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Rose-hip tea: equilibrium and kinetic study of L-ascorbic acid extraction

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The concentration of L-ascorbic acid (AA) has been measured in aqueous infusions of four different rose-hip teas (Chilean, French, German and Italian) sieved into narrow size ranges. To prevent aerial oxidation the experiments were carried out under anaerobic conditions. The L-ascorbic acid concentrations in the original teas were obtained and correlated with the particle colour, and the AA partition constant was determined at 80°C for the German rose-hip tea. The density of the dry and of the water-swollen German tea was also measured as well as the extent to which it absorbed water. The rate of AA extraction from the various teas was found to decrease with increasing particle size but it showed little variation with temperature from 70 to 90°C or with the pH of the extracting medium. Electron micrographs were taken of several rose-hip tea samples.

INTRODUCTION

Our health-conscious society has seen a steady rise in the consumption of herb teas (tisanes). An increasingly popular one is rose-hip tea, sold either as whole dried hips or as ground dried hips. The latter are also on sale in tea-bags, often mixed with hibiscus or mallow leaves. The tea is marketed as a refreshing caffeine-free drink with a fruity flavour and an additional dietary source of vitamin C. Rose-hips are also known to contain carotenoids (Razungles *et al.*, 1989), pectin carbohydrates (Kirchev *et al.*, 1981), non-volatile acids (Jarczyk *et al.* 1970) and mineral elements (Kurt & Yamankaradeniz, 1983). However, little information is available on the comparative composition of dried rose-hips from different sources and no work has been published on the rates of extraction of key components. The present paper deals with the structure of rose-hip tea and physicochemical aspects of the extraction of L-ascorbic acid (AA) while the following paper (Chen & Spiro, 1993) reports on the mineral ion components.

MATERIALS AND METHODS

Of the various rose-hip teas studied, only German ones (sold as Fluet rose-hip by A.N. Woodhams & Co. Ltd, London EC2A 2AN) were supplied in the ground form. The whole dried rose-hips used came from Chile, France (both from Hambleden Herbs, Hambleden, Oxon RG9 6SX) and Italy (Aboca S.N.C., obtained through Neal's Yard, London NW1 8AN). Whole hips were cut in half, the seeds and hair were removed by hand, and then ground with an electric coffee grinder (Moulinex type 28). All the ground hips were sieved with an Endecott mechanical sieve shaker using a set of stainless steel sieves. The fractions in the ranges 600–710 μm, 850–1000 μm and 1180–1400 μm were chosen for most of the runs.

In order to determine the amount of water absorbed by rose-hip particles, 2 g of German hips (850–1000 μm) were infused in 100 ml de-oxygenated water at 80°C for 30 min. The contents were then filtered through a sintered glass funnel. The solvent-swollen particles on the filter were briefly sucked dry and weighed. The filtrate was evaporated in a rotary evaporator and the mass of the remaining residue (the non-volatile soluble constituents) was also weighed.

In another experiment, solvent-swollen hip particles were prepared as above, their surface water gently removed with filter paper, and their density determined by the displacement method using a 25 ml pycnometer (Bauer & Lewin, 1959). Toluene was chosen as the water-immiscible liquid and all measurements were carried out at 20°C. A similar procedure was employed for the determination of the density of dried hips.

Scanning electron micrographs of cross-sections of hips as well as of ground samples were taken with a Jeol JSM-T220A SEM. The samples were mounted on clean dry aluminium stubs with Araldite. The edges of the specimens were painted with a silver solution and the samples were then sputter-coated with a thin gold film.

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The extraction system consisted of a 150 ml round-bottomed flask fitted with a Drechsel head. The end of the Drechsel tube had been shortened and fitted with a glass frit to allow efficient degassing. The requisite amount of distilled water was put in, the flask was weighed and thermally equilibrated in a thermostat bath usually set to give a temperature of 80°C inside the flask. During this period the water was purged with a flow of pre-warmed water-saturated nitrogen through the frit. To start a run, a weighed mass of sieved rose-hip was added through one of the (normally stoppered) side-arms, and periodic 0·5 ml samples were taken with a graduated 1 ml syringe (Sabre). Short pieces cut from compact paper-pulp filters (Anachem H 23535) were stuck on to the needle tip of the syringe to ensure the removal of any solid material from the sample. The filter pieces were left in the infusion medium so that, when the flask and contents were weighed again at the end of the run, the correction due to solvent evaporation could be evaluated.

