Chapter 48

BIOTECHNOLOGICAL POTENTIALITIES OF POLYPHENOLIC COMPOUNDS OF COFFEE AND COMPARISON WITH OLIVE

M. Labat[1], C. Augur[2], I. Perraud-Gaime[2], B. Rio[1], S. Roussos[1], S. Sayadi[3]

[1]IRD (ex-ORSTOM) Institut de Recherche pour le Développement, Laboratoire de Microbiologie, Université de Provence, CESB/ESIL, Case 925, 163 avenue de Luminy, F-13288 Marseille cedex 9. France; e-mail: labat@esil.univ-mrs.fr [2] UAM-I, Depto. Biotecnologia; Ave. Michoacán-Purísima, Iztapalapa, C.P. 09340, A.P. 55 535, México D.F. [3]CBS Centre de Biotechnologie de Sfax, BP"K", 3038 Sfax, Tunisie

Running title: Potentialities of polyphenolic compounds of coffee

1. Introduction

Micro-organisms are unique « cell factories » able to valorize agricultural by-products instead of only degrading or mineralizing them for depollution or methanisation processes. The difficulties encountered in treating such compounds often result from high concentration of pollutants and/or high toxicity to the microflora. Liquid effluents with high chemical oxygen demand (COD) (> 100 g COD/litre) are often rich in aromatic compounds.

Olive mill wastewater (OMW) is an exemple of high polluting industrial by-product especially rich in polyphenolic compounds. Difficulties in the treatment of such a polluting compound are due both to the high concentration of organics which are mainly composed of phenolic compounds toxic to the microflora. Indeed the polluting charge is exceptionnally high, generally over 120 g and can reach 200g of COD/litre of OMW. Polyphenolics of OMW span from monoaromatic to high molecular-mass polyphenols.

Coffee husk and coffee pulp represent another example of agro-industrial co-products rich in polyphenolic compounds. Information is available essentially for coffee pulp, where flavonoids were first extensively studied with two-dimensional paper chromatography

In Coffee Biotechnology and Quality; Sera T., Soccol C.R., Pandey A., Roussos S.,(eds) Kluwer, Dordrecht, pp 517-531

techniques (Lopes-Longo, 1972). Values of total phenolics from lyophilized pulp (6.3 %) and sun dried pulp (6.6 %) were reported (Zuluaga, 1981), and new phenolic structures progressively identified. HPLC techniques enable the identification and quantification of acid phenolics from fresh coffee pulp (Ramirez-Martinez, 1988). Polyphenolic compounds are homo or heterocyclic aromatic structures, where hydroxylic functions are substituted to the benzenic structure. Thus hydroxylated benzenic and cinnamic acids derivatives (acid phenolics), hydroxylated phenols, flavonoids, anthocyans and tannins are polyphenolic compounds. Microbial degradation occurs aerobically or anaerobically. Hydroxylated aromatic compounds are metabolizable in pure anaerobic or aerobic cultures but anaerobic degradation is restricted mostly to sufficiently oxidated aromatics. As an example, methane production from benzoate is achieved only in mixed cultures (Ferry and Wolfe, 1976), as no organisms able to undergo such a methanisation in pure culture were isolated. Moreover, some biotopes or hindguts are specialized in the degradation of specific, usually poorly degradable aromatics. As an example, termite species possess in their hindgut, bacteria that enable the degradation of aromatic compounds with methane production (Brauman *et al.*, 1992). Degradation of complex aromatic compounds is often more efficient aerobically, even if anaerobic degradation was demonstrated with oligognols, or compounds generated from aerobic degradation of lignin (Crawford *et al.*, 1983), and effective with tannins (Field and Lettinga, 1987), and various other complex compounds.

In this review, analytical information is given concerning polyphenolics reported in coffee arabica, a plant species especially rich in polyphenolics and largely cultivated in Latin America. Coffee husk and coffee pulp represent two models of solid effluents containing polyphenolic compounds. Besides olive (*Olea europeae* L.), rather poorly cultivated and consumed in latin America (except Argentina), emphasis is on coffee (*Coffea arabica* L.). These two examples of agricultural products or by-products containing aromatics are then presented together with known biological activities attributed to these aromatics.

