CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part I. Bitter Principles of Pamparapanas (Indian Shaddock)

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The bitter taste of the fruits of the citrus group has been attributed to the existence of certain crystalline compounds the most important of which is naringin. Their study is of great interest in connection with the fruit industry. Though some element of bitterness is agreeable too much of it is a serious disadvantage. Two important points to be noted in this connection are (1) the bitter principles are found to reside mostly in the peels, rags (placenta and vascular bundles) and the seeds and (2) they are capable of conversion into non-bitter derivatives. The second phenomenon takes place particularly when the fruit ripens or when it is stored. There is therefore large scope for producing fruit juices without much bitterness by suitably adjusting the conditions. Further, the by-products, peels and seeds have found use in medicine mainly because of the existence of bitter principles in them.

Pamparapanas (Indian Shaddock) is a very large sized fruit commonly available in the coastal tracts. The peels are thick, with definite flavedo and albedo and the cellulose coatings enclosing the different sections can be easily removed by hand. The seeds are large and have a rough surface. The peels and rags are found to contain naringin as the bitter principle and in this respect this fruit resembles the grape fruit. In appearance, the nature of the different parts and other characteristics, however, the two fruits differ markedly. Regarding the peels of pamparapanas the method that is usually advocated for the preparation of naringin from the peels of the grape fruits is not quite suitable.\(^1\) A preliminary extraction of the dry sample with ether considerably improves the efficiency of the subsequent extraction with aqueous alcohol. This is due to the removal of the oily and resinous matter. The above operation is not necessary in the case of the rags since they contain very little of oil in them. The fresh wet rags contain a high percentage of naringin (1%) and hence during manufacture of the juice great care has to be taken to avoid crushing these rags and extracting them.
The seeds from which the oil had been removed by extraction with light petroleum were employed for studying the bitter principles. Further extraction with alcohol removed all the bitterness of the seeds. The bitter components could be divided into two parts: (1) water-soluble and (2) water-insoluble. The first portion was identified as naringin and the second as a mixture of limonin and isolimonin. It may be remarked here that the presence of the last two in orange kernels was noted by Koller and Czerney and that Feist and Overberg recorded the presence of limonin in lemon pips. The occurrence of naringin in citrus seeds does not seem to have been observed till now. The point of interest is that naringin is intensely bitter and because of its solubility in water its taste is readily felt. On the other hand limonin and isolimonin are sparingly soluble in water and hence the solids when placed on the tongue do not give rise to the bitter taste. However when an alcoholic solution is diluted with a large volume of water, the dilute solution tastes markedly bitter. It is possible therefore that the marked bitterness of the seeds is mainly due to the naringin though the others may also add to it.

Naringin isolated from the different parts of the pamparapanas fruit was identified by a detailed study of its composition, properties and reactions and by comparison with an authentic sample of grape fruit naringin. The investigation definitely establishing the final constitution of naringin as a glycoside having the disaccharose group in the seventh position of naringenin has already been reported. Though limonin has been known for a long time as the bitter principle of lemon seeds the first detailed investigation was published by Koller and Czerney in 1936. They obtained it from orange kernels and gave the molecular formula as \(\text{C}_{22}\text{H}_{20}\text{O}_{7}\), the melting point as 280° and the specific rotation as \(-142°\). Immediately after, Feist and Overburg gave a brief account of the properties of citrolimonin obtained from lemon seeds. This seems to be the same as limonin. The melting point however was given higher as 302°, the rotation as \(-135°\) and the molecular formula as \(\text{C}_{26}\text{H}_{36}\text{O}_{8}\). Koller and Czerney also isolated a small quantity of a second bitter principle called isolimonin to which they gave the molecular formula \(\text{C}_{23}\text{H}_{29}\text{O}_{7}\). More recently Higby has reported that isolimonin occurs as the main bitter principle of the peels, rags and seeds of Navel oranges and limonin in Valencia oranges, that the two are isomeric and that the former yields on hydrolysis with alkali limonin as one of the products.

The seeds of the shaddock probably owe their main part of the bitterness to the presence of naringin. However a mixture of limonin and isolimonin occurs to the extent of about 0.6% of the dry weight of the seeds and of