# Reactions of Calcium Phosphate with Some Fruit Juices

T.V.R.K. RAO
*Department of Chemistry*
*Purnia College, Purnia-854 301, India*

Reactions of calcium phosphate with some fruit juices, *viz.*, juice of jamiri, gagal and kagzi lemons (*Citrus limon*), orange (*Citrus aurantium*), sweet orange (*Citrus sinensis*), cherries (*Prunus cerasus*) and grapes (Vitis vinifera) have been studied. Solubility of calcium phosphate in the fruit juices has been determined. Conductometric titrations evidenced complexation of calcium phosphate by the complexone (hydroxy acid) of fruit juices. The juices have been standardised with respect to their hydroxy acid content by a comparative method. A calcium phosphato citrate (1 : 3) complex has been isolated and characterised from the reaction mixture of calcium phosphate and kagzi lemon juice.

## INTRODUCTION

Calcium phosphate is a biologically important mineral. It forms one of the insoluble ingredients of urinary stones[1]. Interaction of calcium phosphate with different compounds has been studied earlier[2–4]. Presently we are reporting the reactions of calcium phosphate (tribasic) with some fruit juices, *viz.*, juice of jamiri, gagal and kagzi lemons (*Citrus limon*), orange (*Citrus aurantium*), sweet orange (*Citrus sinensis*), cherries (*Prunus cerasus*) and graphes (*Vitis vinifera*). Conductometric titrations evidenced complexation of calcium phosphate by the hydroxy acids of fruit juices. Solubility of calcium phosphate in the fruit juices has been determined. The juices have been standardised with respect to their hydroxy-acid content. A calcium phosphato citrate (1 : 3) complex has been isolated and characterised from the reaction mixture of calcium phosphate and kagzi lemon juice.

## EXPERIMENTAL

Juices of the fruits were extracted with the help of an ordinary fruit juicer. In case of cherries and grapes, the fruits were crushed. The thick juices, thus obtained, were passed through a mesh and then suction-filtered through ordinary filter paper. All the juices used were un-diluted and were used out within the minimum possible time after their extraction. Suspensions of known weights of calcium orthophosphate (tribasic) in 100 mL conductivity water were titrated conductometrically against the fruit juices on a direct reading conductivity meter (Systronics 303) delivering 1 mL in each lot. After each addition of the titrant a time period of 5 min for stirring followed by 1 min for settling down was allowed before taking the reading. Simultaneous blank titrations, *i.e.*, without calcium phosphate, were been carried out under similar experimental and volumetric conditions. Solubilities of calcium phosphate in the fruit juices were determined by finding the volume of juice necessary for dissolving 50 mg calcium phosphate suspended in 100 mL water.

The calcium phosphate citrate (1 : 3) complex was isolated from the reaction mixture of calcium phosphate and kagzi lemon juice by the method as follows. Calcium phosphate was treated with kagzi lemon juice till all the phosphate dissolved; a little more juice was added to keep it in excess. The reaction mixture was stirred well over a magnetic stirrer for a few minutes and then was evaporated to dryness on a water bath. The residue was then charred at 150–200°C in an oven, to destroy the decomposable materials of the reaction mixture at this temperature. The charred mass was extracted with excess of water and filtered. The filterate was treated with a pinch of animal charcoal, warmed and filtered. The filtrate was then concentrated on a water bath for crystallisation. Upon cooling the concentrate, a white compound separated out which was filtered out from the slightly brownish coloured mother liquor, washed with water and dried at 110°C.

## RESULTS AND DISCUSSION

Solubilities of calcium phosphate in standard solution of hydroxy acids (citric, malic and tartaric acids) and in fruit juices are recorded in Table-1 and Table-2 respectively. Strength of fruit juices with respect to their hydroxy-acid content is recorded in Table-3. Conductometric titration data is recorded in Table-4. Physical and analytical data and selected infrared bands of solid compound isolated are mentioned in Table-5. Lemon varieties, orange and sweet orange contain citric acid, cherries contain malic acid and grapes contain tartaric acid. These hydroxy acids are good complexing agents for calcium ions. Solubilisation of calcium phosphate by the fruit juices seem to be due to soluble complex formation between the former and hydroxy acids of juices. Standardisation of the juices with respect to their hydroxy acid content has been done by comparing solubilities of calcium phosphate in fruit juices with those in pure hydroxy acid solutions.

TABLE-1
SOLUBILITY OF CALCIUM PHOSPHATE IN HYDROXY ACID SOLUTIONS

| Acid | Strength of solution | Volume requried (in mL) to dissolve completely 50 mg calcium phosphate suspended in 100 mL water |
|---|---|---|
| Citric | M/2.5 | 1.4 |
| Malic | M/2 | 2.4 |
| Tartaric | M/2 | 1.4 |

For each set of conductometric titration the specific conductivities were plotted against the volume of titrant added and the break (inflection) points on the curves were located. The specific conductivities continued to increase with the addition of titrant; at the break point, however, the rate of increase decreased. Initially taken suspension of calcium phosphate ultimately went into the solution during titration. Juices were also titrated against distilled water only, to serve as blank sets. Such breaks on the curves (calcium phosphate *vs.* fruit juice) corresponding to which there is no break on the respective blank titration (water *vs.* juice) curve, indicate some soluble complex formation between calcium phosphate and the hydroxy acid of the juice. Pure hydroxy acids (present in the currently studied fruits) have been found[5] to form soluble complexes with calcium phosphate.

