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Rose-hip tea: equilibrium and kinetic study of mineral ion extraction

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The concentrations of sodium, potassium, magnesium, calcium, chloride, phosphate, sulphate, formate and acetate ions in infusions at 80°C of sieved German rose-hip tea have been measured by ion chromatography. From the equilibrium concentrations of the infusion the ionic contents of the rose-hip tea were evaluated and compared with sparse and contradictory information in the literature. The main species present was found to be potassium, followed by calcium.

From the rates of increase of the ionic concentrations with time, first order rate constants of infusion were determined and interpreted in terms of slow diffusion of the ions through the rose-hip particles. The resulting internal diffusion coefficients were found to be 30–80 times smaller than the corresponding diffusion coefficients of the ions in water at 80°C.

INTRODUCTION

The documented evidence on the mineral content of rose-hips is sparse, scattered and contradictory. The latest McCance and Widdowson compilation (Holland *et al.*, 1991) states that undiluted rose-hip syrup contains 0·28 wt% Na and 0·026 wt% K. Touyz & Smit (1982), writing in a South African dental journal, reported the calcium and fluoride concentrations in 100 ml infusions of 1·5 g of a German rose-hip and hibiscus tea mixture; their figures lead to a minimum content in the original mixed tea of 2·15 wt% Ca and 0·008 wt% F. They found the pH of the infusion to be 2·83 as against our value of 4·1 for an infusion of rose-hip tea alone (Spiro & Chen, 1993). The most detailed information appears in a Turkish paper (Kurt & Yamankaradeniz, 1983) in which the mineral content of rose-hip pulp for making jam is given as 0·461–0·795 wt% K, 0·001–0·0059 wt% Na, 0·094-0.138 wt% Ca, 0·056–0.124 wt% Mg and 0·337–0·934 wt% phosphorus.

The present paper reports the concentrations of a set of nine inorganic and organic cationic and anionic species in a German rose-hip tea as determined by ion chromatography. Data have also been obtained for the first time on the rate of extraction of these constituents into an aqueous infusion.

MATERIALS AND METHODS

German rose-hip tea, sold as Fluet rose-hip by A. N. Woodhams & Co. Ltd, London EC2A 2AN, was mechanically sieved and the size fraction 0·85–1·00 mm was studied. The extraction system was similar to that used previously (Spiro & Chen, 1993). A blank experiment carried out with 12 of the filters (Anachem H 23535) used for excluding solid pieces of rose-hip from the samples showed the presence of significant concentrations of Na^+ (1 ppm) and Ca^{2+} (5 ppm) and appropriate corrections were made in analysing the results. Nitrogen gas was again used to stir the infusions. As there was now no need to de-oxygenate the solvent, the gas was turned on just before introducing the rose-hip tea. The infusion medium was deionised water obtained from a Millipore RO6 + Q50 system.

The ion chromatography system employed was a Dionex 2010i with a CS3 cation separator column or an AS4 anion separator column, preceded by the appropriate guard columns, and followed by a suppressor system and the conductivity detector. To prevent column degeneration by impurity species in the analyte, organic components were removed from the samples by forcing them through Sep-Pak C18 cartridges (Millipore). These cartridges were preconditioned by wetting with 2 ml methanol followed by 5 ml deionised water. The diluted sample solution was then injected into the Dionex sample loop with a 2·5 ml syringe which had been assembled with a disposable syringe filter holder to remove small particulates. Minisart NML (Sartorius) filters were used for cation analysis but for anion analysis these had to be replaced by OnGuard-H (Dionex) sample pretreatment cartridges to remove transition metal and alkaline earth cations as well as particulate matter. The OnGuard cartridges had previously been flushed with 2 ml deionised water to remove ionic contaminants. Each aliquot was diluted

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with deionised water by a factor of 5–100 prior to analysis to optimise the peak areas in the chromatograms. Calibration plots were carried out with standard solutions of Na^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, HPO_4^{2-}, SO_4^{2-}, formate and acetate in deionised water. For several ions, solutions were also made up in an acidic medium (HCl) of pH 4·7, the pH of the anaerobic rose-hip infusions, but no significant differences were found with this pH change.

The concentration of iron in the infusions was measured with an atomic absorption spectrophotometer (GBC Scientific Equipment Pty Ltd) at 248·3 nm.

