the determination of coagulable nitrogen by the Kjeldahl-Gunning method, and 100 cc. of the filtrate were taken for the non-coagulable nitrogen. The rest of the solution was used for the determination of volatile nitrogen by Polin’s method, on the addition of sodium carbonate and aeration for a number of hours into 25 cc. of 0.1 N acid. In another case the filtrate from the coagulable nitrogen was used for the Van Slyke amino nitrogen test.

Results of Analysis and Comparison with Other Eggs.

The following table gives the percentage of the three parts in four Chinese eggs, and, for comparison, in fresh ducks’ eggs. The first figures for the fresh eggs are those given by Lührig as the average of nineteen eggs that he worked with, and the second are those of Wood and Merrill.

The loss in weight in opening and weighing the eggs, averaging 0.6 gm., or about 1 per cent of the total, is probably chiefly water, but also a little ammonia. Eggs 1 and 4 were bought at a different place from 2 and 3.

As shown in Table I, our eggs weighed less than most of the

18 Quoted by Leach, p. 264, from Wood and Merrill, Maine Agric. Exp. Station, Bull. 75, 90.
published weights of fresh ducks' eggs, and the whites without exception were far lighter. The percentage of the shell and the yolk of pidan are decidedly higher, while the percentage of the white is only about half that of fresh eggs. That some of the water of the white of pidan must have gone over to the yolk during preservation is further definitely shown in the analysis of pidan given in Table II. Here the percentage of water is 54.0 in the yolk and 69.8 in the white, instead of 45.8 and 87.0 for fresh eggs (Table III). There has thus been a marked transfer of water from white to yolk and a marked loss of water from the white to the air. The difference is still more marked when the actual quantities of water in white and yolk are computed for Egg 1 and for fresh eggs: in the whites, 12.4 gm. in pidan, and 32 gm. in fresh eggs; and in the yolks, 17.1 gm. in pidan, and 11 gm. in fresh ones. Greenlee found a similar though much slighter change in hens' eggs kept in cold storage. He reports a change in the moisture of the yolks during 40 days from 47.17 to 50.60 per cent, and in the whites from 87.60 to 84.74 per cent.

In Tables II and IV are brought together the results of the analyses of the yolk and white of pidan, and in Table III, the average composition of fresh ducks' eggs as given by Langworthy. The first two lines of figures for yolks and whites of Table II, except the nitrogen, are all for the same egg (No. 1), the other figures are for other eggs, possibly of different age, and show considerable variation.

A number of differences between pidan and fresh eggs are shown in Tables II and III, in addition to the marked water changes. First, pidan is decidedly higher in ash. Compared with other eggs preserved in alkaline solutions, this high percentage is not surprising. König quotes that eggs kept in wood ashes, if somewhat moist, show in 4 months an increase of ash from 1 to 3 per cent. The ash in these eggs has been found as high as 6.5 per cent. The alkalinity of the ash of König's eggs was also found to be high, whether preserved in wood ashes or in too strongly alkaline water-glass, but not so high as in the yolk of pidan.

The ether extract of the yolk is surprisingly low, 21.1 per cent as compared with Langworthy's 36.2 per cent of the yolks of fresh ducks' eggs. The difference is still marked even when the results are calculated on the dry basis, 44 per cent for pidan and 67 per cent for fresh eggs. Also the acidity of the ether extract is high,
8 per cent free acid calculated as oleic acid. This was determined by titrating duplicate extracts of the yolk of several eggs, using Marcusson's\textsuperscript{20} two indicator method, phenolphthalein, and alkali blue B 6. In view of Pennington's observations\textsuperscript{21} on the occurrence of lipase in hens' eggs, a high acidity is not unexpected. It is possible also that some of the acid from the action of the lipase and the alkali from the preserving material may have formed soaps. These of course would not be extracted by the ether and would give an alkaline ash.

To test this idea of soap formation several of the residues from the ether extraction were ground up with hydrochloric acid, dried, and reextracted with ether. They all gave further substance to the ether which was completely soluble in warm alcohol. It amounted on the average to 3.1 per cent of the original yolk and titrated roughly as 95 per cent oleic acid. This quantity of substance is, of course, not great enough to account for more than part of the loss in ether extract.

