TRANSFORMATION OF COFFEE CHLOROGENIC ACIDS INTO MULTI-FUNCTIONAL MOLECULES

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Introduction

Chlorogenic acid [CA] (5-*O*-caffeoylquinic acid) (Figure 1) occur ubiquitously in plants (coffee, artichoke, sunflower, potatoes, apple...). It was discovered by Robiquet and Boutron in 1837 in the *Coffea arabica* bean. CA corresponds to an ester of an hydroxycinnamic acid (caffeic acid) with quinic acid. Different isomers of CA have been isolated, for example, the 3,4-, 3,5- and 4,5-di-*O*-caffeoylquinic acids, the 3-*O*-caffeoylquinic acid (neochlorogenic acid) and the 4-*O*-caffeoylquinic acid (cryptochlorogenic acid) (Colonna, 1970).

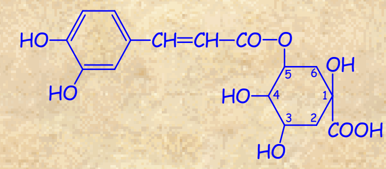

Figure 1. Chemical structure of the 5-*O*-caffeoylquinic acid (chlorogenic acid).

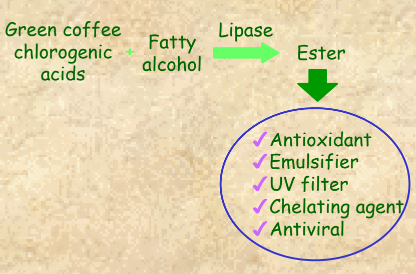

Figure 2. Properties of the lipophilised chlorogenic acid.

Chlorogenic acids present antioxidant, chelating, antiviral, anti-carcinogenic and UV filter properties (Morishita and Ohnishi, 2001).

The aim of this work was to esterify a fatty alcohol to CA using a lipase (Guyot *et al.*, 2000). Pure CA and a green coffee extract rich in chlorogenic acids were tested. The final objective was to obtain amphiphile multi-functional molecules (Morishita and Ohnishi, 2001 ; Scholz *et al.*, 1994) (Figure 2). The antioxidant activity of the mix containing the lipophilised chlorogenic acids was also measured.

Materials and Methods

Commercial coffee extract [MMP] (M.M.P., Inc., NJ, U.S.A.). Novozym 435 [N435] from *Candida antarctica* (Novo Nordisk, Denmark). Papain (Recco, Uganda). Chlorogenic acid [CA] and fatty alcohols (Sigma Aldrich Co, Germany).

3,75 mL of fatty alcohol were reacted with 150 mg of N435 and 20 mg of MMP or 10 mg of CA at 55°C, under agitation and darkness. Samples were filtered (0,45 µm) and analyzed by HPLC (Hypersil C18 high purity 5 µm column) (Guyot *et al.*, 2000). Antiradical activity was measured using DPPH$^{\bullet}$ and expressed as antiradical power ($ARP=1/EC_{50}$) (Brand-Williams *et al.*, 1995).

Results and discussion

No esterification between CA or MMP with the fatty alcohols was observed when using papain as catalyst, whereas when using N435, lipophilisation yields superior to 50% were observed (Table 1). The best esterification yields of CA and of MMP chlorogenic acids were obtained with dodecanol.

Two esters were formed during the MMP lipophilisation. Only one ester was observed from the CA esterification. In MMP, the 5-*O*-caffeoyl- and the feruloyl-quinic acids decreased the most in the presence of the enzyme.

When comparing with the blank (without enzyme), the ARP increased with lipophilisation in N435 added CA hexanol and octanol samples (Figure 3). The ARP was inferior in the case of lipophilised MMP with both alcohols, and with hexanol no changes in ARP were observed.

Table 1. Esterification yield of pure [CA] and of a coffee extract [MMP] chlorogenic acids in presence of Novozym 435 and different fatty alcohols.

Fatty alcohol	Sample	Esterification yield (%) 24 h	48 h	72 h
Hexanol	MMP	67,5	75,7	72,8
Hexanol	CA	97,0	98,9	98,8
Octanol	MMP	67,4	77,2	75,9
Octanol	CA	97,7	99,2	99,2
Decanol	MMP	59,9	76,1	75,4
Decanol	CA	98,6	99,3	99,2
Dodecanol	MMP	76,5	78,6	78,6
Dodecanol	CA	98,6	100,0	99,7

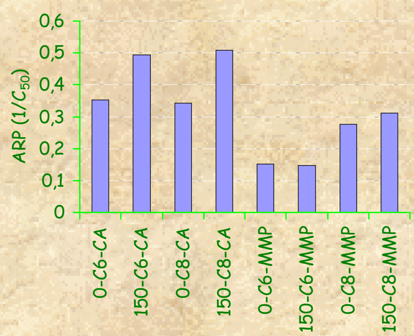

Figure 3. Antiradical power (ARC) of pure (CA) and coffee (MMP) chlorogenic acids after 13 days of reaction without (0-) and with (150-) 150 mg of N435. C6=hexanol, C8=octanol.

Conclusions

Pure and coffee extract chlorogenic acids lipophilisation was possible using a lipase from *Candida antarctica*. Yields superior to 75% were obtained after 48 h of reaction. Apparently, ARP increases with lipophilisation. Supplementary studies must be done to test the esters emulsifying properties.

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