TABLE-2
SOLUBILITY OF CALCIUM PHOSPHATE IN FRUIT JUICES

| Fruit | Volume of juice (in mL) necessary for dissolving 50 mg $Ca_3(PO_4)_2$ suspended in 100 mL water |
|---|---|
| Jamir lemon | 6 |
| Gagal lemon | 6 |
| Kagzi lemon | 7 |
| Orange | 75 |
| Sweet orange | 125 |
| Cherry | 45 |
| Grape | 17.5 |

TABLE-3
STRENGTH OF FRUIT JUICES WITH RESPECT TO HYDROXY ACID CONTENT

| Fruit Juice | Strength | With respect to the acid |
|---|---|---|
| Jamir lemon | 0.093 M | Citric acid |
| Gagal lemon | 0.093 M | Citric acid |
| Kagzi lemon | 0.080 M | Citric acid |
| Orange | 0.0075 M | Citric acid |
| Sweet orange | 0.0045 M | Citric acid |
| Cherry | 0.026 M | Malic acid |
| Grape | 0.038 M | Tartaric acid |

Solid compound, isolated from the reaction mixture of calcium phosphate and kagzi lemon juice agreed analytically with the value required for a 1 : 3 complex between calcium phosphate and citric acid. In the infrared spectra of calcium phosphate a strong band at 1044 $cm^{-1}$ and a weak band at 974 $cm^{-1}$ may be assigned to the asymmetric ($\nu_3$) and symmetric ($\nu_1$) P—O stretching vibrations respectively[6, 7]. In the spectra of currently isolated calcium phosphato citrate (1 : 3) complex the $\nu_3$ band shows up as a double-headed peak of weak intensity at 1079 and 1086 $cm^{-1}$. The region of $\nu_3$ bands and its split into two suggests the phosphate group in the complex to be monobasic and unidentate[8]. Tentatively this complex might be formulated as $[Ca_3(H_2PO_4)_2(HCit)_2(H_3Cit)]$, (where Cit = Citrate).

TABLE-4
CONDUCTOMETRIC TITRATION DATA at 25°C

| Titrate | Titrant | Break point indicating complexation (mL of titrant) |
|---|---|---|
| 0.05 g $Ca_3(PO_4)_2$ in 100 mL water | Jamir lemon juice | 8.6 |
| 0.05 g $Ca_3(PO_4)_2$ in 100 mL water | Gagal lemon juice | 9.9 |
| 0.05 g $Ca_3(PO_4)_2$ in 100 mL water | Kagzi lemon juice | 8.3 |
| 0.05 g $Ca_3(PO_4)_2$ in 100 mL water | Orange juice | 8.8 |
| 0.05 g $Ca_3(PO_4)_2$ in 100 mL water | Sweet orange juice | 9.4 |
| 0.01 g $Ca_3(PO_4)_2$ in 100 mL water | Cherry juice | 10.1 |
| 0.02 g $Ca_3(PO_4)_2$ in 100 mL water | Grape juice | 10.0 |

TABLE-5
PHYSICAL, ANALYTICAL AND INFRARED DATA OF COMPLEX ISOLATED

| Compound | Colour | Decomp. temp. (°C) | Analysis (%) Found (Calcd.) | | | Infrared bands ($cm^{-1}$) Asymmetric P—O stretch ($\nu_3$) |
|---|---|---|---|---|---|---|
| | | | Ca | C | H | |
| Calcium phosphato citrate (1 : 3) $[Ca_3(H_2PO_4)_2(HCit)_2(H_3Cit)]$ | White | 260 | 14.03 (13.54) | 25.39 (24.38) | 3.58 (2.71) | 1086–1079 |

## REFERENCES


1. James S. Ellict, *J. Urol.*, **109,** 82 (1973).
2. J.W. Mellor, A Comphrehensive Treatise on Inorganic and Theoretical Chemistry, Longmans Green & Co., London, Vol. III, p. 874.
3. H.W. Johnston, *New Zealand J. Sci-Technol.*, **36B,** 48 (1954).
4. ———, *New Zealand J. Sci-Technol.*, **36B,** 281 (1954).
5. T.V.R.K. Rao, Ph.D. Thesis, Patna University, Patna, p. 111 (1981).
6. T.R. Narayanan Kutty, *Indian J. Chem.*, **8,** 655 (1970).
7. Foil A. Miller and Charles H. Wilkins, *Anal. Chem.*, **24,** 1253 (1952).
8. R. Coomber and W.P. Griffith, *J. Chem. Soc. (A)*, 1128 (1968).


(*Received*: 9 February 2000; *Accepted*: 7 April 2000) AJC-2005