

Review

Chlorogenic acids and other cinnamates – nature, occurrence and dietary burden†

Michael N Clifford

Food Safety Research Group, School of Biological Sciences, University of Surrey, Guildford, Surrey, GU2 5XH, UK

Abstract: This review defines the range of forms in which cinnamates (*p*-coumarates, caffeates, ferulates and sinapates) occur in foods and beverages subdividing them into (i) the classic chlorogenic acids and close allies, (ii) other esters, amides and glycosides, and (iii) transformation products formed during processing. Cinnamate derivatives which would not release cinnamic acid by hydrolysis are excluded. The quantitative data are reviewed concisely and attention is drawn to certain shortcomings, in particular a complete absence of data for certain commodities (breakfast cereals, baked goods, tomato products and nuts) and minimal data for pulses, legumes and processed or cooked foods. In addition, more data are required for the edible portion of modern varieties. By extrapolating from such data as are available the important source(s) (i) of individual cinnamates (regardless of the conjugate type) and (ii) of each major class of conjugate, have been identified as follows:

- (i) *Cinnamates*: caffeic acid: coffee beverage, blueberries, apples, ciders; *p*-coumaric acid: spinach, sugar beet fibre, cereal brans; ferulic acid: coffee beverage, citrus juices, sugar beet fibre, cereal brans; sinapic acid: broccoli, kale, other leafy brassicas, citrus juices.
- (ii) *Conjugates*: caffeoylquinic acids: coffee beverage, blueberries, apples, ciders; *p*-coumaroylquinic acids: sweet cherries; feruloylquinic acids: coffee beverage; tartaric conjugates: spinach, lettuce, grapes and wines; malic conjugates: lettuce, spinach, possibly legumes; rosmarinic acid: culinary herbs, mixed herbs, possibly stuffings; cell wall conjugates: spinach, sugar beet fibre, cereal brans.

It seems likely that the UK population will fall into several categories depending on (i) their consumption of coffee, (ii) their consumption of bran, and (iii) their consumption of citrus. Those who drink several cups of coffee per day augmented by bran and citrus might easily ingest 500–800 mg *cinnamates* (or even 1 g for the greatest coffee ingest consumption) whereas those who eschew all these and take little fresh fruit or vegetables might struggle to consume 25 mg.

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INTRODUCTION

Possibly the first report referring to chlorogenic acids was that published in 1837 by Robiquet and Boutron,¹ but the term itself does not seem to have been introduced until 1846 by Payen.^{2,3} In 1932 chlorogenic acid was shown to be a caffeic acid conjugate of quinic acid.⁴

Since then a vast literature has developed and it has become apparent that there are many cinnamoylquinic conjugates, that these are only one of many conjugated forms of the cinnamic acids, and

that such conjugates are extremely widespread in the plant kingdom. It is not easy to summarise this literature and even less easy to put this information into the context of human food. Many of the data available relate to non-food sources although some plants studied may be close botanical relatives of plants consumed and others may be of interest as herbal remedies. Even when foodstuffs have been analysed, data are often qualitative, or for a very limited number of samples and varieties (not necessarily those of current horticultural or agricultural

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* Correspondence to: Michael N Clifford, Food Safety Research Group, School of Biological Sciences, University of Surrey,

Guildford, Surrey, GU2 5XH, UK

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importance) and quite often not solely for edible tissue. Only occasionally has consideration been given to maturity or season and rarely to the effects of processing or cooking.

It is not easy to identify unequivocally one component as a particular conjugate among many possible and structurally similar substances and it is now known that some early identifications were in error. For example, the original identification of cinnamoyl-glycerols in pineapple as 1,4-di-*p*CoQA,⁵ the incorrect identification of a caffeoyltartaric acid glucoside in grapes and of 1,5-diCQA in coffee, corrected by Baranowski and Nagel⁶ and Clifford⁷ respectively, and the early confusion over the conjugates in cranberries discussed by Marwan and Nagel.⁸ There may be others as yet unrecognised, especially in view of some apparent inconsistencies in the data available.

THE NATURE OF THE CINNAMATE CONJUGATES

The chlorogenic acids

Classically, chlorogenic acids (CGA) are a family of esters formed between certain *trans*-cinnamic acids and quinic acid (1L-1(OH),3,4/5-tetrahydroxycyclohexane carboxylic acid) which has axial hydroxyls on carbons 1 and 3, and equatorial hydroxyls on carbons 4 and 5. During processing, *trans* isomers may be partially converted to *cis*.

Using the preferred IUPAC numbering,⁹ the commonest individual chlorogenic acid is 5-*O*-caffeoylquinic acid (5-CQA). It is the only one commercially available and is still often called chlorogenic acid or 3-CQA (pre-IUPAC numbering) but the use of both terms should be discouraged. (Please note that in this review all citations will use the IUPAC system and if necessary numbering has been changed for consistency and clarity.)