2. Potentialites of phenolic compounds found in olive and coffee

2.1 PHENOLIC CHEMICALS IN OLIVE PLANT (*OLEA EUROPAEA L.*)

Various phenolic chemicals are reported from different parts of the olive plant. Hydrophilic phenolic compounds are estimated between 20 and 500 ppm in olive (Léger, 1999), and o-diphenolics between 60 to 100 mg/l of olive oil (Ryan and Robards, 1998). Other cyclic compounds, like cyclo-olivil (branches), cinchonine (leaf) are not phenolic chemicals (N heterocyclic compounds). Sterols (beta-sitosterol-glucoside reported in olive leaf), carotenoids (1.8 - 8.3 ppm beta-carotene reported in olive fruit) and cyclic

N

compounds without phenolic alcohol are excluded from this list; but verbascoside (reported in olive fruit), esculin (reported in olive stem) or estrone (reported in olive seed) are listed as they exhibit a true phenolic function.

Table 1. Part A - List of phenolics reported in olive plant and by-product (alphabetical order).

Chemical name of the phenolic compound Chemical name of similar phenolic compound	Part of the olive plant
d-acetoxypinoresinol	4
d-1-acetoxypinoresinol-4"-o-methyl-ether	4
d-1-acetoxypinoresinol-4'-beta-d-glucoside	4
apigenin (pulp absent)	2, 8
apigenin-7-di-o-xyloside	2
apigenin-7-glucoside	2, 6, 8
caffeic-acid (oil 0.0-1.0 ppm, OMW 90 ppm)	1, 8, 9
1-caffeyl-glucose	1
catechin	1
catechol-melanin	1
chlorogenic acid	2
cinnamic acid	8
cornoside	6
p-coumaric acid (oil 0.0-0.6 ppm)	1, 2, 8, 9
o-coumaric acid	6, 8
cyanidin-3-monoglycoside	2, 5, 6
cyanidin-3-rutinoside	1
cyanidin-3-rhamnosylglucosylglycoside	1
3,4-dihydroxyphenylethanol (oil 0.0-351.2 ppm)	1, 2, 6, 8, 9
linked with dialdehydic form of elenolic acid	8
3,4-dihydroxyphenylethanol-4-diglucoside	1
3,4-dihydroxyphenylethanol-4-monoglucoside	1
3,4-dihydroxyphenylpropane	2
elenolic acid	2, 6, 8
elenolic acid glucoside (leaf absent)	6,8
esculin	4
esculetin	4
estrone	7
ferulic acid (oil 0.0-2.4 ppm)	6, 8, 9
gallic acid	1, 6, 8, 9
hesperidin	2, 6

Table 1. Part B - List of phenolics reported in olive plant and by-product (alphabetical order)

Chemical name of the phenolic compound / Chemical name of similar phenolic compound	Part of the olive plant
4-hydroxybenzoic acid	8
4-hydroxyphenylacetic acid (oil 0.2-2.8 ppm, OMW 145 ppm)	6, 8, 9
3,4-dihydroxyphenylacetic acid	1
4-hydroxyphenylethanol (oil 0.1-123.1 ppm)	1, 6, 8, 9
4-hydroxyphenylethanol glucoside	6
4-hydroxyphenylethanol derivative (oil 0.0-113.4 ppm)	8
linked with dialdehydic form of elenolic acid (oil 0.0-79.8 ppm)	8
d-1-hydroxypinoresinol	4
d-1-hydroxypinoresinol-4"-o-methyl-ether	4
kaempferol	1, 4
glycosylated kaempferols	1, 4
ligstroside (oil 25 ppm)	2, 6, 8
luteolin	1, 2, 6
luteolin-4'-glucoside	2, 6
luteolin-5-glucoside	1
luteolin-7-glucoside	2, 6
luteolin-7-rutinoside	2
luteolin-tetraglucoside	2
nuezhenide	7
nuezhenide oleosid	7
oleuropein (oil 67 ppm)	1, 2, 6, 8
demethyl-oleoeuropein	1
oleuropeic acid	3
deacetoxyoleuropein aglycon	1
oleuropein aglycon isomer (oil 0.0-83.5 ppm)	8
oleuroside	2
oleoside	
olivin	2
olivin-4'-diglucoside	2
protocatechuic acid	1, 8, 9
quercitin	2, 4, 5, 6
quercitin-3-rhamnoside	5
quercitin-3-rutinoside (or rutin)	2, 5, 6
quinone	1