The samples were injected into coded sample tubes containing 0·5 ml of 4 wt% HPO_3 (BDH) to stabilise the ascorbic acid. These tubes stood on a shallow dish of ice. These diluted aliquots were then analysed by reverse phase isocratic HPLC. The chromatographic conditions adopted were modified versions of those used by Ziegler *et al.* (1986, 1987). The 27·5 cm column containing 5 μm ODS2 was preceded by a 5 cm guard column filled with 10 μm ODS. The mobile phase was 0·5 wt% HPO_3 (for aliquots of pH ~ 4) and 0·25 wt% HPO_3 (for aliquots of pH ~ 7), pumped at 1·1 ml min^{-1} by a Beckman 110B solvent delivery module. The detector was a Cecil CE 515 double beam scanning monitor set to 243 nm (for analytes of pH ~ 4) or 267 nm (for analytes of pH ~ 7), and the output was recorded on a Milton Roy CI4000 computing integrator. The retention time for ascorbic acid varied from 4·6 to 4·95 min, similar to the values reported by Ziegler *et al.* (1986, 1987). Calibration plots using known solutions of L-ascorbic acid (BDH AnalaR) showed peak area rising strictly proportionately with concentration.

Changes in pH during a kinetic run were monitored with a calibrated digital pH meter (Kent EIL 3055) and a combined glass/calomel electrode.

RESULTS AND DISCUSSION

Physical properties

Table 1 lists the appearance of different sieve fractions of the rose-hip teas investigated. In the case of the German rose-hips, which were already supplied in the ground form, the sieve sizes 0·85–1·00 mm and 1·00–1·18 mm represented the most highly populated fractions and together accounted for 50% of the material. Only 12% of the German particles exceeded 1·18 mm. As the table shows, there were clear variations in colour even within the narrow size ranges from a given source.

Table 1. Colour and description of rose-hips according to particle size

Type	Particle size (mm)	Colour	Particle shape
German	1·18–1·40	Dark red with specks of black and brown	Overall spherical with irregular cut edges
	0·85–1·00		
	0·60–0·71	Dark orange red with specks of black, dark brown and very light orange	Flattened spheres, irregularly shaped
	0·425–0·50	Light and dark orange with specks of dark red and black and some fine hairs	As above[a]
Chilean	1·18–1·40	Mixture of dark red and orange red with specks of brownish red	Spherical with cut edges
	0·85–1·00		
	0·60–0·71	As above but with much less brownish red	As above
French	1·18–1.40	Dark red with mixtures of lighter and darker shades	Spherical with cut edges
	0·85–1·00		
	0·60–0·71	As above but with a larger percentage of lighter shades	As above
Italian	All sizes	Dark or pale brownish-black	Spherical with cut edges

[a] 'As above' denotes a parameter similar to the one written immediately above.

The electron micrograph in Fig. 1 shows large cavities indicative of the porous nature of the particle. Both large and small cavities appeared in the micrograph (not shown) of the cut edge of a fragment of Chilean rose-hip. Craters of various sizes and grouped cavities were seen on micrographs (not shown) of the cut edge of a fragment of French rose-hip and also on a Chilean specimen. Figure 2 of a French rose-hip shows a very rough surface (perhaps due to the grinding) pitted with tiny cavities and unevenly spread patches of crust which are clearly seen attached to the particle surface. Under a light microscope (magnification 150×), yellow jelly-like patches were observed on the surface of the hip wall which could be related to this crusty material.

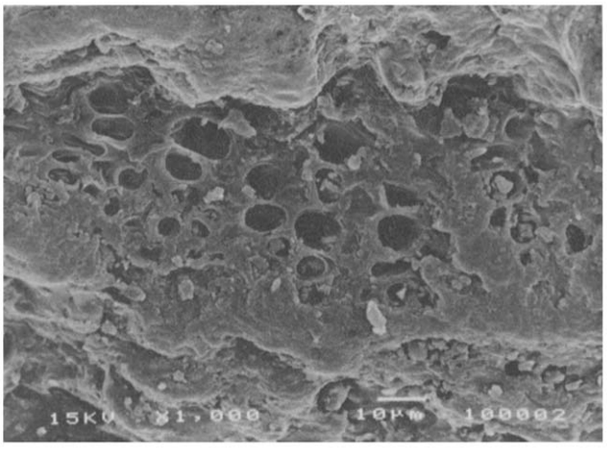

Fig. 1. Electron micrograph of a red ground German particle.