These classic CGA may be subdivided by the identity, number and position of the acyl residues. The following subgroups are known:

- the relatively widespread mono-esters of caffeic acid, ie caffeoylquinic acids (CQA), *p*-coumaroylquinic acids (*p*CoQA) and feruloylquinic acids (FQA);
- di-esters, tri-esters and the single tetra-ester of caffeic acid, ie diCQA, triCQA and tetraCQA, the latter two groups being characteristic of Asteraceae;^{10–14}
- mixed di-esters of caffeic and ferulic acid, ie caffeoylferuloylquinic acids (CFQA) which are characteristic of robusta coffee (*Coffea canephora*, Rubiaceae)^{15–18} or caffeic and sinapic acid, ie caffeoylsinapoylquinic acids (CSiQA) as found in *Gardenia jasminoides* (Rubiaceae);¹⁹
- mixed esters involving various permutations of between one and three residues of caffeic acid with one or two residues of a dibasic aliphatic acid (eg glutaric, oxalic, succinic) which are characteristic of Asteraceae.^{20–22}

It is convenient to extend this list of classic CGA to include the galloyl conjugates of quinic acid and the cinnamoyl conjugates of quinic acid derivatives such as shikimic acid,^{23–26} methyl or butyl quinate,^{27,28} 4-deoxyquinic acid²⁹ and the recently characterised *muco*-quinic acid³⁰ which differs from the isomer described above by having an equatorial hydroxyl on carbon 3.

Other cinnamate conjugates

Cinnamic acids may be conjugated to many molecules other than quinic acid and its close relatives, although sometimes as very minor components of limited distribution. This second category includes:

- (1) esters of other hydroxy acids, particularly α -hydroxyhydrocaffeic, malic and tartaric but including galactaric, glucaric, gluconic, hydroxycitric, methoxyaldaric, phenylpyruvic and tartronic;
- (2) amides of amino compounds including aromatic amino acids, choline, anthranilic acids and diamines;
- (3) esters of polysaccharides, simple sugars, sugar alcohols including glycerol and *myo*-inositol, and glycosides including those of anthocyanins, flavonols and diterpenes;
- (4) esters of lipids including alkanols, alkandiol, ω -hydroxy-fatty acids and sterols; and
- (5) glycosides.

Cinnamate transformation products

There is little information on cinnamate transformation during food preparation and processing. It has been well established that cinnamic acids may be released from conjugates by hydrolysis and subsequently decarboxylated either by heat³¹ or microorganisms yielding various alkylphenols, but little consideration has been given to the possibility that food processing might generate novel transformation products. Possibly the first to be recognised was the grape reaction product (GRP) 2-*S*-glutathionylcaftaric acid and 2,5-di-*S*-glutathionylcaftaric acid formed from caftaric acid (caffeoyl tartaric acid) during wine making.^{32–35} Red wine contains adducts formed by the interaction of anthocyanins with vinyl phenol from *p*-coumarate decarboxylation^{36,37} and caffeic acid released during coffee roasting is partially converted to tetrahydroxy-phenylindans.^{38,39} These products will not be further discussed here as the cinnamate residues have been lost irretrievably.

Hydrolysis of CGA during coffee roasting also releases the 'typical' quinic acid residue (*vide supra*) which is then converted to the full theoretical complement of quinic acid and quinic lactone (quinide) diastereoisomers.^{40,41} Unhydrolysed CQA and FQA can be converted similarly to the corresponding 1,5-lactones or quinides^{42–44} and it seems possible that other diastereoisomers, either of the lactones or the original acids, might also be formed.

CINNAMATES IN FOODS AND BEVERAGES

Quantitative data are presented on a fresh weight basis unless specified otherwise.

Coffee

Coffee beans are one of the richest dietary sources of CGA and for many consumers must be the major dietary source. The CGA in coffee and coffee products have been extensively reviewed^{31,45} and only a summary is presented here. Depending on the species, green coffee beans contain some 6–10% CGA on a dry matter basis. During roasting there is a progressive destruction and transformation of CGA with some 8–10% being lost for every 1% loss of dry matter but substantial amounts survive to be extracted into domestic brews and commercial soluble coffee powders.

It has been estimated⁴⁶ that a 200 ml cup of roast and ground coffee might supply from 20 mg CGA (weak brew, very dark roast) up to 675 mg CGA (strong brew, very pale roast robusta). More recent studies (Clifford and Balyaya, unpublished data) suggest that 70–200 mg per 200 ml cup of arabica and 70–300 (or even 350) mg per 200 ml cup of robusta are more representative. Soluble coffee powder as sold in the UK during 1983–1984 (2 g per cup) might supply from 70 to 220 mg CGA consisting of 50–150 mg CQA, 4–21 mg FQA and 15–38 mg diCQA.^{31,47,48} Beverage prepared from Angolan robusta coffee beans, which have a unique composition, has been reported to contain some 12–44 mg litre⁻¹ caffeoyl-tyrosine and some 33–66 mg litre⁻¹ of a similar but unidentified conjugate.^{49–51}