N

Table 1. Part C - List of phenolics reported in olive plant and by-product (alphabetical order)

Chemical name of the phenolic compound Chemical name of similar phenolic compound	Part of the olive plant
salidroside	7
sinapic acid	1, 8
syringic acid (oil 0.0-2.3 ppm, OMW 710 ppm)	1, 6, 8, 9
3,4,5-trimethoxybenzoic acid (OMW 80 ppm)	9
alpha-tocopherol (oil 40-130 ppm)	8
beta- tocopherol (oil 10-20 ppm	8
gamma-tocopherol (oil 13 ppm)	8
veratric acid (OMW 500 ppm)	6, 9
verbascoside	1,6

1 = fruit, 2 = leaf, 3 = root, 4 = stem, 5 = pericarp, 6 = pulp, 7 = seed, 8 = olive oil, 9 = liquid by-product (olive mill wastewater or OMW).

Phenolic compounds listed above were detected in olive fruit or other parts of the plant (if specified), and in olive oil and its liquid by-product (OMW). This list includes free and glycosylated monomeric (p-coumaric acid; protocatechuic acid; quinone) and polymeric (catechin, cyanidin-3-rutinoside, tannin) phenolics.
This list of phenolic chemicals with ppm (or mg/kg) values is adapted from various bibliographical sources: Balice and Cera, 1984; Salvemini, 1985; Nefzaoui, 1991; Duke, 1992a and 1992b; Labat *et al.*, 1996 and 1997; Baldioli *et al.*, 1996, Léger, 1999; Montedoro *et al.*, 1993; Ryan and Robards, 1998. Chemical names are mentioned with reported concentrations when available. Few compounds are not true phenolic compounds (but associated with). As olive oil generates liquid by-products most of these values in ppm are re-calculated from % f.w. (fresh weight) of OMW, and few from mg/l of oil (with d=0.91). For this reason, this table cannot be directly compared with values in ppm calculated from solid by-products (coffee pulp).

2.2 PHENOLIC CHEMICALS IN COFFEE PLANT (*COFFEA ARABICA L.*)

Various phenolic compounds are reported from different parts of the coffee plant or solid by-products (pulp and husk). Total phenolic compounds are often estimated in mg gallic acid per 100 mg of dry weight (d.w.) of pulp. Values between 6.3 (lyophized pulp) and 6.6 (sun dried pulp) were reported (Zuluaga, 1981). With HPLC techniques, mean value of total phenolics was 1.27 % (d.w.) (Ramirez-Martinez, 1988).

N

Table 2. Part A - List of phenolics reported in coffee plant and by-product (alphabetical order).

Chemical name of the phenolic compound Chemical name of similar phenolic compound	Part of the coffee plant
caffeic acid (pulp 3,100-16,000 ppm)	3, 4
caffeol	2
caffesterol (or coffeasterol)	5
caffetannic acid (seed 84,600 ppm)	3
catechin (flavanol) (pulp 2200 ppm)	4
epicatechin (pulp 1900-4400 ppm)	4
chlorogenic acid (or caffeoyl-quinic acid ester or CGA) (seed 50,000-100,000 ppm, pulp 3,600-27,000 ppm)	3, 4
3-caffeoyl-quinic acid (pulp 200-1,400 ppm)	3, 4
4-caffeoyl-quinic acid (pulp 200-1,400 ppm)	3, 4
5-caffeoyl-quinic acid (pulp 2400-8800 ppm)	3, 4
p-coumaric acid	4
p-coumaric ester derivative	5
p-cresol	5
o-cresol	5
m-cresol	5
cyanidin-3-glycoside (or cyanidin-3-monoglycoside)	4
cyanidin-3,5-diglycoside	4
cyanidin-3-diglycoside	4
cyanidin-3-glycorhamnoside	4
3,4-dicaffeoylquinic acid (3,4-isochlorogenic acid) (pulp 5,700 ppm)	3, 4
3,5-dicaffeoylquinic acid (3,5-isochlorogenic acid) (pulp 19,300 ppm)	3, 4
4,5-dicaffeoylquinic acid (4,5-isochlorogenic acid) (pulp 4,400 ppm)	3, 4