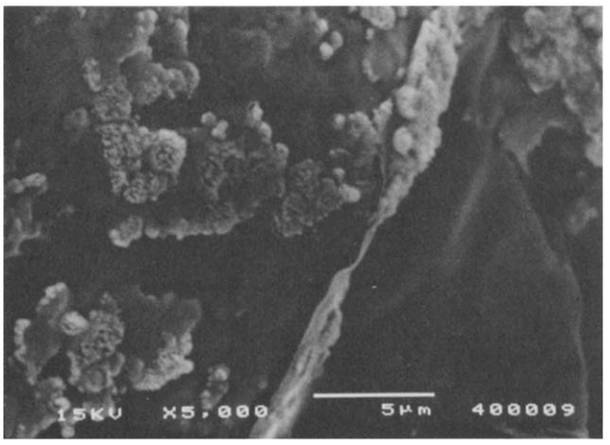

Fig. 2. Electron micrograph of a red ground French rose-hip at high magnification.

These micrographs show that the rose-hip particles are made up of dead woody type material, with the surfaces and edges exhibiting considerable structural heterogeneity. The porous sections consist of large cavities as well as isolated regions of compressed honeycomb-like cavities. Selective compressibility of the cellular structures of the tissues before ripening could have caused this uneven distribution of pores in terms of shape, size and intensity (S. Archer, private communication). The yellow gel-like patches on the surface could be resinous material exuded from the oil ducts within the fruit wall or else polysaccharide pectin. Pectin solutions are known to be able to gelate.

Extent of water absorption by rose-hips

The density of the dried German rose-hips supplied (0·85–1·00 mm) was found to be $1{\cdot}50_4$ g ml^{-1} by the displacement method with toluene in a pycnometer while that of the water-swollen hips was $1{\cdot}019_3$ g ml^{-1}.

The swelling ratio A_s, the mass of the solvent-swollen hips divided by that of the dried hips (Spiro & Kandiah, 1990), was found to be 1·635. Thus

$$1{\cdot}635 = A_s = \frac{m_{swo}}{m_{dry}} = \frac{\rho_{swo} V_{swo}}{\rho_{dry} V_{dry}} = \frac{1{\cdot}0193 V_{swo}}{1{\cdot}504 V_{dry}} \quad (1)$$

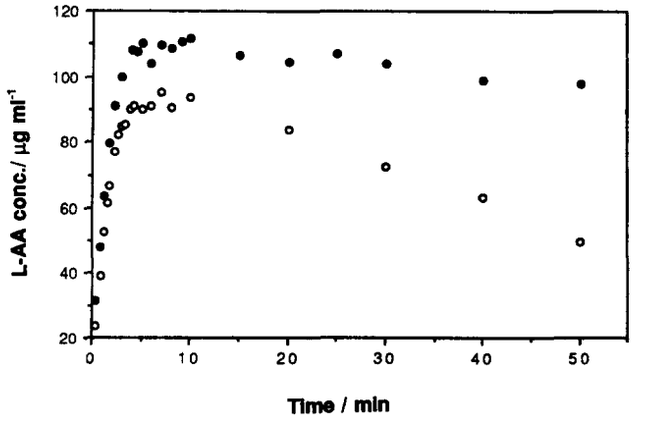

Fig. 3. Concentration–time plot of the extraction of L-ascorbic acid from German rose-hips at 80°C under aerobic conditions. ○, into distilled water; ● into 2 wt% HPO_3.

where m, ρ and V stand for mass, density and volume, respectively. Hence

$$V_{swo} = 2{\cdot}4\ V_{dry}$$

Rose-hip particles therefore swelled by a factor of 2·4 on immersion in water and increased their mass by 63·5%.

