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Profiling the chlorogenic acids of sweet potato (*Ipomoea batatas*) from China

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Abstract

The leaves, stem and root of sweet potato cultivated in China have been analysed qualitatively for chlorogenic acids by structure-diagnostic LC–MS^3. Chlorogenic acids were not detected in the root. Caffeoylquinic acids were quantitatively the major subgroup of chlorogenic acids detected in the stem and the only subgroup detected in the leaves. This subgroup was dominated by 5-caffeoylquinic acid. The stem also contained three feruloylquinic acids, 3,5- and 4,5-dicaffeoylquinic acid, and small amounts of at least four caffeoyl-feruloylquinic acids. This is the first report of feruloylquinic and caffeoyl-feruloylquinic acids from sweet potato. Two chemically unrelated and coeluting substances with the same molecular mass ($M_r = 530$) extracted from the Chinese sweet potato interfered with the characterisation of the caffeoyl-feruloylquinic acids. At least five caffeoyl-feruloylquinic acids were detected in the peel of sweet potato cultivated in Tanzania that lacked these interfering substances.

Keywords: Caffeoylquinic acids; Caffeoyl-feruloylquinic acids; Chlorogenic acids; Dicaffeoylquinic acids; Feruloylquinic acids; *Ipomoea batatas*; Sweet potato

1. Introduction

Sweet potato, *Ipomoea batatas* (L.), is an herbaceous perennial grown in more than one hundred countries including barren mountain areas in China. This important staple food crop has attracted attention because of its content of potentially bioactive phytochemicals, including chlorogenic acids. Sweet potato has long been known to contain chlorogenic acids (Uritani & Miyano, 1955) and several caffeoylquinic and dicaffeoylquinic acids, and at least one tricaffeoylquinic acid have been reported in the leaves of Japanese plants (Islam et al., 2002; Kurata, Adachi, Yamakawa, & Yoshimoto, 2007; Takenaka, Nanayama, Isobe, & Murata, 2006), but there have been no studies on plants grown in China.

Chlorogenic acids have interesting properties *in vitro*, such as inhibition of Na^+-dependent D-glucose uptake in rat intestinal brush border membrane vesicles (Welsch, Lachance, & Wasserman, 1989) and coffee beverage rich in chlorogenic acids has been shown to modify gastrointestinal hormone secretion and glucose tolerance in humans (Johnston, Clifford, & Morgan, 2003) although the mechanism(s) has not been fully elucidated.

Chlorogenic acids are a large family of esters formed between quinic acid and one to four residues of certain *trans* cinnamic acids, most commonly caffeic, *p*-coumaric and ferulic: sinapic and dimethoxycinnamic acid also occur and in some plant species various aliphatic acids may replace one or more of the *trans* cinnamic acid residues (Clifford, 2000, 2003; Clifford, Knight, Surucu, & Kuhnert, 2006). In the IUPAC system (−)-quinic acid is defined as 1L-1(OH),3,4/5-tetrahydroxycyclohexane carboxylic acid and that nomenclature is used throughout this paper (IUPAC, 1976). Chlorogenic acid analysis in plant extracts

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is made difficult by the lack of authentic standards and by the difficulty of discriminating between positional and geometric isomers (Clifford, 2003). These difficulties have been partially overcome by the development of structure-diagnostic LC–MS^n procedures that can define a chlorogenic acid by its molecular ion and discriminate between positional isomers by their patterns of fragmentation (Clifford, Johnston, Knight, & Kuhnert, 2003; Clifford, Knight, & Kuhnert, 2005; Clifford et al., 2006; Clifford, Marks, Knight, & Kuhnert, 2006; Clifford, Wu, Kirkpatrick, & Kuhnert, 2007; Clifford, Wu, & Kuhnert, 2006; Clifford, Zheng, & Kuhnert, 2006) without the need for isolation and purification of individual compounds. In this paper we report the application of these analytical methods to sweet potato stem and leaves that are popular as vegetables in China.

2. Material and methods

2.1. Materials

The purple sweet potato (*Ipomoea batatas* L.) was harvested from the dedicated sweet potato cultivation plots at Hunan Agricultural University in July 2004. All other reagents used were good quality products from normal commercial sources.