The two major chlorogenic lactones (3-CQL and 4-CQL) are found at levels of 800–2400 and 200–1600 mg kg⁻¹ in roasted coffees.^{43,44} Coffee brew also contains traces of diterpene glycosides esterified with the relatively rare 3,4-dimethoxy-cinnamic acid.⁵²

Green and black tea

Tea leaf is the major dietary source of theogallin (5-GQA) and is accompanied by small amounts of *p*CoQA and CQA. These substances are not substrates for tea polyphenol oxidase and appear to survive fermentation and may thus be found in black tea as well as green tea. There are no data for their contents in tea brew, but 10–50 g kg⁻¹ has been reported for green and black tea leaf.^{53–56} Rooibos or bush tea (*Aspalathus linearis*), consumed in southern Africa, is quite different, but contains a novel conjugate between caffeic acid and the enol form of phenylpyruvic acid.⁵⁷

Maté

Maté is a traditional South American beverage prepared from the leaves of *Ilex paraguariensis* which is rich in CQA and diCQA. There have been few studies of the brew composition but green maté

material bought and brewed in Europe provided 107–133 mg CGA per approx 200 ml of which diCQA represented approximately one third. In contrast, roasted maté provided 16–41 mg CGA per approx 200 ml.⁵⁸ Components originally assigned tentatively as FQA are now thought to be caffeoyl-quinic lactones (Clifford, unpublished data). Mazzafera⁵⁹ doubted the authenticity of the plant material purchased in Europe and reported that when authentic material was brewed in the traditional manner (50–60 g leaf per litre boiling water), some 480–520 mg 5-CQA and 340 mg caffeic acid were extracted. However, due to significant differences in the methods of analysis, these data are not directly comparable with the former.

Cocoa

The caffeoyl amide of dihydroxyphenylalanine and the *p*-coumaroyl amide of hydroxyphenylalanine have been reported in cocoa.⁶⁰

Pome fruits – apples and pears

Apples are one of the more extensively studied fruits. CGA are found at similar concentrations in the isolated flesh and skin (mean values 30–60 mg kg⁻¹) but are absent from the seeds and pomace.^{61,62} Whole apples have been reported to contain 62–385 mg kg⁻¹ CQA (with 5-CQA always dominant), up to 40 mg kg⁻¹ *p*CoQA (with 4-*p*CoQA dominant in some cases) and smaller amounts of caffeoyl-, *p*-coumaroyl- and feruloyl-glucoses (up to 6, 6 and 9 mg kg⁻¹, respectively).^{63–65} Values of 100–200 mg kg⁻¹ total CGA on a dry matter basis are consistent with the foregoing.⁶⁶ It is clear that composition varies markedly with variety, cider varieties being richer than culinary. Commercial juices and ciders are also variable in composition with juices providing from undetectable up to 208 mg litre⁻¹ CQA^{65,67} and ciders 11–480 mg litre⁻¹ (Clifford and Mitchell, unpublished data) or even higher when produced from single varieties of apples (for example, >700 mg litre⁻¹ CQA and >400 mg litre⁻¹ *p*CoQA for cv Vilberrie).⁶⁸ Heat processing reduced the CGA content of apple juice significantly, especially when accompanied by treatment with pectic enzymes, but the fate of the cinnamates was not discussed.⁶⁹ The fruit of *Sorbus domestica*, used in Germany as an adjunct in cider making, contains some 1500 mg kg⁻¹ CQA.⁷⁰

According to some investigators^{63–65,67} pears and pear juices are similar in composition with some 60–280 mg kg⁻¹ CQA in whole fruit and up to 240 mg litre⁻¹ in juice but others^{71–73} have also reported the presence of caffeoyl- and *p*-coumaroyl-L(-) malic acids (ie 2*S* malic acid) and 3,5-diCQA (1–8 mg kg⁻¹).

Stone fruits

Stone fruits contain CQA and *p*CoQA with mean contents in the range 150–600 mg kg⁻¹ and 3–

200 mg kg⁻¹, respectively, at least in cherries found mainly adjacent to the peel. Compared with apples and pears, the 3-isomers are more prominent relative to the 5-isomers. Cherries and plums are rich in *p*CoQA compared with peaches and apricots.⁶⁴ Studies on commercial juices and nectars (containing added sugar syrup)⁶⁵ are not entirely in agreement with the foregoing. Levels of 5-CQA were some 3–4 × greater than 3-CQA in peach and apricot juice with total CQA reaching ≈9 and ≈4 mg litre⁻¹, respectively: *p*CoQA was not detected but some 0.5 mg litre⁻¹ of free cinnamic acids was noted. Heat treatment of peach juice caused significant losses of CQA and *p*CoQA especially when combined with pectic enzyme treatment.⁶⁹