Evaporation of the filtrate of a rose-hip infusion gave the net amount of non-volatile solubles extracted per unit mass of rose hips, Y, as 0·625. The net amount of water absorbed by unit mass of rose-hips, X, is then given by (Spiro & Kandiah, 1990).

$$X = A_s + Y - 1 = 1{\cdot}635 + 0{\cdot}625 - 1 = 1{\cdot}26 \quad (2)$$

L-Ascorbic acid extraction: exploratory experiments

The initial extraction experiments were carried out in a three-necked round-bottomed 150 ml flask fitted with an open condenser and a magnetic stirrer (Rank Bros., Bottisham, Cambs.) immersed in the thermostat bath. The results of a run with 3 g German rose-hips (1·00–1·40 mm) and 100 ml distilled water are shown in Fig. 3. The concentration of AA is seen to increase rapidly at first and then, after reaching a maximum value at 7 min, to decrease due to aerial oxidation to dehydroascorbic acid (DHAA) possibly followed by irreversible degradation to diketogulonic acid (DKA) (Coultate, 1988). A similar run with 3 g French rose-hips reached a maximum AA concentration of 15 mg litre^{-1} after 5 min, followed by a rapid concentration drop to 2 mg litre^{-1} after 25 min. Since metaphosphoric acid is known (Ziegler *et al.*, 1986) to inhibit oxidation to DHAA, a repeat run was carried out with the German rose-hips but using 2 wt% HPO_3 as the infusing medium. This appreciably stabilised the AA although, as Fig. 3 indicates, there remained a slow decline in the AA concentration at longer times.

An alternative procedure was then tried, based on the fact that DHAA can be reduced back to AA by dithiothreitol (DTT) (Okamura, 1980; Ziegler *et al.*, 1987). The German hips were again infused in distilled water but the 0·5 ml samples were added to 0·5 ml DTT reagent (2 mmol litre^{-1} in phosphate buffer) and allowed to incubate at room temperature for 10 min. After this 0·1 ml ice-cooled 1·1 wt% HPO_3 was added to the samples which were kept in ice until analysed by HPLC. With this procedure the AA concentration reached a maximum of 113 mg litre^{-1} at 8 min and then gradually declined, at a rate slower than in the first run in Fig. 3 but faster than in the second run with an HPO_3 medium.

It became clear from these experiments that the aerial oxidation of AA could be prevented only by the total exclusion of oxygen. This was confirmed by carrying out infusion runs using water which had been purged with nitrogen for at least 30 min followed by continuous passage of nitrogen over the surface of the liquid after the addition of the rose-hips. With this procedure the AA concentration remained constant

after reaching its maximum value. This method was therefore adopted for all the equilibrium and kinetic runs reported in this paper.

A further problem was the gradual disintegration of the rose-hip particles during the runs. Stirring the infusions was necessary to ensure homogeneity for sampling, but the magnetic stirrer bar tended to break up the water-softened particles soon after the start of a run. The kinetics could therefore not be related to the particle size. Even the use of a mechanical stirrer (Spiro & Kandiah, 1989) proved unsuccessful because the paddles still broke up some of the particles. The problem was solved by stirring the infusion with the purging nitrogen bubbles, as described above.

The pH of the rose-hip infusions at 80°C under anaerobic conditions slowly decreased from 4·9 some 2 min from the start of a run, to 4·4 after 60 min. Under aerobic conditions the pH was 4·1 after 30 min. Rose-hip tea is thus a relatively acidic beverage.

Certain qualitative observations are worth mentioning. In most runs, foaming developed after 5–10 min. This was at first attributed to the formation of CO_2, one of the products of the anaerobic decomposition of AA. However, from the rates of decomposition at pH 4 at 100°C reported by Huelin *et al.* (1971), the extent of AA decomposition after 10 min should have been less than 0·6% even at 100°C. This would have liberated less than 0·006 ml CO_2, much too small a volume to account for the observed foam. Moreover, no foam was seen in a kinetic run in 0·1 mol litre^{-1} HCl where AA is least stable, whereas considerable foaming occurred in a buffered phosphate medium at pH 7 where the rate of AA destruction is low (Huelin *et al.*, 1971). No foam was observed either in a blank run or in an infusion carried out in air although aerobic loss of AA is often ten times greater than anaerobic loss (Liao & Seib, 1988). All these points suggest that CO_2 evolution was not the correct explanation. Instead, the foam probably resulted from the release of saponins and fatty acids which could have acted as surfactants to stabilise the formation of any foam. The hydrophilic nature of the polar ends of these molecules, and hence the surfactant action, will have been enhanced by ionisation and this may well be the reason for the observed increase of foaming with rising pH. The release of these solubles, and more especially the introduction of pectin polysaccharides into the solution, explains another phenomenon: the gradual rise in viscosity of the infusion. This was particularly noticeable when larger amounts of rose-hip (up to 8 g) were added in some of the equilibrium experiments.