RESULTS AND DISCUSSION

Equilibrium studies

When a mass *w* of rose-hip tea is infused in a volume *V* of water, the equilibrium concentration c_∞ of any given constituent in the solution is given by the equation (Spiro & Siddique, 1981; Spiro & Kandiah, 1990).

$$\frac{1}{c_\infty} = \frac{V}{w x_0} + \frac{1}{K' x_0} \tag{1}$$

where x_0 is the initial concentration of the constituent in the rose-hip and K' is its notional partition constant. Experiments were carried out at 80°C with five different masses of rose-hip ranging from 0·5 to 8 g, all in 100 ml of deionised water. The equilibrium concentrations were obtained from samples taken after 30 min infusion and were corrected for evaporation losses. Estimates based on calibration data indicate that the uncertainties in the concentrations of Mg^{2+}, Ca^{2+} and SO_4^{2-} are *c.* ± 4% while those of K^+ and HPO_4^{2-} are *c.* ±7%. The plots of $1/c_\infty$ against $1/w$ for these ions were linear but with least squares intercepts which were always small, positive for some ions and negative for others. In the latter cases, positive intercepts could be obtained by introducing error bars and drawing appropriate lines. It was clear, however, that the uncertainty limits of the intercepts were too large to provide reliable partition constants. The uncertainty limits of the slopes were much smaller (2–11%). The ionic contents of the original rose-hips, x_0, calculated from the slopes are listed in Table 1.

The other ions require separate comment. The small Na^+ peaks from the infusion samples were sometimes split while the Cl^- peaks were not distinct, so only very approximate values are available for these ions. The peak initially attributed to F^- gave a fluoride concentration much higher than that reported by Touyz & Smit (1982). The ions $HCOO^-$ and CH_3COO^- are known to possess similar retention times, a point confirmed by calibration experiments (F^- 1·23 min, CH_3COO^- 1·25 min, $HCOO^-$ 1·31 min). Repeat anion analyses were carried out using tetraborate eluent which separated the three peaks (F^- 1·99 min, CH_3COO^- 2·15 min, $HCOO^-$ 2·62 min). With this modified procedure no fluoride was detected in equilibrium rose-hip infusions but both formate and acetate ions were found to be present, in roughly equal concentration.

Table 1. Concentrations of various ionic constituents in dried German rose-hip tea (0·85–1.00 mm) as determined from equilibrium infusions at 80°C

Ion	x_0/the concentration in the dried rose-hips in:		
	ppm	wt%	mol/kg
Na^+	*c.* 1 800	*c.* 0·18	*c.* 0·08
K^+	11 600	1·16	0·30
Mg^{2+}	1 540	0·15	0·06
Ca^{2+}	6 000	0·60	0·15
Cl^-	*c.* 250	*c.* 0·03	*c.* 0·007
HPO_4^{2-}	370	0·04	0·004
SO_4^{2-}	2 130	0·21	0·02
$HCOO^-$	*c.* 105	*c.* 0·01	*c.* 0·002
CH_3COO^-	*c.* 100	*c.* 0·01	*c.* 0·002

The atomic absorption analysis of an undiluted aliquot of a rose-hip tea infusion gave an absorbance of only 0·006. According to the calibration plot, this corresponds to only *c.* 2 ppm and shows that the tea contained only a trace amount of iron.

The concentrations of K^+ and of Mg^{2+} in rose-hip tea in Table 1 are larger than, but of the same magnitude as, the figures for rose-hip pulp given by Kurt & Yamankaradeniz (1983). The major cation present is seen to be K^+, as would be expected for a typical plant material, and the surprisingly low potassium content listed in the McCance and Widdowson compilation (Holland *et al.*, 1991) is probably a mistake. Our rough estimate for Na^+ of *c.* 0·18 wt% is smaller than (but of the same magnitude as) that of Holland *et al.* (1991) though far higher than in the Turkish report. The concentration of the second most important cation, Ca^{2+}, lies between the much lower figure of Kurt & Yamankaradeniz (1983) and the very high one given by Touyz & Smit (1982). The latter result was probably affected by the hibiscus present in their tea mixture. The contribution of the hibiscus may also explain why they reported the presence of fluoride ion which we were unable to detect. No figure for sulphate content has been published previously, and the fact that the Turkish group's value for total phosphorus is so much greater than the HPO_4^{2-} content in Table 1 points to the presence of other phosphorus-containing species in rose-hips. Indeed, it is clear from Table 1 that other anionic species must be present to balance the much higher concentrations of cations. Many of these anions are likely to be organic even though only small concentrations of low molecular weight carboxylate ions were detected.

Kinetic studies

As in the case of L-ascorbic acid infusions (Spiro & Chen, 1993), the concentration (*c*) versus time (*t*) plots for the extraction of cations and anions were not very reproducible. The replicate runs in Fig. 1 for K^+ illustrate this point well. The run marked with open

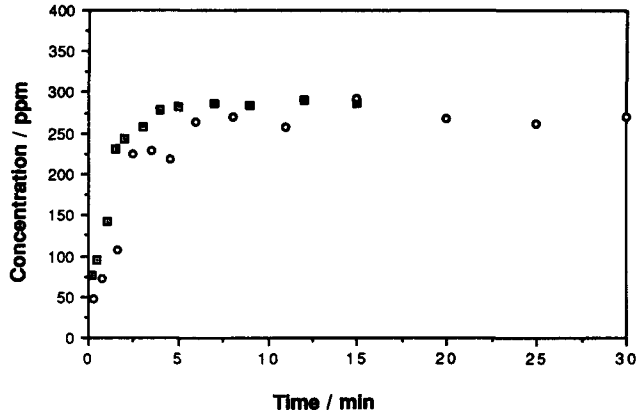

Fig. 1. The increase in concentration of K^+ ions with time in duplicate infusions of 2 g German rose-hip tea (0·85–1·00 mm) in 100 ml deionised water at 80°C.