Table 2. Part B - List of phenolics reported in coffee plant and by-product (alphabetical order).

N

Chemical name of the phenolic compound / Chemical name of similar phenolic compound	Part of the coffee plant
4-ethylphenol	5
2-methoxy-4-ethylphenol	5
2-ethylphenol	5
eugenol	5
isoeugenol	5
ferulic acid (pulp 1,000 ppm)	4
ferulic ester derivative	5
caffeoylferuloylquinic acid	3
guaiacol	5
2,4-methylenephenol	5
4-methoxy-4-vinylphenol	5
protocatechuic acid (pulp 200-7,000 ppm)	4
rutin (or quercitin-3-rutinoside) (pulp 2200 ppm)	4
sinapic acid	1
tannin (seed 90,000 ppm, pulp 18,000-86,000 ppm)	3, 4
gallotannins* (hydrolysable tannins)	4
ellagitannins* (hydrolysable tannins)	4
flavonoids (pulp 28,000-40,000 ppm)	3, 4
leucoanthocyanidins (condensed tannins)	4
proanthocyanidins (condensed tannins)	4
alpha-tocopherol	1
beta-tocopherol	1
gamma-tocopherol	1
2,3,5-trimethylphenol	5
p-xylenol (dimethylphenol)	5
o-xylenol	5

* = not confirmed, 1 = plant, 2 = leaf, 3 = seed, 4 = solid by-product (coffee pulp), 5 = plant part not mentioned

Compounds such as caffeine (seed 600 - 32,000 ppm); theobromine (leaf and seed 18 ppm) and theophylline (leaf and seed) are not phenolics (N heterocyclic compounds) and are not listed below. Sterols, carotenoids and cyclic compounds without phenolic alcohol are excluded of this list but tocopherols are listed as they exhibit a true phenolic function.

This list of phenolic chemicals with ppm (or mg/kg) values is adapted from various bibliographical sources: Bressani *et al.*, 1972; Bressani et Elias, 1976; Clifford *et al.*, 1989 and 1993; Duke, 1992a and 1992b; Molina *et al.*, 1974; Ramirez-Martinez, 1988; Ramirez-Martinez and Clifford, 2000; Zuluaga *et al.*, 1975. Chemical names are mentioned with reported concentrations when available. As coffee plant generates solid by-products (pulp and husk), most of these values in ppm are calculated from % d.w. (dry weight). For this reason, this table cannot be directly compared with values in ppm calculated from liquid by-products (OMW).

3. Potentialites of three major phenolic compounds found in coffee

Coffee (*Coffea arabica* L.) is a plant species especially rich in polyphenolics. Three polyphenolic compounds found within this plant (seed, leaf and other parts) are chosen for their high potential in terms of biological activities. Chlorogenic and caffeic acids as monoaromatic models and tannin as polyaromatic model of polyphenols, is described.

3.1. CHLOROGENIC ACID CONTENT IN COFFEE AND OTHER PLANTS

Table 3. Plant species reported to contain high amount of chlorogenic acid (> 100 ppm)

Plant name	Concentration	Plant part
Coffee (*Coffee arabica* L)	50,000 - 100,000 ppm	seed
Sunflower (*Helianthus annuus* L.)	1,900 - 28,000 ppm	seed
Damask rose (*Rosa damascena* M.)	15,000 ppm	pollen or spore
Blueberry (*Vaccinium corymbosum* L.)	3,000 ppm	fruit
Coriander (*Coriandrion sativum* L.)	305 - 320 ppm	plant
Wall germander (*Teucrium chamaedrys* L.)	200 ppm	plant