L-Ascorbic acid content and partition constant

Infusion experiments were carried out under nitrogen for seven different masses, w, of German rose-hip (0·85–1·00 mm) in 100 ml water at 80°C. After 30 min, when equilibrium had been reached, the AA concentrations, c_∞, were determined. Figure 4 shows that the resulting plot of $1/c_\infty$ versus $1/w$ was linear, as

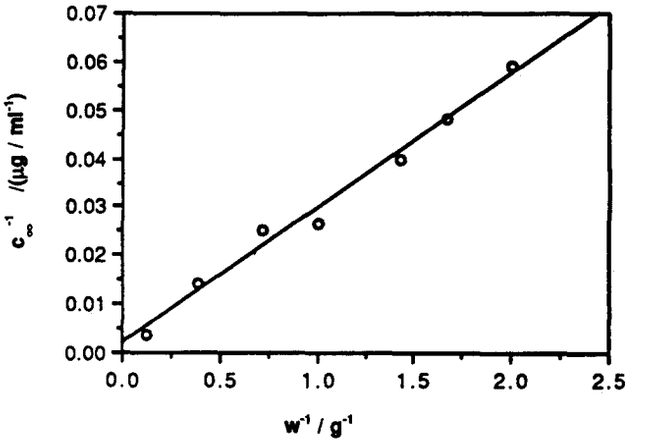

Fig. 4. Plot of $1/c_\infty$ versus $1/w$ for anaerobic equilibrium infusions of German rose-hip tea (0·85–1·00 mm) at 80°C.

predicted by the equation (Spiro & Siddique, 1981; Spiro & Kandiah, 1990)

$$\frac{1}{c_\infty} = \frac{V}{wx_0} + \frac{1}{K'x_0} \qquad (3)$$

where V is the volume of solution, x_0 the initial concentration of AA in the rose-hips, and K' the notional partition constant for AA. The slope of the least squares line in Fig. 4 led to x_0 = 3·59 g (0·0204 mol) L-ascorbic acid per kg rose-hip, or 0·36 ± 0·02 wt %. This value is above the minimum requirement of 0·20–0·25 wt% stipulated by Hungarian Standards (1969, 1971) for rose-hip fruit and pulp. It also lies within the range of 0·25–0·7% laid down by the London Herbal Tea Bureau (80 Kensington High Street, London W8 4SG) as an acceptable vitamin C content for rose-hip tea. Ziegler *et al.* (1986) reported that commercial rose-hips contained 0·04–0·54% dry weight L-ascorbic acid, frozen and lyophilised hips contained 0·7–1·3%, while rose-hips in tea bags only contained 0·15%.

While similar equilibrium plots were not carried out for all the different size fractions of the various rose-hip teas, estimates of their AA content can be obtained from the c_∞ values in Table 2. These show that, for both German and Chilean rose-hips, c_∞ fell with decreasing particle size. This may have been caused by the destruction of AA on progressively greater grinding, or by the larger surface area of the smaller particles and the consequent increased exposure to air and moisture which would chemically degrade the vitamin (Erdman & Klein, 1982). In comparison with the corresponding German tea infusions, the Chilean tea produced at least 10% more AA while the French rose-hips produced only about one-third as much. The infusions from the black Italian hips contained no detectable AA at all. This result ties in with the work of Bakos *et al.* (1981) who found the vitamin C content was highest at the onset of ripening when the hips are a pale red colour, and lowest when the hips become over-ripe and turn dark. Moreover, rose-hips grown in the more northerly parts of Europe are known to contain more vitamin C that those grown further south, and our results show a

definite correlation between AA content and distance from the equator.

