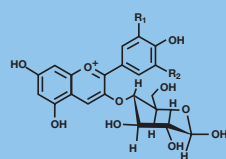


The relevance of soft fruit to human nutrition

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A recent joint expert report by the World Health Organisation and the Food and Agriculture Organisation of the United Nations concerning the relationship between nutrition and chronic and degenerative diseases concluded that a convincing association exists between the consumption of fruits (including berries) and vegetables and reduced risk of cardiovascular disease (CVD) and cancer. In addition to these epidemiology-based conclusions it is now generally accepted that both of these degenerative diseases are initiated by the oxidative reaction of free radicals with lipids, proteins and DNA within the human body. Logic, therefore, suggests that increased consumption of antioxidants should alleviate, or at least retard, the onset of these diseases and this has been the focus of much research.



Rutinoside – (rhamnosyl-1→6-glucose)
 Sophoroside – (glucosyl-1→2-glucose)
 Sambubioside – (xylosyl-1→2-glucose)

R ₁	R ₂	Anthocyanin	Recovery (%)
OH	H	Cyanidin-3-glucoside	61
OH	H	Cyanidin-3-rutinoside	81
OH	H	Cyanidin-3-sambubioside	40
OH	H	Cyanidin-3-sophoroside	85
OH	OH	Delphinidin-3-glucoside	40
OH	OH	Delphinidin-3-rutinoside	59
OH	OH	Delphinidin-3-sambubioside	29
OH	OH	Delphinidin-3-sophoroside	65
OCH ₃	OCH ₃	Malvidin-3-glucoside	81
OCH ₃	OCH ₃	Malvidin-3-rutinoside	90
OCH ₃	OCH ₃	Malvidin-3-sambubioside	55
OCH ₃	OCH ₃	Malvidin-3-sophoroside	90
H	H	Pelargonidin-3-glucoside	80
H	H	Pelargonidin-3-rutinoside	71
H	H	Pelargonidin-3-sambubioside	35
H	H	Pelargonidin-3-sophoroside	82
OCH ₃	H	Peonidin-3-glucoside	49
OCH ₃	H	Peonidin-3-rutinoside	75
OCH ₃	H	Peonidin-3-sambubioside	80
OCH ₃	H	Peonidin-3-sophoroside	81
OCH ₃	OH	Petunidin-3-glucoside	40
OCH ₃	OH	Petunidin-3-rutinoside	70
OCH ₃	OH	Petunidin-3-sambubioside	79
OCH ₃	OH	Petunidin-3-sophoroside	72

Table 1 The recoveries of anthocyanins following *in vitro* digestion.

Our previous studies have identified the (sub)classes and diversity of antioxidants present in three soft fruit species relevant to the Scottish economy - *Rubus*, *Ribes* and *Fragaria*. These species are also important sources of nutritional value in Europe and North America along with other species including cloudberry (*Rubus chamaemorus*) and Rowan (*Sorbus spp.*) etc. As bioavailability is a pre-requisite of efficacy in humans we are assessing, using a validated *in vitro* digestion system, the ability of phytochemicals to survive unchanged in transit through the stomach and upper gastrointestinal tract.

LC-MS analyses of *in vitro* digestion products from a range of soft fruit anthocyanins and phenolics showed that resistance to digestion was related to both the degree of methoxylation and glycosylation, as well as the type of glycosylation (Table 1). Without exception, the diglycosylated anthocyanins rutinoside and sophoroside both exhibited greater resistance to *in vitro* digestion than the corresponding mono-glycosylated compounds with the rutinoside generally the more resistant. However the sambubiosides were invariably the least resistant to digestion with the xylose-glucose linkage predominantly responsible for their lability.

The lability of these disaccharide (and, if present, tri-oligosaccharide) linkages does not necessarily compromise nutritional value since degradation of the disaccharide (or oligosaccharide) ultimately leads to the generation, at least transiently, of the mono-glycosylated forms which most likely enter human cells via the intestinal glucose transport (SGLT1) pathway.



