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Raman spectroscopic characterization of different regioisomers of monoacyl and diacyl chlorogenic acid

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ABSTRACT

We have investigated the Raman spectra of different regioisomeric forms of monoacyl and diacyl chlorogenic acids. Raman spectra of 3-caffeoylquinic acid, 4-caffeoylquinic acid, 5-caffeoylquinic, 3,4-di-*O*-caffeoylquinic acid, 3,5-di-*O*-caffeoylquinic acid, 4,5-di-*O*-caffeoylquinic acid, and a synthetic derivative of 3-feruloylqunic acid were recorded using visible Raman spectroscopic technique and vibrational bands are assigned. Additionally, a theoretical study of 5-caffeoylquinic acid was performed using Gaussian 03.

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1. Introduction

Classically, chlorogenic acids (CGAs) are a family of esters formed between quinic acid and certain *trans*-cinnamic acids, most commonly caffeic, *p*-coumaric, and ferulic acid [1–3]. Representative structures are shown in Fig. 1. In the IUPAC system (−)-quinic acid is defined as 1L-1(OH),3,4/5-tetrahydroxycyclohexane carboxylic acid, but Eliel and Ramirez [9] recommend 1α,3*R*,4α,5*R*-tetrahydroxycyclohexane carboxylic acid. Chlorogenic acids are widely distributed in plants [2,3] occurring in most dietary plants. Average CGA consumption is estimated at around 2 g per day per human with CGAs showing additionally favorable pharmacokinetic behavior resulting in high levels absorption either intact or as gut floral metabolites [4,5]. The green coffee bean is remarkably rich in CGAs, containing around 10% of its dry weight as CGAs, with at least 85 chlorogenic acids that are not acylated at C1 of the quinic acid moiety previously identified [6]. Further dietary plants containing large amounts of CGAs include yerba maté, most *Asteraceae* plants and many more [7,8].

Recently, LC–MS^n has been used to characterize cinnamoyl-amino acid conjugates [7] and to discriminate between individual isomers of monoacyl and diacyl chlorogenic acids [10–13]. The MS fragmentation patterns in tandem MS spectra, UV spectrum, retention time, and relative hydrophobicity have been utilized to develop structure-diagnostic hierarchical keys for the identification of chlorogenic acids. In particular fragmentation patterns observed in tandem MS spectra are highly diagnostic with respect to the regiochemistry of CGA substituents. All regioisomers, independent on whether they are monoacyl, diacyl or triacyl derivatives of quinic acid, show distinct fragmentation patterns that can be rationalized in terms of different hydrogen bonding arrays within the different regioisomers. Thus, a reliable and predictive structure diagnostic tool, using tandem MS, has become available resulting in the identification of more than 500 novel chlorogenic acid derivatives in dietary material in the last five years. For hetero diacyl quinic acids and hetero triacyl quinic acid derivatives (hetero designates the presence of at least two different acyl substituents) 2-D NMR usually fails to provide reliable structure information due to unfavorable signal overlap in $^1H^{13}C$-HSQC and $^1H^{13}C$-HMBC spectra in the olefinic and aromatic region. Hence, for this type of compounds, tandem MS provides currently the most successful structure elucidation method.

In this study, we apply Raman spectroscopy to the analysis of CGAs. While Raman spectroscopy does not necessarily provide a detailed insight into the regiochemistry of chlorogenic acids, it provides as recently shown a rapid and simple tool for the non-destructive characterization of CGAs in the green coffee bean directly, thus enabling a fast and efficient screening