Berry fruits

Berry fruits encompass several distinct botanical families and thus differ markedly in their composition. Relatively few quantitative data are available. Blueberries contain 0.5–2 g kg⁻¹ CQA^{74,75} and only small amounts (≈60 mg kg⁻¹ in total) of other conjugates, mainly glucosides. Blackcurrants supply some 140 mg kg⁻¹ of total conjugates in which CQA dominate (≈40%), *p*CoQA and caffeoyl-glucose account for some 15% each and feruloyl-glucose, *p*-coumaroyl-glucose and total cinnamate β-D-glucosides for some 8% each. Blackberries provide some 70 mg kg⁻¹ with CQA dominant. Raspberries, strawberries, redcurrants and gooseberries are poor sources by comparison with the berries mentioned above, providing mainly glucose esters and β-D-glucosides totalling some 20–30 mg kg⁻¹.^{74,76} Cranberries contain a complex series of sugar derivatives involving both ester and glycosidic linkages, sometimes both, and varying numbers of sugar residues.⁸ Bilberry wine has been reported to contain 50 mg litre⁻¹ of CGA.⁷⁵

Citrus fruits

Citrus fruits contain the comparatively rare conjugates of glucaric (feruloyl, *p*-coumaroyl and diferuloyl) and galactaric acids (feruloyl, *p*-coumaroyl) and some associated lactones. These occur mainly in the peel (170–250, 27–62, 55–67 mg kg⁻¹ in oranges, grapefruit and lemon respectively), and at ≈25, ≈17 and ≈2 mg kg⁻¹ in the flesh.^{77,78} A range of other conjugates, involving sugars and anthocyanins, have also been reported.

The following data relate to the total cinnamates released by hydrolysis. The flavedo of oranges (and juice) supplied the following in bound form: ≈30 (8–18) mg kg⁻¹ sinapic, ≈130 (40–50) mg kg⁻¹ ferulic, ≈18 (8–12) mg kg⁻¹ *p*-coumaric and ≈4 (11–25) mg kg⁻¹ caffeic for which there is known to be a low recovery: the corresponding data for grapefruit were ≈50 (12–20), ≈152 (30–40), ≈72 (15–20) and ≈4 (5–8) mg kg⁻¹.^{79,80} Juice from blood oranges contains these same cinnamates at a total concentration in the range 50–160 mg litre⁻¹ again with ferulic

acid (30–64 mg litre⁻¹) dominant.⁸¹ Some workers have reported up to 2 mg litre⁻¹ 5-CQA and smaller amounts of free cinnamic acids and feruloylglucose in commercial orange juices and nectars (containing added sugar syrup).⁶⁷

Grapes and wines

Grapes are characterised by *cis*- and *trans*-cinnamoyltartrates (ie esters of L(+)-tartaric acid, ie 2R3R tartaric acid), in the pulp and juice as well as the skin, and the classic chlorogenic acids are absent.⁸² As usual caffeoyltartaric (caftaric) acid dominates but is accompanied by *p*-coumaroyltartaric (coutaric), feruloyltartaric (fertaric) and *trans*-coutaric glucoside.⁸³ The composition depends on the species and cultivar to a greater extent than season, ripeness and growing location, and may serve as a chemotaxonomic criterion^{84,85} but literature values vary considerably. Grape juice from red and white varieties of *Vitis vinifera* grown in America varied from ≈10 to 430 mg litre⁻¹ caftaric in one study but up to 600 mg litre⁻¹ in another, with little variation between skin (150 mg kg⁻¹) and flesh (110 mg kg⁻¹) although the skin is usually richer: coutaric ranged to 55 mg litre⁻¹ and fertaric to 16 mg litre⁻¹.^{65,67,85–87} Levels in grapes from Tuscany were in the range 2–7 mg kg⁻¹ caftaric, 0.4–5 mg kg⁻¹ coutaric and up to 3 mg kg⁻¹ fertaric.⁸⁸ Juice from *V. aestivalis* and *V. labrusca* contained 1350 and 460 mg litre⁻¹ caftaric respectively, whereas it was barely detectable in juice from *V. rotundifolia*.⁸⁵

Levels of caftaric and coutaric decline markedly by oxidation during the wine-making process and become more variable but levels of fertaric change less. Wines are extremely variable, with contents increasing with time of skin contact.^{89,90} Some American wines contained 9–116, up to 9 and up to 16 mg litre⁻¹ for caftaric, coutaric and fertaric respectively. Some 43 mg litre⁻¹ caftaric was reported for some French wines,^{86,91} but only 2–12 mg litre⁻¹ for some Spanish wines.^{92–94} Japanese Koshu wines contained appreciably higher concentrations of caftaric (40–304 mg litre⁻¹) and coutaric (28–127 mg litre⁻¹) although Japanese Semillon wines were very similar in this respect to French Semillon.⁹⁵