According to eqn (3), the partition constant of L-ascorbic acid can be evaluated from the intercept of Fig. 4. Because of the scatter of the points the resultant value of $K' = 0{\cdot}16 \pm 0{\cdot}17$ g ml^{-1} is subject to considerable uncertainty. The notional partition constant K' is related to the mass partition constant of AA, K_m, by the relation (Spiro & Kandiah, 1990)

$$\frac{1}{K'} = \frac{1}{\rho_{water}}\left(\frac{A_s}{K_m} + Y - X\right) \quad (4)$$

whence $K_m = 0{\cdot}24$. Thus at equilibrium the AA concentration in the water-swollen hip is some four times greater than in the aqueous infusion. Mass partition constants ranging from 0·2 to 0·7 have frequently been found for solubles extracted from food plant materials (Spiro & Kandiah, 1990).

Rate of L-ascorbic acid infusion

In the anaerobic infusion experiments, *c.* 2·000 g ground and sieved rose-hip were infused in 100 ml water. All the measured AA concentrations were corrected for loss of solute and solvent through sampling and for loss of solvent by evaporation. As Fig. 5 shows, these corrected concentrations, c, at first increased rapidly with time, t, and eventually levelled out to a final equilibrium value, c_∞. Within this overall pattern, replicate runs are seen to exhibit significant differences from each other. In some experiments, as in the ones marked + and □ in Fig. 5, there were signs that the infusion proceeded in two or even three separate steps or stages, sometimes with quasi-equilibrium plateaux between them. Step-wise processes have been reported for related systems, as in the extraction of [6]-gingerol from ginger rhizome (Spiro & Kandiah, 1989) and in the uptake of amino acids and glucose from external solutions into plant cells (Shtarkshall & Reinhold, 1974). These phenomena have been attributed to a

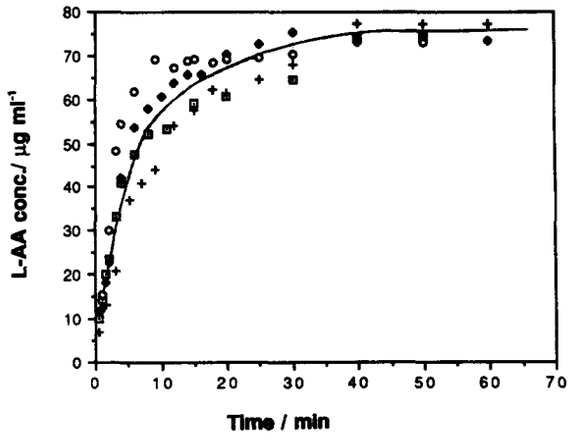

Fig. 5. Plots of L-ascorbic acid concentration against time for anaerobic infusions at 80°C of German rose-hip tea in the size range 1·18–1·40 mm. The different symbols refer to replicate runs.

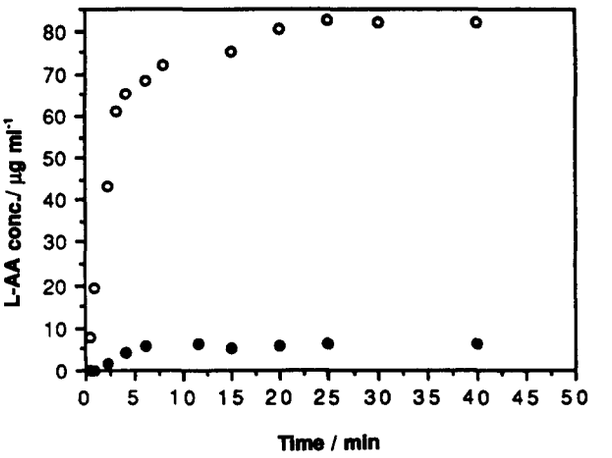

Fig. 6. Plots of L-ascorbic acid concentration versus time for anaerobic infusions at 80°C of Chilean rose-hips (0·85–1·00 mm). ○, Red particles; ●, black particles.

variety of causes including solvent inflow producing non-uniform cell rupture, thermal denaturation of membranes, and different transport mechanisms. Although explanations of this kind could well apply to rose-hip extraction, Fig. 5 demonstrates that these concentration steps could not always be reproduced in subsequent infusion runs. A large part of the variability within and between runs can actually be accounted for by an uncertainty of *c.* ±5% in the individual concentration points. The heterogeneous nature of the particles will have also played a significant role. This point is dramatically illustrated in Fig. 6 where the infusion pattern of 2 g of red particles of Chilean rose-hips of size 0·85–1·00 mm differed markedly from the same weight of black particles from the same source and size fraction. In any given sieve range, then, the particles will have come not only from rose-hips of different degrees of ripeness which have probably been dried to different extents, but also from different locations within the hips and hence with different cellular morphologies and ascorbic acid contents. When all this is borne in mind, the lack of reproducibility of the runs in Fig. 5 and the stepped nature of some of the curves are not too surprising.

