

# THE ACID CONTENT OF SOME OF OUR VEGETABLE FOODSTUFFS.

Part II. Amchur or *Mangifera Indica*.

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“MEN and animals must ingest considerable quantities of compounds like citric, malic, tartaric and oxalic acids. Yet the dietary function of these organic acids of vegetables is almost entirely unknown. How do they function in alimentation? Do they find their way into the systematic circulation or are they disposed of in the liver?”<sup>1</sup> Whatever answer future research may make to this query of Professor Mendel, it is true that in India, more than anywhere else, a very large variety of vegetables and vegetable products is known, and extensively used, for their acid contents. Sometimes raw, sometimes cooked, these are used, throughout the length and breadth of the country, for flavouring dals, curries, vegetables, condiments, pickles, achar and even drinks. Tradition has handed down a mass of information regarding the suitability and the precise uses in diet of every one of these, while the Ayurvedic and the Unani physicians have even a more crystallised knowledge of the peculiar advantages and the specific dangers attending the use and abuse of each, either as an article of diet or of medicine. In addition to this knowledge, there are other factors to regulate their use, the chief of which are the economic, the geographic and the climatic conditions. These acid foods have scarcely received due attention, as a class, however, at the hands of the chemists, analytical and physiological alike. It is to be hoped that, at a time when nutrition itself is attracting a new and world-wide attention, these invariable articles of our daily food will not have long to wait.

Of a few members of this class, a considerable analytical knowledge does undoubtedly exist. The *Citrus* family is an example in point. In health as well as in disease, members of this family have been considered, in India particularly, as of first rate importance. The discovery of their vitamin and mineral contents has lately pushed them into the forefront in the dietary of the civilised

world and has also thrown an interesting light on their dietetic value ; but this should not succeed in throwing in the background the more ancient and the more deeply human interest of their acid contents. Though analytical figures of the acids contained are available in literature, a fresh survey of the acid contents of those varieties popularly used would undoubtedly be useful.

The next in importance, perhaps, is tamarind, *Tamarindus Indica*. While the stone or the seed is not without use, the dried fruit, often salted and preserved for the year, finds its way into ever so many foods, drinks and even medicines, particularly in the south and southwest of India. The acid is reported to be mainly tartaric and investigations have also been made to utilise tamarind for the industrial production of tartaric acid, tartrates and alcohol,<sup>2</sup> though no commercial application is so far known.

The place of tamarind is taken, in many homes and in several provinces, by two species of *Garcinia* or by raw dried mango.

Of the *Garcinia*, the lesser known *Garcinia Cambogia* goes also by the nickname of *Vilayati Imli*, and its dried fruits, after the removal of the stone, are used very much like those of tamarind, particularly in the south, in Travancore, in Cochin and in South Malabar. "It is also used as a condiment and eaten with fish as a substitute for tamarind."<sup>3</sup> Like tamarind, it is found also to contain mainly tartaric acid and in about the same proportion, *viz.*, 10%.<sup>4</sup>

*Garcinia Indica*, better known as Kokam, is a much more popular stuff. Its acid contents are under investigation in this Laboratory.

The United Provinces know nought of Kokam and employ as a souring element the raw dried mango fruit, which is locally known as amchur [or mango-powder], or as Khatai, the generic term for all sourness. After the removal of the stone the raw mangoes are cut into slices and dried in the sun, and these find their way into markets and homes, as they can then keep for a year or more. A reference, very kindly supplied by Lt.-Col. R. N. Chopra from *Die Pflanzen-stoffe* by C. Wehmer (2nd Edition, Vol. I, 1929, Vol. II, 1931), says that the acid variety of *Mangifera Indica* contains the acid citric. Beyond this we have been unable to find any reference to the investigation of its acid contents.

The samples investigated by us were obtained from the local market. Three organic acids, tartaric, citric and oxalic, have been found in the amchur, in proportions of 6, 4 and 1% approximately. The ash was rather low, about 5%, and showed the presence of phosphates in addition to that of aluminium, iron, calcium, magnesium, sodium and potassium. The total acidity,

found by direct titration against alkali and calculated in terms of tartaric acid, was as high as about 15%. The presence was also detected of starch and glucose or glucosides.

*Experimental.*

*Moisture.*—The amchur, though sun-dried, still contained appreciable amounts of water. Weighed amounts were kept in an air-oven, at a little above 100° C., and the loss determined till the last weight was constant. Two samples gave respectively 14.73 and 14.75%, or 14.74% as the average moisture content.