Table 2. Rate constants for the extraction of various mineral ions from 0·85–1·00 mm German rose-hips at 80°C

Ion	c_∞ (ppm)	k (min^{-1})	D_{hip} (10^{-10} m^2 s^{-1})	D_{aq} (10^{-10} m^2 s^{-1})	HF
K^+	270	0·24	0·71	58·4	82
Mg^{2+}	31	0·11(0·54)	0·33	21·2	64
Ca^{2+}	82	0·15	0·45	23·6	52
HPO_4^{2-}	10	0·24	0·71	21·8[a]	31
SO_4^{2-}–	44	0·33	0·98	31·8	32
AA^{-}[b]	70	0·20	0·60	24·2[c]	40

[a] Calculated from the conductance figure given by Selvaratnam & Spiro (1965).

[b] L-Ascorbic anion, rate data from Spiro & Chen (1993).

[c] Diffusion data from Shamim & Baki (1980), scaled up by eqn (5).

circles shows another feature noted previously, namely an apparent series of discrete steps in the infusion pattern. Similarly shaped patterns have been reported for the uptake of ions by plant materials (Cram, 1974; Vange *et al.*, 1974) and were discussed in structural terms. Whether such an interpretation can be applied to rose-hip tea infusion is debatable in view of the uncertainty attached to each concentration measurement and the lack of reproducibility of the curves. Both these phenomena, the occasional stepped patterns and the irreproducibility, can more appropriately be attributed to the heterogeneous nature of the sieved rose-hip tea samples (Spiro & Chen, 1993). Further work needs to be done with colour-matched and hand-picked particles.

Since according to the quasi-steady-state theory of extraction from spherical particles (Spiro & Selwood, 1984).

$$\ln\left(\frac{c_\infty}{c_\infty - c}\right) = k_{obs}t + a \tag{2}$$

where c_∞ is the final equilibrium concentration of the ion in question and a is a semi-empirical parameter, plots were drawn of the ln function against time. For most of the runs a single straight line could be drawn through almost all the data points. In the case of magnesium, the points appeared to fall on two intersecting straight lines. Here the slope of the first section is given in Table 2, with the slope of the second section in brackets.

If diffusion of the ion through the rose-hip particle is the rate-determining step, then it follows from the quasi-steady-state model (Spiro & Selwood, 1984) that

$$k_{obs} = 12D_{hip}/r^2 \tag{3}$$

where r is the radius of the particle (0·463 mm). The resulting values of the diffusion coefficient within the rose-hips, D_{hip}, are given in the fourth column of Table 2.

The values of D_{hip} can now be compared with the corresponding diffusion coefficients of the ions in water at 80°C, D_{aq}. To evaluate the latter we first calculate the tracer diffusion coefficients of the ions at 25°C, D_i, from the known limiting equivalent conductances λ_i at 25°C (Robinson & Stokes, 1959) using the Nernst equation

$$D_i = (RT/F^2)(\lambda_i/z_i) \tag{4}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant and z_i the charge number of ion i. Scaling the D_i values at 25°C up to 80°C is then carried out by means of the equation

$$D_{aq} = D_i[T(80°C)/T(25°C)][\eta(25°C)/\eta(80°C)] = 2{\cdot}984D_i \tag{5}$$

where η is the viscosity of water at the stated temperature (Robinson & Stokes, 1959). Equation (5) is based on the Stokes–Einstein relation together with the assumption that the hydrodynamic radii of the ions are independent of temperature. The resulting values of D_{aq} at 80°C, listed in the fifth column of Table 2, are seen to be considerably greater than the corresponding values of D_{hip}. The ratio D_{aq}/D_{hip}, called the hindrance factor HF, is listed for each ion in the last column of the table. These HF values are of similar magnitude, though larger for cations than for anions. It is interesting that the figure for the large ascorbate ion AA^- lies inside the range of values of the mineral ions. The origins of the hindrance factor, principally the tortuous passage of the soluble species through the internal structure of the plant material, have been discussed by Spiro *et al.* (1989). The magnitude of the HF values found for rose-hips lies within the range reported for other food materials (Spiro *et al.*, 1990).

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