2.2. Methods

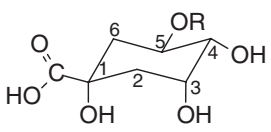
2.2.1. Extraction

Sweet potato stem, leaves or root (500 mg) was extracted (3 × 40 ml, 20 min each) with 70% v/v aqueous methanol using an HT-1043 solid–liquid continuous extraction system (Tecator, Bristol, UK). The solvent cups containing the extract were allowed to cool for a few minutes and filtered via Whatman No. 1 filter paper into a 100 ml volumetric flask and made up to volume with 70% aqueous methanol. An aliquot (10 ml) was treated with Carrez reagents (0.5 ml reagent A plus 0.5 ml reagent B), mixed by inversion and vortexing at least five times for 20 s at 1-min intervals, and centrifuged (2000*g*, 20 min). An aliquot of supernatant (7 ml) was transferred to a glass-tube and evaporated to dryness under nitrogen at 60 °C. The residue was dissolved in 200 µl methanol and transferred with washing (4 × 200 µl) into a volumetric flask (5 ml), made up to volume with water, centrifuged at (13,400*g*, 10 min), syringe filtered (0.45 µm), stored at −12 °C until required, thawed at room temperature, and used directly for LC–MS^n.

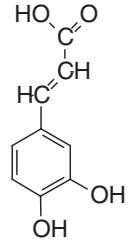
2.2.2. LC–MS^n

The LC equipment comprised a Surveyor MS Pump, autosampler with a 20 µl loop, and a PDA detector with a light-pipe flow cell (recording at 325, 280 and 254 nm, and scanning from 240 nm to 600 nm). This was interfaced with an LCQ Deca XP Plus mass spectrometer fitted with an ESI source (Thermo Finnigan, San Jose, CA, USA) and operating in data-dependent MS^n mode to obtain fragment ion *m*/*z*. As required, more sensitive targeted MS^n experiments were used to seek compounds with a particular molecular ion, for example, *m*/*z* 353, 367, 515, 529 and 677 for caffeoylquinic, feruloylquinic, dicaffeoylquinic, caffeoylferuloylquinic and tricaffeoylquinic acids, respectively. MS operating conditions (negative ion) had been optimized using 5-caffeoylquinic acid (Sigma Chemical Company, Poole, Dorset, UK) with a collision energy of 35%, ionization voltage of 3.5 kV, capillary temperature 350 °C, sheath gas flow rate of 65 arbitrary units, and auxiliary gas flow rate of 10 arbitrary units (Clifford et al., 2003).

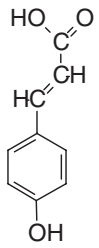
Chlorogenic acids separation was achieved on a 150 × 3 mm column containing Luna 5 µm phenylhexyl packing (Phenonemex, Macclesfield, UK). Solvent A was water:acetonitrile:glacial acetic acid (980:20:5 v/v, pH



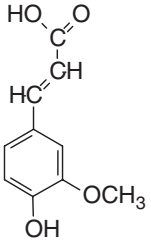
Quinic acid R = H, or
5-CQA R = caffeic acid



Caffeic acid



p-Coumaric acid



Ferulic acid

Name	Number	R_1	R_3	R_4	R_5
3-*O*-caffeoylquinic acid	1	H	C	H	H
5-*O*-caffeoylquinic acid	2	H	H	H	C
4-*O*-caffeoylquinic acid	3	H	H	C	H
3-*O*-feruloylquinic acid	4	H	F	H	H
5-*O*-feruloylquinic acid	5	H	H	H	F
4-*O*-feruloylquinic acid	6	H	H	F	H
3,4-di-*O*-caffeoylquinic acid	7	H	C	C	H
3,5-di-*O*-caffeoylquinic acid	8	H	C	H	C
4,5-di-*O*-caffeoylquinic acid	9	H	H	C	C
3-*O*-feruloyl, 4-*O*-caffeoylquinic acid	10	H	F	C	H
3-*O*-caffeoy, 4-*O*-feruloylquinic acid	11	H	C	F	H
3-*O*-feruloyl, 5-*O*-caffeoylquinic acid	12	H	F	H	C
3-*O*-caffeoy, 5-*O*-feruloylquinic acid	13	H	C	H	F
4-*O*-feruloyl, 5-*O*-caffeoylquinic acid	14	H	H	F	C
4-*O*-caffeoy, 5-*O*-feruloylquinic acid	15	H	H	C	F

C = caffeic acid; F = ferulic acid

Fig. 1. The structure of chlorogenic acids found in sweet potato (*Ipomea batatas*).