
Preliminary Report.

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Flowers of “Tsuyukusa” Commelina communis are beautiful azure blue and the extracted flower juice colours fabrics blue, hence the name “Tsukikusa” or “Awobana,” meaning a paint grass or a blue flower. This colouring matter is one of the most well known and the oldest of its kind in Japan and the usage has a historical interest. Though no longer practical as a dye, as the colour can be easily washed away, it is still employed for drawing patterns in the art of Yuzen silk print and Shiborizome (tied dyeing). In some regions, therefore, the plant is especially cultivated for the production of “Awobana paper” which is painstakingly prepared by painting the flower juice on sheets of paper and drying them in the sun.

Concerning the chemistry of this colouring matter, no record has been found.

For the studies described here, the above mentioned “Awobana paper” was used for the material. As this paper is usually moist and becomes even mouldy in the summer, it was treated with methyl alcohol in the beginning. In soaking the paper in the solvent, it was freed from mixed yellow colouring matter and sugar which were removed by going into the solution. Then the paper was washed well with methyl alcohol. On drying, the material was made suitable for preservation.

For the separation of the colouring matter, the above mentioned paper was treated with a small amount of water. On adding methyl alcohol to this water solution, it gave a powdery separation of the colouring matter. The precipitate was then filtered by suction, washed several times with methyl alcohol and finally with ether. The dried powder thus obtained resembles ultramarine in appearance and is convenient for storing.

This colouring matter is insoluble in methyl alcohol, but dissolves in water readily. Because of this latter property it may be considered to exist as a metallic double compound. After combustion, it leaves about
14.5–15% of ashes, the chief metallic constituents of which are K and Mg (traces of Fe, Al, Ca), while PO₄ and SO₄ are the important acid radicals. Ammonia is produced when Awobana is heated with an aqueous alkaline solution. By heating the colouring matter with MgO, the ammonia produced is estimated to be about 1%. Therefore NH₄ also seems to be one of the basic components. This study of ashes seems extremely important as well as interesting in its relation to the characteristic property of Awobana, namely its great solubility in water.

This colouring matter when acidified turns gradually purple to red without losing its solubility in water.

The next important consideration is that the substance in question may be a glucocide, since it gives sugar when boiled with mineral acid. For an example, if the blue Awobana powder (2 g) is dissolved in water (10 cc) and conc. HCl (12 cc) is added and heated (2 hrs), it gives a separation of red powder (approximately 0.6 g); and glucosazone (approximately 0.6 g) is obtained on treating the aqueous solution. The sugar content is about 31%, and it appears to be one molecule of monosaccharose. The semicarbazone formed is identical with that of glucose. While this red aglycon is very soluble in alcohol, it is insoluble in other organic solvents and it has not yet been insolated in crystalline form.

Decompositions with caustic alkali and alkaline fusions were carried out under various conditions. Among several substances formed, the two of the most important are P- coumaric acid (this and its acetyl derivative were confirmed by analyses and comparison with the synthetic products) and P- oxy-acetophenon (confirmed by the analysis and comparison with the synthetic substance). Compared with flavonol or anthocyane, such a dissimilarity in the decomposition products seems remarkable. But P- coumaric acid is obtained when treated with even cold 1% aqueous alkali while to obtain P- oxy-acetophenon, it seems necessary to heat with alkali and the amount of the latter produced is the same whether P- coumaric acid is first removed or not. On the other hand P- coumaric acid seems to be produced in an aqueous Awobana solution which has been left standing for several weeks after an addition of fairly concentrated HCl. It is also noteworthy that any assumption for a nucleus of polyhydric phenol is hitherto unconfirmed without the isolation of a phloroglucinol derivative. The methoxy determination gave only such
a trace that might be accounted by impurities. Further attempts for the isolation of a polyhydric phenol nucleus are being made as well as the studies to complete the other problems already mentioned.

Experiments in acetylation and methylation are also in progress.

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