Catalytic Lipophilization of Natural Antioxidants

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About

Green Coffee Bean

Roasted Coffee Bean

Silverskin

Project

Paper

In the frame of CirCO project (acronim of Circular Coffee) founded by Fondazione Cariplo-Innovhub, coffee silverskin, CS, the main dry by-product of the roasting process, was valorized.

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Cosmetics

CS is a thin tegument covering the coffee beans with no commercial value, rarely used as fertilizer, livestock feed or energy source, but usually discarded as solid urban waste. However, it could be broken up into cellulose, lignin, lipids and some phenolic compounds, such as caffeine and chlorogenics acids.

Cellulose

Extraction

Fat

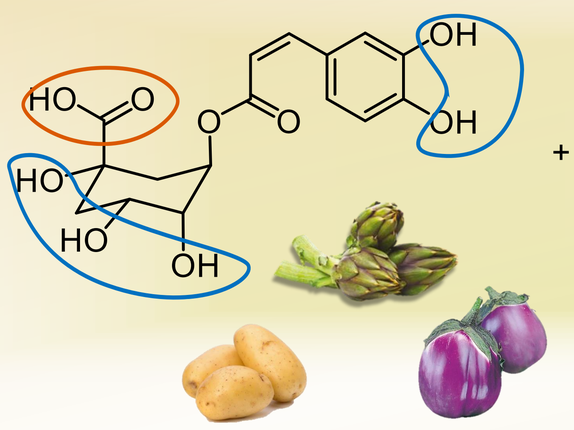
Polyphenols

Extraction

Esterification

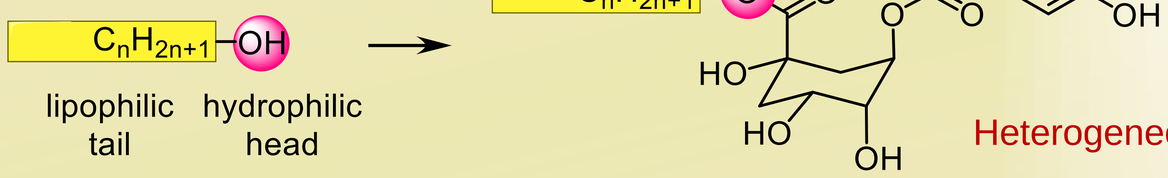
Chlorogenic acid

Chlorogenic acid, CGA, is a polyphenol widespread in nature that enjoys several pharmacological and biological activities, such as antioxidative, antibacterial, antihypertensive, antitumor, antidiabetic, hypolipidemic, anti-inflammatory, antiviral.



However, the highly hydrophilic structure hinder the use into oil-based products and limits its permeability through the skin tissues and its bioavailability.

Aims

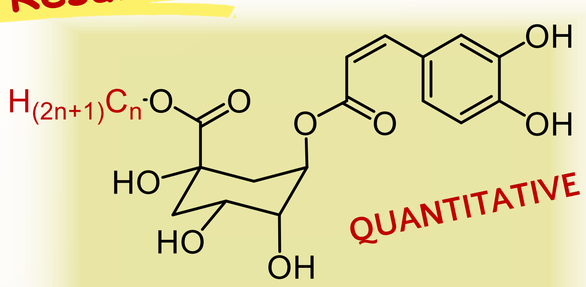


To overcome these drawback, CGA was lipophilized through esterification with a fatty alcohol using sulphonic resins as heterogeneous Brønsted solid acid catalysts.

Heterogeneous catalysis

"Green" solvents, Safe reaction conditions
Easy catalyst separation and recovery,
Low costs

Results



n = 2, 4, 8, 12, 16, 18

Alcohol	molar ratio	T (°C)	Time (h)	Conv (%)	Yield (%)	Sel (%)
Ethyl	1/30	75	6	94.3	93.8	99.5
Butyl-	1/10	80	6	97.6	91.1	93.3
n-Octyl-	1/7	"	16	97.0	90,6	93.4
Lauryl-	1/5	"	40	95.0	74.3	78.2
Cetyl-	1/4	"	48	91.5	66.0	72.2
Stearyl-	1/4	"	60	96.9	62.9	64.9

The sulphonic resins Amberlyst® 15 resulted greatly effective in the direct acylation of CGA with fatty alcohols (2-18 carbon atoms) in a sustainable, solvent free, one-pot process with quantitative conversions and high selectivities.