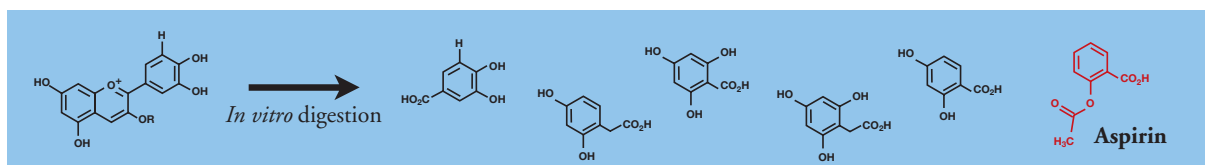


Figure 1 Some of the products produced following the *in vitro* digestion of the anthocyanin cyanidin.

The chemistry of the anthocyanidin moiety itself has a direct bearing on its *in vitro* digestibility. In general, the balance between methoxylation and hydroxylation is directly related to lability to digestion. Malvidin, a dimethoxylated anthocyanin, exhibits the greatest level of resistance to digestion with the tri-hydroxylated anthocyanin, Delphinidin, the least resistant. Interestingly, the progression from tri-, di- to mono-hydroxylation (delphinidin, cyanidin and pelargonidin, respectively) is accompanied by an increasing resistance to digestion for a given glycoside. The analogous progression from di-, mono- to non-methoxylation (malvidin, peonidin and pelargonidin, respectively) is less clear but is broadly related to an increased susceptibility to *in vitro* digestion.

The products of an *in vitro* (and by implication an *in vivo*) digestion process, whilst including aglycones and compounds with reduced levels of glycosylation, also include metabolites with potential pharmacological impact (Fig. 1). Many of these compounds are structurally similar to aspirin, the common anti-inflammatory and pain relief drug which is now prescribed to prevent CVD and strokes. It is estimated that globally, 50 billion aspirin tablets are taken annually. The link between health benefits associated with fruit intake, degenerative diseases and the production of such compounds during digestion warrants further study.

Studies to determine the ability of fruit phenolics to survive *in vitro* digestion showed that differences exist between the species examined, with rowan and lingonberry exhibiting the highest and lowest recoveries, respectively (Fig. 2). The proportion of fruit juice phenols that survived *in vitro* digestion and remained available to reach the 'serum fraction' was generally *c.* 5-10%. However, these values represent a simple digestion model and factors such as active uptake and food-matrix interactions will invariably cause the actu-

al *in vivo* values to be much lower. In addition to this the differences in the polyphenolic composition of the berries will obviously contribute to variations in overall bioavailability of phenolics. However, the model acts as a robust and reproducible way of determining

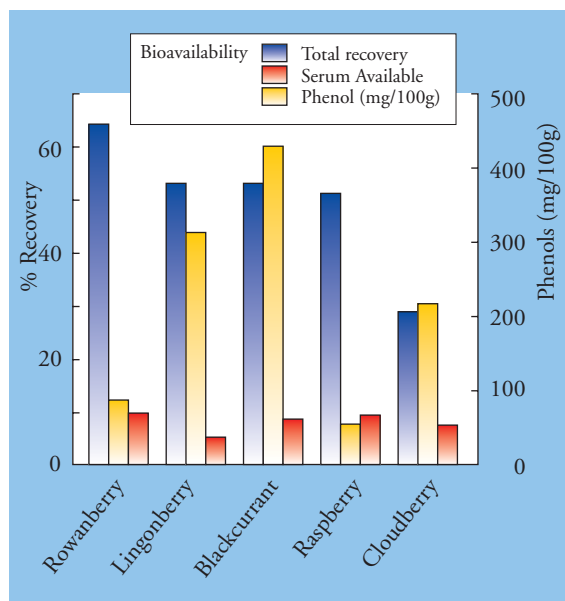


Figure 2 The recoveries and bioavailabilities of selected soft fruit phenolics following *in vitro* digestion. The values are represented as the % of the total phenols recovered or bioavailable to the serum relative to the total phenol added at the start of the *in vitro* digestion, and the absolute sample phenol concentration. The phenol values refer to the total phenol contents of the original juices.

the relative ability of fruit phytochemicals/bioactive compounds to survive the digestive processes.

Data from model digestion/bioavailability assessments will be used to test hypotheses on modes of action. This in turn will help drive breeding programmes on nutritional enhancement.