2-S-Glutathionylcaftaric acid has been reported in juices and wines at 6–8 mg litre⁻¹.^{65,93} Prolonged maturation can result in release of up to 3 or 4 mg litre⁻¹ caffeic and *p*-coumaric acid by hydrolysis, and ethyl esters may form by transesterification.^{32–35,83,95} Red grapes also contain several 6-*O*-*p*-coumaroyl- and caffeoyl-glucosides of various anthocyanidins at levels which vary considerably with cultivar.^{88,96,97}

Other fruits

Pineapple is characterised by the presence of the caffeoyl- and *p*-coumaroyl-glycerols but no quanti-

tative data are available.⁵ Other workers have reported small amounts of free cinnamic acids, 5-*p*CoQA and feruloylglucose totalling about 3 mg litre⁻¹.⁶⁷ Some dates contain caffeoylshikimic acids.^{24,25} Kiwi fruit contains ≈ 11 mg kg⁻¹ conjugated caffeic acid, about a quarter of which is fibre-associated.⁹⁸

Brassica vegetables

3-CQA, 3-*p*CoQA and 3-FQA have been reported^{99,100} in the leafy Brassicas (kale, cabbage and Brussels sprouts) at levels of 6–120 mg kg⁻¹, up to 104 mg kg⁻¹ and up to 37 mg kg⁻¹ respectively along with smaller amounts of the 4-isomers and little or none of the 5-isomers. Significant amounts of sugar derivatives have also been reported with feruloyl glucose and sinapoyl glucose dominating and levels up to 350 mg kg⁻¹ in kale and up to 80 mg kg⁻¹ in the others and, in red cabbage and radish, cinnamoyl esters of anthocyanins. Broccoli contained about 60 mg kg⁻¹ CGA plus about 20 mg kg⁻¹ sugar esters, but cauliflower and radish contained not more than 20 mg kg⁻¹ of CGA and sugar esters combined. More recent studies¹⁰¹ indicate that some broccoli florets contain several mixed feruloysinapoyl esters of gentiobiose totalling > 300 mg kg⁻¹. Radish leaf contained a series of malic acid esters at levels totalling 240–550 mg kg⁻¹. The corresponding levels in tuber peel were 40–120 mg kg⁻¹ but only 2–23 mg kg⁻¹ in peeled tubers. Only traces of sugar and quinic acid esters were found.¹⁰² Sinapoyl-choline is a characteristic component of mustard seed (*Sinapis alba* and *Brassica nigra* = *B juncea*), mustard and mustard containing products but quantitative data are not available. Small amounts (up to 3 mg kg⁻¹) were found in some cabbages.⁹⁹

Chenopodiaceae – spinach and beetroot

Spinach is dominated by *p*-coumaroyl-*meso*-tartaric acid at levels around 200 mg kg⁻¹ along with *p*-coumaroylmalic acid (25–30 mg kg⁻¹) and glucose esters totalling some 60–80 mg kg⁻¹. Beetroot root provides traces of quinic acid and glucose esters and the leaf slightly larger amounts of the glucose esters but the tartaric acid derivative found in spinach leaf was not detected.^{103,104} Cell wall-bound cinnamates are dealt with under fibre, *vide infra*.

Asteraceae

The Asteraceae is a very large group of plants which vary markedly in their profiles and contents of cinnamates. In some cases the profile does not differ with tissue for a given species (for example dandelion¹⁰⁵) but it should not be assumed that this is always the case.

The leaves of lettuce, endive and chicory provide quinic acid, malic acid and tartaric acid esters among which caffeic derivatives, especially dicaffeoyltartaric acid (chicoric acid), dominate. The total cinnamate contents were, respectively, 50–120 mg kg⁻¹, 200–500 mg kg⁻¹ and some 20 mg kg⁻¹.¹⁰⁴ CQA and

diCQA have been found in chicory root (total 2.6 g kg⁻¹) and in dandelion and chicory root-based coffee substitutes (some 100–400 mg kg⁻¹).^{106,107} Although these workers saw no evidence of mono- or di-caffeoyltartaric acid in the coffee substitutes these have been found throughout all parts of dandelion.¹⁰⁵ Another study found caffeoylshikimic acid but not the quinic acid esters referred to above in endive.²⁶

Artichoke (*Cynara scolymus*) and scorzonera provide some 450 and 180 mg kg⁻¹ CQA respectively with little or none of the other conjugates.¹⁰⁰ Artichoke is characterised by significant amounts of 3,5-diCQA and 1,5-diCQA.^{108–110} These isomers are not easily resolved and 1,5-diCQA is unstable in aqueous solutions, isomerising rapidly to 1,3-diCQA, otherwise known as cynarin(e). These factors may account for Herrmann⁸⁶ failing to mention these isomers although cynarin forms 800–1300 mg kg⁻¹ dry basis of the capitula.¹¹¹ It is not known whether any cinnamates occur in the artichoke-based beverage marketed as Cynar, but cynarin is found in some herbal medicines.¹¹² The relatively scarce triCQA, tetraCQA and caffeoylsuccinoyl-quinic acids (*vide supra*) have been reported in Asteraceae used as herbal medicines. These conjugates have not been reported in food plants other than burdock (*Arctium lappa*),^{20,21} an extract of which was once used in preparing the cordial 'Dandelion and Burdock'. Absinthe (*Artemisia absinthum*), tarragon (*A dracunculus*) and mugwort (*A vulgaris*) contain significant amounts of imperfectly defined quinic acid esters of caffeic acid¹¹³ but it is not known if these are transferred to vermouth and similar beverages in which extracts of absinthe are traditionally used.