In Fig. 5 a smooth curve has been drawn through all

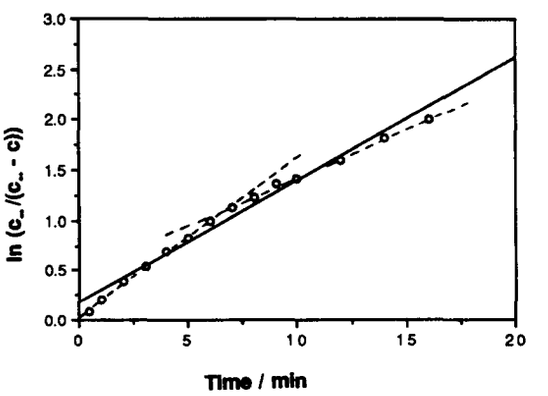

Fig. 7. Plot of ln $[c_\infty/(c_\infty - c)]$ versus time for the overall curve in Fig. 5.

the points. Figure 7 shows the resultant kinetic plot of the first-order equation.

$$\ln\left(\frac{c_\infty}{c_\infty - c}\right) = k_{obs}t + a \qquad (5)$$

derived from a quasi-steady-state model (Spiro & Selwood, 1984), where k_{obs} is a first-order rate constant and a is a semi-empirical intercept (Spiro, 1988). As can be seen, the points for the 1·18–1·40 mm German rose-hips are better represented by two intersecting straight lines than by one overall line, indicative of a faster infusion process followed by a slower one. Such situations have already been encountered with other food systems (Spiro & Kandiah, 1989). For 0·85–1·00 mm German rose-hips, however, the points fell on a single straight line. In order to make viable comparisons, only the best single line parameters have been listed in Table 2. For the Chilean and French rose-hips these parameters are the results of individual kinetic runs while for the German rose-hips, where replicate runs were carried out, they refer to the smooth curves drawn through all the data points as in Fig. 5.

Inspection of Table 2 reveals a general trend of rising c_∞ values with increasing particle size. This clearly points to a rising proportion of AA-rich particles in the larger size ranges, especially in the German rose-hip tea (cf. also Table 1 and Fig. 6). The rate constants tend to decrease with increasing radius, but not in a uniform manner. Nor is the decrease in k_{obs} as large as in the extraction of solubles from other food solids such as coffee beans (Spiro & Selwood, 1984) and ginger rhizome (Spiro & Kandiah, 1989). In these cases k_{obs} was found to vary inversely with the square of the radius of the particles, indicative of a rate-determining step of diffusion of the soluble species through the particles. If the rate determining step for the extraction of AA were also its diffusion through the rose-hip particles with a diffusion coefficient D_{hip}, then according to the quasi-steady-state model for dilute suspensions (Spiro & Selwood, 1984)

$$k_{obs} = 12D_{hip}/r^2 \qquad (6)$$

The failure of the k_{obs} values in Table 2 to obey such a relationship may be attributed to the factors enumerated above and especially to the increasing fraction of AA-rich material as the particle size increased. However, it is interesting to note that, if the first quasi-equilibrium concentrations which manifested themselves in several of the c–t plots, were employed as the c_∞ values in eqn (5), the resulting rate constants for the German rose-hips did vary approximately as $1/r^2$. Further research with hand-picked particles may be able to shed light on the appearance of steps in the infusion patterns and on the reality or otherwise of the quasi-equilibrium plateaux.