Another possible source of loss of ether extract might be decomposition of the phospholipoids.\textsuperscript{22} To find whether this had taken place, we determined the total phosphorus of the yolk and the phosphorus in the extract obtained by successive extractions of the dried yolk with anhydrous ether (12 hours), absolute alcohol (12 hours), and again with ether (18 hours). The phosphorus was determined in the usual way as magnesium pyrophosphate after oxidizing the material with sodium carbonate and potassium nitrate. We found 0.77 per cent total and 0.39 per cent lecithin phosphoric anhydride. This is much lower than figures given by Lührig\textsuperscript{17} for fresh eggs. According to these the yolk of ducks' eggs contains 1.255 per cent total P$_2$O$_5$, 0.643 per cent "soluble in ether, pure lecithin," and 0.218 per cent "soluble in alcohol, lecithin bound to nuclein," or altogether 0.861 per cent lecithin P$_2$O$_5$. Of course to compare these figures with ours from our abnormally moist yolk, all should be calculated on the dry basis. If this is done the lowness of our figures is even more striking, although the yolk we used contained less water than most of

\textsuperscript{20} Marcusson, J., \textit{Z. angew. Chem.}, 1911, xxiv, 1297.
\textsuperscript{22} We wish to thank Dr. David Klein for suggesting this.
ours—49.6 per cent—and weighed much less. Lührig’s fresh yolks contained 45.0 per cent moisture. This gives us on the dry basis 2.28 per cent total and 1.59 per cent lecithin phosphoric acid for the fresh yolks, as opposed to 1.53 and 0.76 per cent for ours. Both total and lecithin phosphoric acid are low in pidan, by approximately the same amount—0.8 per cent. The actual quantities in the whole yolks are 0.2987 and 0.2050 gm. for the fresh eggs, and 0.169 and 0.086 gm. for pidan. Thus not far from half the lecithin phosphorus has apparently disappeared, has not been transformed into some other phosphorus compound insoluble in alcohol or ether, but is actually gone from the yolk. Of course the data are insufficient for accurate determination of the amount of change, but there can be little doubt that the lowness of the ether extract of pidan is in part due to some decomposition of phospholipoids.

Besides the change of water, ash, and ether extract in pidan, the figures in Tables II and III seem to show increase in the protein of the white (N × 6.25). This increase is apparent only, however, and due merely to decrease in moisture. Recalculation on the dry basis shows loss rather than gain, 65 per cent of the total solids instead of the 85 per cent of the fresh, probably because of actual increase of ash. The yolk protein so calculated shows little difference between pidan and fresh eggs (29 and 31 per cent).

The distribution of the nitrogen of pidan is given in Table IV. It is compared with some of Pennington’s figures for fresh hens’ eggs in Table V.

It should be remembered that the figures for pidan are for three different eggs. As might be expected, they are not perfectly concordant, but show definite variations from fresh eggs. The average for Pennington’s non-coagulable nitrogen is 9.1 per cent of the average for total nitrogen; whereas the corresponding figures for pidan are 16 per cent for the white and 18 per cent for the yolk. The non-coagulable nitrogen is thus decidedly higher in pidan than in fresh hens’ eggs. No figures were found for fresh ducks’ eggs.