Solanaceae

Potato tubers provide some 500–1200 mg kg⁻¹ dry basis total CGA^{114,115} (mainly CQA plus a little diCQA¹¹⁶) at harvest and the content rises slowly on storage especially in the light¹¹⁷ and during wound healing.¹¹⁸ These are concentrated in the peel where they may reach levels of 2–5 g kg⁻¹ (Ref 119) or even higher.¹²⁰ *p*-Coumaroyl conjugates of anthocyanins are present in peel (up to 7 g kg⁻¹) and flesh (up to 2 g kg⁻¹).¹¹⁹ Bell peppers contain caffeoyl and feruloylputrescine in the placenta during fruit development but only small amounts of glucose derivatives in mature fruit. Aubergines have a significant CQA content (600 mg kg⁻¹) and small amounts of FQA and anthocyanin conjugates (15 mg kg⁻¹). During the ripening of tomatoes, CQA in the pulp are partially replaced by glucosides in the peel – ripe fruit contain some 10–80 mg kg⁻¹ CQA, 5–15, 15–50 and 20–70 mg kg⁻¹ glucosides of ferulic, caffeic and *p*-coumaric respectively, plus up to 20 mg kg⁻¹ *p*-coumaroyl-glucose.^{104,116,121} Caffeoylglucaric acid is found in tomato leaf.¹²² It has not been possible to trace any compositional data for tomato juice or purée.

Apiaceae

Celery contains a modest but variable amount of CQA (2–65 mg kg⁻¹), *p*CoQA (up to 3 mg kg⁻¹) and FQA (up to 8 mg kg⁻¹),^{123,124} as do carrots (20–120 mg kg⁻¹)¹⁰⁰ but it should be noted that seedsmen attribute the root fly-resistance of modern varieties to the virtual absence of CGA.

This botanical group also supplies a range of spices and some of these have substantial contents of quinic acid conjugates (predominantly CQA but with appreciable FQA and *p*CoQA) and reaching 3 g kg⁻¹ in the case of anise, just over 2 g kg⁻¹ in fennel, approaching 2 g kg⁻¹ in caraway, but only some 200 mg kg⁻¹ in coriander.¹²⁵

Lamiaceae and Boraginaceae

The Lamiaceae supply many leafy herbs (basil, marjoram, melissa, oregano, peppermint, rosemary, sage, spearmint and thyme) characterised by the occurrence of rosmarinic acid, the caffeic acid conjugate of α -hydroxyhydrocaffeic acid, at concentrations ranging from 1 to 17 g kg⁻¹ dry basis¹¹³ or even in excess of 20 g kg⁻¹ (dry basis) in some samples of basil and rosemary.^{126,127} A smaller quantity (500 mg kg⁻¹ dry basis) has been found in borage.¹¹³ Melissa also contains a series of dimeric and trimeric caffeic acid conjugates.¹²⁸ It has not been possible to trace data for mixed herbs, stuffings, forcemeats, etc.

Fabaceae – legumes and pulses

There have been various reports of cinnamates in legumes and pulses^{23–26,129} but the distribution is variable across tissues, at least in Faba (*Phaseolus* spp) type beans where the largest concentrations of L(-)-malic acid conjugates (phaseolic acids) are found in leaves, with moderate but variable contents (up to 100 mg kg⁻¹) in pods and traces only in the seeds.¹⁰⁴ Peas contain *p*-coumaroyl, caffeoyl and feruloyl derivatives of flavonol glycosides¹³⁰ and lentils 0.1 mg kg⁻¹ of bound *p*-coumaric acid.⁹⁸ Caffeoyl and *p*-coumaroyltartronic acids have been found in dry mung beans (*Vigna radiata* = *Phaseolus aureus*).¹³¹

The novel compound, 1-caffeoyl-4-deoxyquinic acid, along with 3-CQA and 5-CQA, has been reported in the foliage of a wild groundnut (*Arachis paraguariensis*) but it is not clear if these compounds occur also in the edible portions of the *A hypogea*.²⁹ Commercial peanut flour and protein isolates have significant cinnamate contents including 500–1350 mg kg⁻¹ *p*-coumaric acid.⁶⁹