SCALE UP

Alcohol	Conv (%)	Yield (%)	Sel (%)	Isolated yield (%)
Ethyl	95.2	94.1	98.8	70
Butyl-	96.4	90.6	94.0	88
n-Octyl-	94.8	93.4	98.5	80
Lauryl-	93.4	76.4	81.8	50

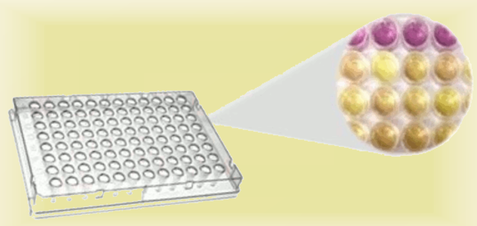
The esters have been easily isolated in high amount by precipitation and subsequent recrystallization processes.

Antiaging and antioxidant evaluation of chlorogenic acid esters

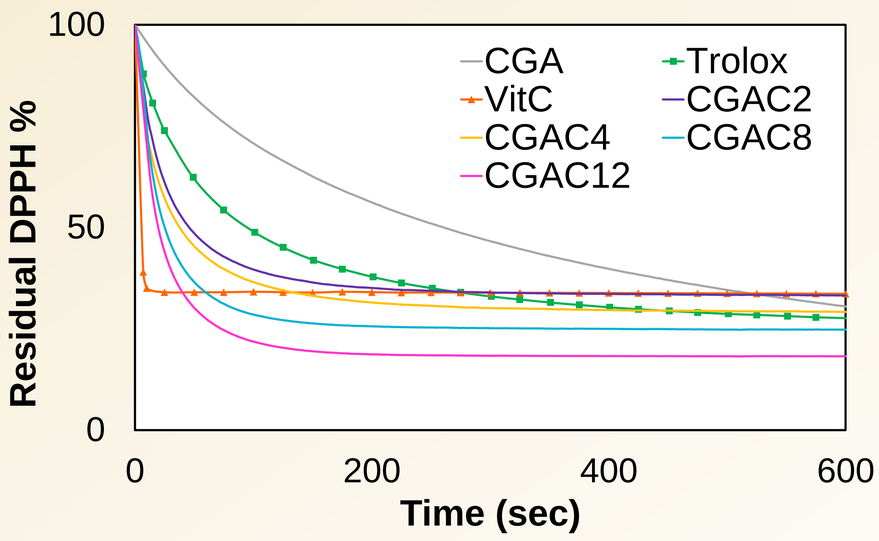
Antioxidant screening – DPPH assay

Sample	EC50 (μM)
Chlorogenic acid	0.214
Ethyl chlorogenate	0.203
Butyl chlorogenate	0.201
Octyl chlorogenate	0.173
Lauryl chlorogenate	0.163
Ascorbic acid	0.203
Trolox	0.184

All the esters have shown an ability greater than CGA and ascorbic acid (the positive control) to halve the starting amount of DPPH radicals.

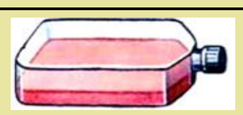


The highest scavenging activity was shown by Lauryl and *n*-octyl CGA that resulted also more potent than Trolox.



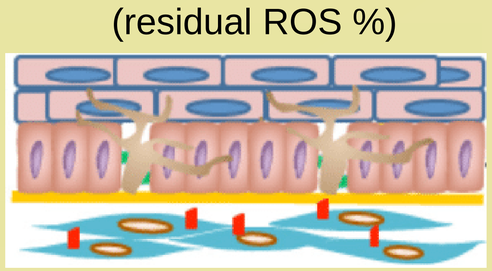
Antiaging screening on human cell cultures

Oxidative Stress
UVA irradiation



Human cells cultures + Sample or Control

Cell viability evaluation (residual ROS %)



KERATINOCYTES

In vitro *n*-octyl chlorogenate reduce the oxidative stress of human keratinocytes after UVA irradiation by reducing the production of ROS.

FIBROBLASTS

In vitro Ethyl chlorogenate improves the viability of human fibroblasts. Moreover, it preserves them from oxidative stress after UVA irradiation by improving the stiffness of the membranes.

In silico studies

In silico predictions of toxicity have shown that all the CGA esters isolated, especially ethyl chlorogenate, are not carcinogenic, quite safe and well tolerated.

Reference

Pappalardo, V.; Ravasio, N.; Falletta, E.; De Rosa, M.C.; Zaccheria, F. A Green Lipophilization Reaction of a Natural Antioxidant. *Antioxidants* **2023**, 12, 218. https://doi.org/10.3390/antiox12020218