The limiting diffusion coefficient of L-ascorbic acid molecules in water at 25°C has been found to be $1{\cdot}053 \times 10^{-9}$ m^2 s^{-1} by Shamim & Baki (1980) while that of the L-ascorbate ion was $8{\cdot}1 \times 10^{-10}$ m^2 s^{-1}. Diffusion coefficients of AA solutions some 25% lower were earlier reported by Schneeberger *et al.* (1975). The values at 25°C can be scaled up to 80°C by applying the Stokes–Einstein equation (Tyrrell & Harris, 1984) to the diffusion coefficient in solution:

$$D_{soln} = k_B T/6\pi\eta r_{AA} \qquad (7)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the medium. If r_{AA}, the effective hydrodynamic radius of the L-ascorbic acid, is assumed to be independent of temperature, then D_{soln} will vary proportionately with T/η. Taking D_{soln} to be $1{\cdot}0 \times 10^{-9}$ m^2 s^{-1} at 25°C, and inserting the known viscosities of water (Robinson & Stokes, 1959), yields $D_{soln} = 3{\cdot}0 \times 10^{-9}$ m^2 s^{-1} at 80°C. Were AA to diffuse through rose-hip particles of 500 μm radius with such a diffusion coefficient, the contribution to k_{obs} would be *c.* 8·6 min^{-1}. Since this is far larger than the experimental rate constants in Table 2, diffusion of AA through rose-hip must be a greatly hindered process if it is the rate-limiting step. Hindered intra-particle diffusion has been found to be the slow step in all other food extraction processes investigated so far (Spiro *et al.*, 1989; Spiro & Kandiah, 1989).

Table 3 summarises the results of AA extraction experiments carried out at other temperatures and in aqueous media of different pH. The equilibrium concentrations are seen to remain roughly constant, except for the larger value in the phosphate buffer run which could have been due to setting the HPLC detectors at

Table 2. Kinetic parameters for the infusion of L-ascorbic acid from ground rose-hips into distilled de-oxygenated water at 80°C

Type	$\langle r\rangle^a$ (μm)	c_∞ (mg litre^{-1})	k_{obs} (min^{-1})	a
German	232	51·2	0·38	0·20
	328	58·8	0·18	0·23
	463	69·5	0·20	0·08
	645	74·0	0·12	0·17
Chilean	328	77·0	0·44	−0·05
	463	80·6	0·46	−0·10
	645	84·8	0·17	0·03
French	328	14·4	0·25	0·02
	463	24·8	0·28	−0·23
	645	18·6	0·15	0·03

[a] The midpoint radii of the sieve size range.

Table 3. Kinetic parameters for the anaerobic infusion of L-ascorbic acid from 0·85–1·00 mm German rose-hips into various media at several temperatures

Temp. (°C)	Medium	pH		c_∞ (mg litre^{-1})	k_{obs} (min^{-1})
		Initial	End		
70	Water			72·6	0·24
80	Water	7·00	4·60	69·5	0·20
90	Water			72·6	0·24
80	0·1 mol litre^{-1} HCl	0·80	0·82	71·2	0·28
80	Phosphate buffer[a]	7·16	6·44	(81·5)	0·18

[a] 0·025 mol litre^{-1} KH_2PO_4 + 0·025 mol litre^{-1} Na_2HPO_4.

243 nm instead of 267 nm. The first quasi-equilibrium concentrations, on the other hand, decreased from 59 mg litre^{-1} at 70°C to 39 mg litre^{-1} at 90°C. Surprisingly, k_{obs} did not change significantly between 70°C and 90°C. However, when the first quasi-equilibrium concentrations were used as c_∞ in eqn (5), rate constants of 0·42, 0·55 and 0·68 min^{-1} were obtained at 70, 80 and 90°C, respectively, leading to an Arrhenius activation energy of 25 kJ mol^{-1}. This lends further credence to the reality of steps in the infusion plots.

The k_{obs} values decreased with increasing pH of the extracting medium. The L-ascorbic acid will have been completely undissociated in the HCl solution and almost completely dissociated in the phosphate buffer since its pK_1 is 4·17 at 25°C (Liao & Seib, 1988). One would therefore have expected a small rise rather than a fall with increasing pH if the ions diffuse in company with positively charged co-ions such as K^+ (Spiro *et al.*, 1987). The result obtained thus points to the presence of new factors such as complexation of the L-ascorbate ion with other constituents like metal ions (Chen & Spiro, 1993).

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