*Ash.*—The ash obtained on incineration was, on an average in two experiments, 5.44%. A qualitative macro-analysis of the ash indicated phosphate, iron, aluminium, calcium, magnesium, sodium and potassium.

*Solubility.*—The amchur dried at 100° C. was found to contain about 13.65% of water-soluble material. For the purpose of extracting the organic acids, trial-extractions were made with a number of solvents, such as water, acetone, alcohol, ether and ethyl acetate. Water was undoubtedly a very suitable solvent, but on account of the presence of starch in the material, became very difficult to work with, as extractions with boiling water gave a pasty mass which could not be easily and quickly filtered. Acidified alcohol was found to be able to avoid the difficulty.

*Organic acids.*—The method finally adopted was as under. 100 g. of the powdered amchur were refluxed with 250 c.c. of ethyl alcohol (rectified about 92–95%), acidified with 10 c.c. of 2N hydrochloric acid. After a few hours, the solvent was removed and the amchur was refluxed with another lot of unacidified alcohol. This was repeated four or five times, till the extract ceased to give an acid reaction. From the accumulated extracts, alcohol was removed by distillation and the residue was treated with sufficient water. This was heated on the water-bath till all the alcohol was evaporated off, when the watery extract, coloured though clear, was treated with lead acetate solution. After the precipitated lead salts were removed, the filtrate was treated with basic lead acetate solution to ensure complete precipitation of the acids. The two precipitates were mixed and the filtrate was kept aside. The residue left after the amchur was exhaustively extracted with alcohol, was also kept for further observations.

The combined lead precipitates were washed with 50% alcohol and then treated with ammonia. The bulk of the precipitate dissolved and passed into the filtrate, leaving only a small residue. The filtrate must contain tartaric, citric and malic acids, and the residue may contain oxalic.<sup>5</sup> This residue was suspended in water and decomposed by hydrogen sulphide and

filtered. The filtrate on evaporation gave an acid liquid, which, in the presence of dilute sulphuric acid, reduced potassium permanganate solution in the warm. From a neutral solution of the syrup, calcium chloride solution gave a white precipitate of calcium oxalate, insoluble in acetic acid, which confirmed oxalic acid.

The filtrate of the ammonium salts, on treatment as described (5, *loc. cit.*), free from lead sulphide, was concentrated; aqueous potassium acetate solution, 95% alcohol and vigorous stirring helped to bring down a sticky precipitate of cream of tartar, which settled on keeping. The solution was poured off, and the precipitate was washed with diluted alcohol (2 parts alcohol and one of water), dissolved in acetic acid, and treated with lead acetate solution. From the precipitated lead salt, the free tartaric acid was separated in the usual way in aqueous solution, which on evaporation gave a syrup, and from the syrup, white crystals. The purified crystals melted at 169° C., alone as well as when mixed with some pure tartaric acid.

It weighed about 1.5 g., and its identity was further confirmed by other tests: such as charring on heating, reduction of ammoniacal silver nitrate solution, the Fenton's test, Mohler's test<sup>6</sup> and Pinerua's test,<sup>7</sup> all of which were found, by trials with the known organic vegetable acids, to be perfectly reliable for tartaric acid.

The liquid separated from the cream of tartar above, was treated with calcium chloride, ammonia and some alcohol. The precipitate formed might be the calcium salts of malic and citric acids: it was washed with hot lime water, whereby the malate would go in solution and the citrate would remain undissolved.

The filtrate was examined for malic acid. Sulphuric acid was added, the precipitated calcium sulphate filtered off, and lead acetate solution added. As it gave no precipitate, malic acid could not be present.

The residue of calcium citrate was treated with a calculated quantity of dilute sulphuric acid and the precipitated calcium sulphate removed by filtration. By means of lead acetate and hydrogen sulphide, the citric acid was again obtained in aqueous solution, which was evaporated to a thick syrup, cooled, kept in a vacuum desiccator for some days, and ultimately evaporated gently, to dryness on a water-bath, when white glistening plates, weighing about one gram, were obtained. It melted at 152° C. (anhydrous citric acid melts at 153° C.). Its identity was further confirmed by its behaviour on heating when it did not char but gave the pungent fumes of aconitic acid; by giving no precipitate in the cold from a neutral solution by the addition of calcium chloride solution, though it appeared immediately on boiling; and by answering Denigès' test.<sup>8</sup>