Miscellaneous vegetables

Corn salad (Valerianaceae) contains approximately 1 g kg⁻¹ CQA. Rhubarb petiole (*Rheum* spp, Polygonaceae) contains traces of glucose esters but the leaf contains *p*CoQA as the only CGA. Leeks (Alliaceae) contain small amounts of FQA (up to 12 mg kg⁻¹) without detectable CQA.¹⁰⁰ The spice star anise contains from 100 to 200 mg kg⁻¹ CGA in which, surprisingly, 4-*p*CoQA dominates at 52–

125 mg kg⁻¹.¹²⁵ Sweet potatoes (*Ipomoea batatas*) contain CQA and diCQA in the range 100–500 mg kg⁻¹,¹³² a series of long chain (C₁₆, C₁₇, C₁₈) alkyl ferulates¹³³ and in pigmented varieties caffeoyl derivatives of anthocyanins.¹³⁴ Red-pigmented yams (*Dioscorea* spp) contain sinapic esters of a cyanidin glycoside.¹³⁵ Chinese water chestnuts (*Eleocharis dulcis*, Cyperaceae) contain cell wall-bound cinnamates, *vide infra*.

Cereals and cereal products including beers and bran

It has not been possible to trace any data for bread, biscuits, cakes, breakfast cereals, etc.

Conjugates of cell wall polysaccharides

Cereals are characterised by cinnamic acids, especially ferulic acid, esterified to arabinose residues in primary cell wall arabinoxylan in the aleurone layer and pericarp. A portion of this total cinnamate exists as ferulate dimers linked in various ways including 5,5' or 5,8' carbon-carbon bonds.^{136–138}

Barley bran contains \approx 50 mg kg⁻¹ bound ferulic, \approx 30 mg kg⁻¹ bound *p*-coumaric and 3 mg kg⁻¹ diferulic acid. The endosperm content is \approx 3 mg kg⁻¹ total and the aleurone is intermediate.⁶⁹ Rice endosperm cell walls contain 12 g kg⁻¹ esterified cinnamic acids comprising \approx 9 g kg⁻¹ ferulic, \approx 2.5 g kg⁻¹ *p*-coumaric and \approx 0.5 g kg⁻¹ diferulic esters.¹³⁹ While whole wheat contains some 20–30 mg kg⁻¹ cinnamic acids esterified to polysaccharides,¹⁴⁰ the derived wheat bran contains some 4–7 g kg⁻¹ and maize bran as much as 30 g kg⁻¹.^{140–142} Maize leaves contain conjugates of hydroxycitric acid.¹⁴³

Water chestnuts (*Eleocharis dulcis*, Cyperaceae) are botanically closer to the cereals than to other common fruits and vegetables and are characterised also by a significant content of cell wall-bound cinnamates (> 7 g kg⁻¹ ferulate and > 4.5 g kg⁻¹ diferulate, the majority of which is 8-*O*-4 linked).¹⁴⁴

Spinach and sugar beet contain cell wall polysaccharides which are esterified with *p*-coumaric and ferulic acids, and to a lesser extent with what is probably cross-linked ferulate dimer.^{142,145} Sugar beet fibre contains some 9 g kg⁻¹ of ferulic acid attached to galactose or arabinose residues in pectic side-chains. Digestion, using an *in vitro* model of the human colon suggests that some 90% of cinnamates are released from sugar beet fibre in 24 h compared with some 35–40% from wheat bran but the released cinnamate may be further metabolised by the gut flora and its bioavailability is uncertain.¹⁴²

Other conjugates and free cinnamates

Wheat, maize and rye contain ferulic and *p*-coumaric esters of sterols and stanols.^{146,147} The leaves of rye contain feruloyl esters of gluconic and methoxyaldaric acids.¹⁴⁸ Oats contain a series of 24 caffeic and ferulic esters of glycerol, long chain alkanols, alkandiol (n = 22, 23, 24) and ω -hydroxy acids

($n = 26, 28$).^{149–153} In addition, there are more than 25 compounds which are esters of anthranilic acid or 5-hydroxyanthranilic acid with either *p*-coumaric, caffeic or ferulic acids (avenanthramides) or with their ethylenic analogues (avenulamides).^{154–156} Oat meal has been reported to contain some 200–300 mg kg⁻¹ of esterified ferulic acid.¹⁴⁰

Barley contains small amounts of free cinnamic acids, mainly *p*-coumaric and ferulic which together range from 8 to 26 mg kg⁻¹ (Ref 157) but this value rises during malting (18 mg kg⁻¹). The content rises further on mashing, presumably by hydrolysis of bound forms, with ferulic acid dominating (115 mg kg⁻¹) and lesser but equal amounts of caffeic and *p*-coumaric making up the total (167 mg kg⁻¹). A limited range of beers (including lagers, stouts, ales, etc) contained 2–8 mg litre⁻¹ but German 'rauchbier' reached almost 20 mg litre⁻¹.¹⁵⁷

DIETARY BURDEN

A major objective of this review, as originally conceived, was to identify the commodities most likely to provide the greatest amount of (i) a particular cinnamate (independent of the conjugate type and extent of hydrolysis in the gastro-intestinal tract) and (ii) of a particular conjugate. These two approaches have been taken since it seems possible that the form of the conjugate might influence absorption as is suggested in the case of flavonol glycosides.¹⁵⁸ With the exception of some beverages, the lack of data for the composition of commodities as consumed, ie the *edible portion after processing, cooking, baking, etc*, effectively make such an assessment impossible. In the circumstances, it is possible only to highlight the sources which have the *potential in normal usage to make a greater contribution than most*.