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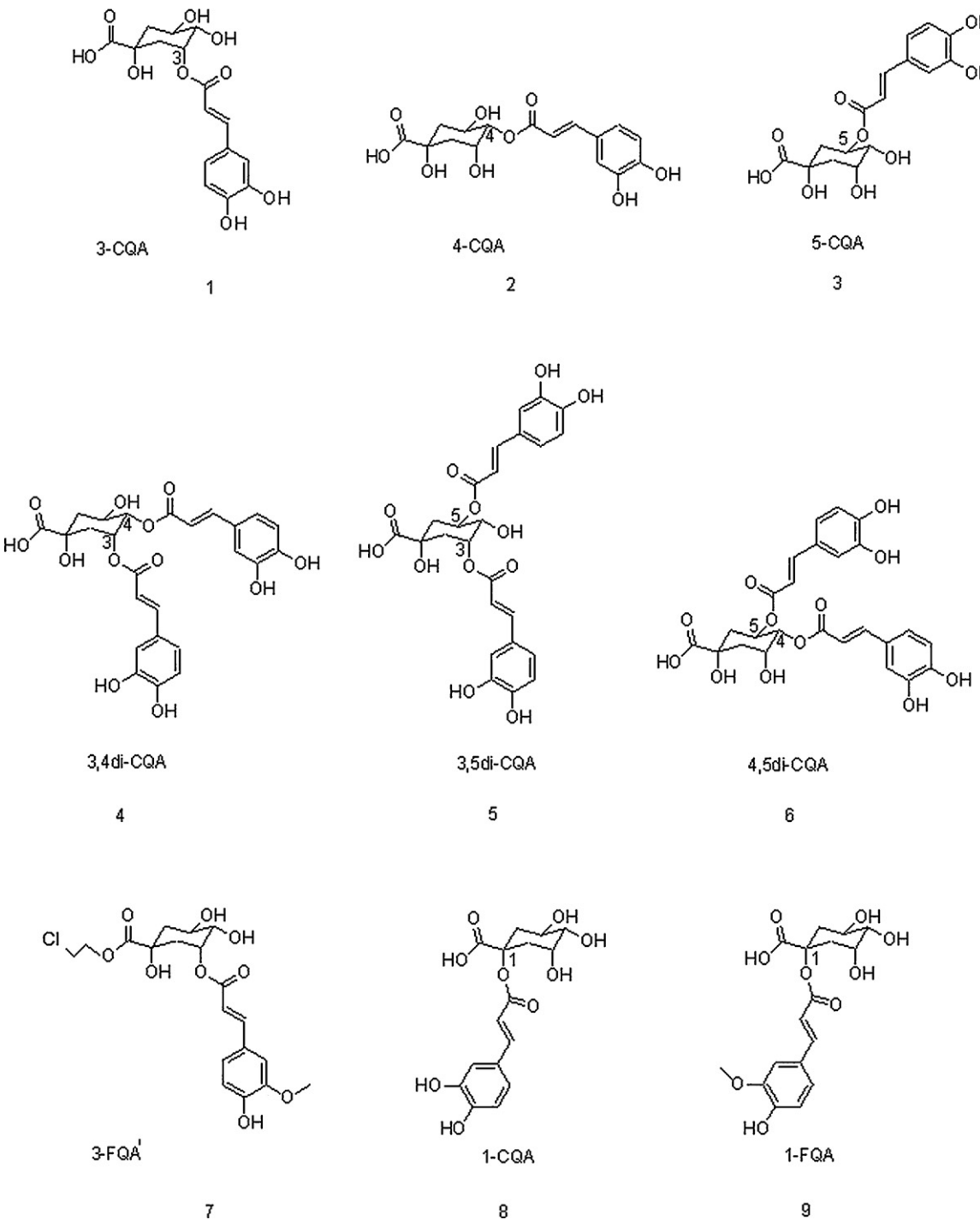

Fig. 1. Chemical structure of 3-CQA (1), 4-CQA (2), 5-CQA (3), 3,4-diCQA (4), 3,5-di-CQA (5), 4,5-di-CQA (6), 3-FQA' (7), 1-CQA (8), and 1-FQA (9).

system for assessment of coffee quality or adulteration [14,15]. In the present study we investigated the Raman spectra of seven selected regioisomeric monoacyl and diacyl chlorogenic acids, commonly present in coffee, using a dispersive Raman spectroscopic technique. A detailed investigation of chemically pure material, including assignments of observed vibrational bands, should allow a meaningful interpretation of differences in Raman spectra obtained from crude coffee extracts [16]. This work is complemented by a detailed theoretical study of 5-caffeoylquinic acid.

2. Materials and methods

2.1. Sample preparation

A total number of seven chlorogenic acids (CGA) which are 3-*O*-caffeoylquinic acid [neochlorogenic acid (3-CQA)], 4-*O*-caffeoylquinic acid [cyprochlorogenic acid (4-CQA)], 5-*O*-caffeoylquinic acid [chlorogenic acid (5-CQA)], 3,4-di-*O*-caffeoylquinic acid (3,4-diCQA), 3,5-di-*O*-caffeoylquinic acid (3,5-diCQA), 4,5-di-*O*-caffeoylqunic acid (4,5-diCQA), and a

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