*Glucose.*—The filtrate left after the removal of the lead salts of the organic acids above, obtained by the first treatment with lead acetate and basic lead acetate solutions, was treated with hydrogen sulphide to remove lead completely, the precipitated lead sulphide was filtered off and the residual liquid was evaporated on a water-bath to a syrup, which gave out no crystals. The syrup indicated carbon, hydrogen and some inorganic materials. It reduced, however, Fehling's solution, reduced copper acetate in dilute acetic acid solution and gave Molisch's reaction for carbohydrates. The syrup was dissolved in water, treated with lead acetate solution, boiled and then ammonium hydroxide was cautiously added till a slight permanent precipitate was formed. On boiling, the salmon-red coloured precipitate, characteristic of glucose, was observed. This was filtered, washed and decomposed by hydrogen sulphide. After the removal of lead sulphide, the filtrate was concentrated and an osazone was prepared from it, which melted at 205° C. (glucosazone melts at 205° C.), and its melting-point was not changed when a mixed melting-point was taken with a known specimen of the glucosazone.

*Starch.*—The residue of the amchur left after the alcoholic extraction of amchur, and weighing, when air-dried, about 70 g., was refluxed with water for about four hours and filtered. This watery extract gave a blue colour on the addition of iodine solution, the colour disappearing on heating and re-appearing on cooling. An equal bulk of alcohol was added, which gave a colourless jelly. After filtering this off, the filtrate gave no colour with iodine solution, while the residue on the filter did as before. Neither the filtrate nor the jelly gave indications of proteins or of alkaloids, though the former showed potassium. The jelly was dried and powdered when it resembled, in appearance as well as in behaviour, starch. It was a white amorphous powder, which, on heating, decomposed, charred and emitted the smell of burning flour. Insoluble in cold water, it dissolved on boiling and did not immediately separate on cooling. This solution gave, besides the starch-iodide test, a white precipitate with lead acetate solution.

*Quantitative determinations of the organic acids: Tartaric Acid.*—10 g. of amchur were refluxed with 92–95% alcohol repeatedly, till all the acids were extracted. This was very carefully filtered, and to the filtrate potassium acetate solution was added. It was vigorously stirred and left for settling overnight. The potassium hydrogen tartrate formed was both sticky and coloured. Instead, therefore, of weighing it directly as usual, it was, after washing, suspended in water and titrated directly against standard NaOH solution. (Trial experiments with pure potassium hydrogen tartrate similarly suspended in water and titrated had given accurate results.) The amount of

tartaric acid found was, in two similar determinations, 6.087% and 6.112% respectively.

*Determination of citric and oxalic acids.*—The filtrate obtained from the potassium hydrogen tartrate was treated with lead acetate till complete precipitation was effected. It was warmed and the lead salts filtered off. Treatment of this precipitate with ammonia left the lead oxalate undissolved. The latter was removed from the dissolved lead citrate and thoroughly washed.

The insoluble lead oxalate was suspended in water, decomposed by hydrogen sulphide, the lead sulphide separated, and the filtrate and washings evaporated till H<sub>2</sub>S was completely removed. The amount of oxalic acid in this was determined by titration against standard potassium permanganate solution. The oxalic acid found in two samples was 1.076% and 1.074% respectively.

The combined filtrate and washings containing the citrate were acidified with acetic acid and the acid was precipitated as the lead salt. This precipitate was filtered off, treated with H<sub>2</sub>S, while suspended in water, the lead sulphide removed and washed, and the filtrate and the washings containing the free citric acid were titrated against standard sodium hydroxide. The citric acid in two determinations was found: 4.218% and 4.236%.

*Determination of glucose.*—The amchur solution was clarified by a preliminary treatment with basic lead acetate solution which brought down the acids and some other impurities. After the removal of these, the remaining filtrate and washings were treated with oxalic acid to remove the excess of lead. In the remaining solution, the glucose was determined by the method of Lane and Eynon, using methylene blue as an internal indicator.<sup>9</sup> Two experiments gave the amount of glucose as 2.9895% and 3.0135% respectively.

*Summary.*

| The mean of two concordant determinations:— |    |    |    | %      |
|---|----|----|----|--------|
| Water in sun-dried amchur                   | .. | .. | .. | 14.74  |
| Water-soluble, in 100° C. dried sample      | .. | .. | .. | 13.65  |
| Total acidity, as tartaric acid             | .. | .. | .. | 15.215 |
| Tartaric acid                               | .. | .. | .. | 6.099  |
| Citric acid                                 | .. | .. | .. | 4.227  |
| Oxalic acid                                 | .. | .. | .. | 1.075  |
| Glucose                                     | .. | .. | .. | 3.0015 |
| Ash   | .. | .. | .. | 5.44.  |

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