The values for burden set out below have been calculated from representative but rounded quantitative data presented in the first part of this review and assuming, for simplicity, that a serving of fruit or vegetable is 100 g, of non-alcoholic beverage is 200 ml, of cider or beer is 500 ml, of wine is 100 ml, of bran is 10 g and of herbs is 1 g.

There is no doubt that caffeic acid is the cinnamate which occurs most extensively, and the various CQA and diCQA are the most ubiquitous conjugates. Usually the 5-isomer dominates, but in stone fruit and brassicas it is the 3-isomer. Because of the quantity commonly consumed, coffee beverage must top the list with 200 ml instant brew (2% w/v) supplying 50–150 mg CQA. The theoretical yield of caffeic acid would be ≈ 25 –75 mg. Blueberries, aubergines, apples, cider and green maté could be important in some populations. Sweet cherries and Savoy cabbage along with apples, apple juice and cider probably supply the majority of the *p*CoQA while coffee must, in the majority of cases, come first for conjugated ferulic acid, followed by citrus juices.

In view of the quantities consumed by some populations, wines may be the major source of the tartaric

acid conjugates, but the literature data are extremely variable probably reflecting differences in wine-making practice across the world. Clearly grapes and grape juice also could make a significant contribution especially of tartaric at up to 60 mg per 200 ml juice. Lettuce, with 5–15 mg 100 g⁻¹, will be the major source of chicoric (dicafeoyltartaric) acid in the UK, but endive may have twice the concentration. Spinach will be the major source of coumaric (albeit *meso*-tartaric) and is almost certainly the richest source of conjugated *p*-coumaric acid at some 30–35 mg per 100 g.

Lettuce, since it is eaten raw, will probably be the main UK source of caffeoylmalic acid (up to 3 mg 100 g⁻¹) but spinach may be richer. Legumes might also be an important source but the quantitative data are inadequate.

Broccoli florets and leafy cruciferous vegetables will be the major source of sugar esters and of conjugated sinapic acid – broccoli florets supplying > 10 mg bound sinapic acid per 100 g. Tomatoes and tomato products are likely to be the major source of glucosides at up to 13 mg 100 g⁻¹ in total, and possibly the second richest source of conjugated *p*-coumaric acid at ≈ 3 mg 100 g⁻¹.

Herbs are the only source of rosmarinic acid. While some are very rich, the levels consumed make this a comparatively poor source of conjugated caffeic acid, generally supplying only low milligram quantities per gram, but up to ≈ 10 mg in some cases.

Cereal bran and bran-enriched products must be the most important source of cell wall-bound cinnamates. Even with small servings, say 10 g, maize or wheat bran could supply up to 30 and 7 mg of ferulate respectively making such products the richest dietary source of this cinnamate although its bio-availability after release in the colon is unclear. However, coffee brew could supply up to 10 mg ferulate (as FQA) per 200 ml cup so, for many people, coffee will be the major source.

There are insufficient quantitative data to allow useful comments to be made about the other conjugates.

CONCLUDING REMARKS

Cinnamate content of foods and beverages is incompletely known yet variable, as are diets. For a meal consisting of two glasses of wine, salad-based starter, main course with potatoes and two other vegetables including broccoli or spinach, a blueberry sweet, plus two large cups of strong coffee, the intake might be as much as 1 g of conjugates (predominantly CGA) or 500 mg of cinnamates (predominantly caffeic). The coffee alone would supply approximately 70% of the total *even if there were no losses in cooking*. In contrast, breakfast consisting of two slices of white toast and a cup (or two) of tea would supply hardly any cinnamates, but replacing white bread with wholemeal, taking a bran-containing cereal and

a glass of citrus juice might supply up to some 60 mg cinnamates (there are inadequate data for conjugates contents) in which ferulate would dominate.

It seems likely that the UK population will fall into several categories depending on (i) their consumption of coffee, (ii) their consumption of bran, and (iii) their consumption of citrus. Those who drink several cups of coffee per day augmented by bran and citrus might easily achieve 500–800 mg cinnamates (or even 1 g for the highest coffee consumption) whereas those who eschew all these and take little fresh fruit or vegetables might struggle to achieve 25 mg.

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