Pennington also determined ammoniacal nitrogen on fresh and old eggs by the Folin aeration method. An increase was found of ammoniacal nitrogen from 0.0012 per cent in well handled eggs
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**TABLE IV.**
Distribution of Nitrogen in Pidan.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
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<tr>
<td>Yolk.</td>
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<td>2.04</td>
<td>0.42</td>
<td>0.06</td>
<td>0.07</td>
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<td></td>
<td>2.32</td>
<td>1.99</td>
<td>0.41</td>
<td>0.06</td>
<td>0.182</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>1.92</td>
<td>0.41</td>
<td>0.06</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>2.22</td>
<td>1.80</td>
<td>0.44</td>
<td>0.06</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>2.14</td>
<td>1.79</td>
<td>0.33</td>
<td>0.06</td>
<td>0.180</td>
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<tr>
<td>Average</td>
<td>2.24</td>
<td>1.91</td>
<td>0.40</td>
<td>0.06</td>
<td>0.299</td>
</tr>
<tr>
<td>White.</td>
<td>3.21</td>
<td>2.89</td>
<td>0.54</td>
<td>0.07</td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>2.84</td>
<td>0.59</td>
<td>0.08</td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>3.06</td>
<td>2.50</td>
<td>0.44</td>
<td>0.10</td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>3.08</td>
<td>2.54</td>
<td>0.44</td>
<td>0.12</td>
<td>0.303</td>
</tr>
<tr>
<td>Average</td>
<td>3.14</td>
<td>2.69</td>
<td>0.50</td>
<td>0.09</td>
<td>0.302</td>
</tr>
</tbody>
</table>

**TABLE V.**
Distribution of Nitrogen in Hen's Eggs.

<table>
<thead>
<tr>
<th></th>
<th>Total.</th>
<th>Coagulable by heat.</th>
<th>In filtrate from coagulum.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td>1.46</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td>1.49</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td>1.59</td>
<td>0.112</td>
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<td>1.71</td>
<td>1.64</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td>1.51</td>
<td>0.152</td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>1.54</td>
<td>0.156</td>
</tr>
</tbody>
</table>

day old, to 0.0030 per cent or more in an egg which was almost a white rot. This author used portions of the whole egg in the determinations, and we used merely the filtrate from the coagulable nitrogen, but even so the ammoniacal nitrogen in pidan is from twenty to forty times as high as that in the oldest and poorest of Pennington's eggs. Higher figures than Pennington's are given by Houghton and Weber. For black rots they give 169.6 mg. of ammonia nitrogen per 100 gm. of moisture and fat-free substance. Our results calculated on the same basis are 240 mg. per 100 gm. of yolk, and 300 mg. per 100 gm. of white. Even

these figures may be too low, since ammonia was undoubtedly lost in opening the eggs.

The presence of ammonia is especially important in connection with the low phosphorus content. At least some of it may have come from the lecithin. If it had all come from protein other signs of protein decomposition should have been more marked. The increase above the normal of the non-coagulable nitrogen in pidan does not seem great enough to correspond with this excessive ammonia. Some proteolysis has undoubtedly taken place during the preservation, but also some decomposition of the lecithin.

The amino nitrogen was determined by Van Slyke's method on the filtrate from the coagulable protein of both yolk and white of one of the eggs, using 14.6 gm. of yolk and 8.0 gm. of white to obtain 100 cc. of solution. This was exactly neutralized, evaporated on the water bath to one-fourth its volume, and 2 cc. portions were used for the determination in the micro apparatus. It was necessary to shake this reaction mixture for 18 to 20 minutes to get concordant results. The yolk showed 0.18 per cent amino nitrogen, and the white 0.30 per cent. No figures on amino nitrogen of fresh or cold storage eggs have been found in the literature.

SUMMARY.

The following changes have been shown to take place during the formation of pidan from fresh ducks' eggs. (1) Water in large quantities has been transferred from the white to the yolk, and water has been lost from the white to the outside. (2) The ash and the alkalinity of ash have increased in a way similar to that of other eggs preserved in alkali. (3) The ether extract has decreased and its acidity is high. (4) Both total and lecithin phosphorus have decreased. (5) The non-coagulable nitrogen has increased and also the ammoniacal nitrogen, the latter to an extraordinary degree, and the amino nitrogen is high. From these changes the conclusion is drawn that decomposition of the egg protein and of the phospholipoids has taken place. The production of pidan from the fresh eggs is probably brought about through the agency of the alkali, bacteria, and enzymes.

Van Slyke, D. D., J. Biol. Chem., 1912, xii, 275
CHINESE PRESERVED EGGS—PIDAN
Katharine Blunt and Chi Che Wang


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