To our knowledge, *Coffea arabica* is the plant species which contains the highest concentration of chlorogenic acid, when compared with other plants known to synthetise this compound. Contrary to expectations coming from the name of the plant itself, caffeic acid is not reported to be in high amount, as a free phenolic compound, in coffee. This compound is reported to be in the highest amount in the tuber of jalap (Ipomoea purga) reaching up to 40,000 ppm (Duke, 1992a). Coffee is not within the 30 plant species with highest amount. Caffeic acid is found only after hydrolysis, where the caffeic structure is issued from chlorogenic acid. The amounts of chlorogenic and caffeic acids depend (1) on the maturity of coffee beans, (2) on the drying method and (3) on the species of *Coffea* studied (Balyaya and Clifford, 1995).

N

3.2. KNOWN BIOLOGICAL ACTIVITIES ATTRIBUTED TO CHLOROGENIC ACID, A MODEL OF DIMERIC PHENOLIC COMPOUND FOUND IN COFFEE

This aromatic compound, an ester of caffeic acid and quinic acid, is a dimer of a phenolic and a cyclic structure respectively. This polyphenolic structure possesses one carboxylic and five hydroxylic functions (two from the caffeic and three from the quinic acid structure). Its hydrolysis produces diphenolic (caffeic) and tetrahydroxylic (quinic) structures. Different related structures have been identified in coffee (caffeoyl-quinic acid esters in position 3-, 4- or 5-, and dicaffeoyl-quinic acid esters in position 3,4-, 3,5 or 4,5 and derivatives), belonging to CGA (chlorogenic acid) group or ICGA (isochlorogenic acid) group (cf. Table 2).

Table 4. Compilation of 51 reported biological activities of chlorogenic acid (adapted from Duke, 1992a)

Biological activity	Biological activity	Biological activity
Allelochemic	Allergenic	Analgesic
Anti HIV	Anti tumor promoter	Anti EBV
Anticancer (colon, forestomach, liver and skin)	Anticarcinogenic	Antifeedant
Antigenotoxic	Antigonadotropic	Antihemolytic
Antihepatotoxic	Antiherpetic	Antihypercholesterolemic
Antiinflammatory	Antinitrosaminic	Antimutagenic
Antioxidant	Antiperoxidant	Antipolio
Antiradicular	Antiseptic	Antisunburn
Antithyroid	Antitumor	Antiulcer
Antiviral	Bactericide	Cancer preventive
CNS active	CNS stimulant	Cholagogue
Choleretic	Clastogenic	Collagen sparing
Diuretic	Fungicide	Hepatoprotective
Histamine inhibitor	Immunostimulant	Insectifuge
Interferon inducer	Juvabional	Larvistat
Leukotriene inhibitor	Lipoxygenase inhibitor	Metal chelator
Ornithine decarboxylase inhibitor	Oviposition stimulant	Sweetener, Vulnerary

As a consequence CGA was reported to exibit various physiological and biological activities.To our knowledge, up to 51 biological activities were attributed to CGA. They are listed below, but still await an unambiguous demonstration (Table 4).

N

3.3. KNOWN BIOLOGICAL ACTIVITIES ATTRIBUTED TO CAFFEIC ACID, A MODEL OF MONOMERIC PHENOLIC COMPOUND FOUND IN COFFEE

Caffeic acid is a monoaromatic compound which possesses an o-diphenolic structure (3,4-dihydroxybenzoic acid), resulting in strong antioxydant properties which continues to attract considerable research. Free caffeic acid was reported in coffee (seed and pulp) but a large part was included in CGA (cf. Table2). Like CGA, caffeic acid was shown to exhibit various physiological and biological activities (up to 65). They are listed below but still remain to be unambiguously demonstrated (Table 5).

Table 5 Compilation of 65 reported biological activities of caffeic acid (adapted from Duke, 1992a).

Biological activity	Biological activity	Biological activity
Allergic	Analgegic	Anti-HIV
Anti-tumor-Promoter	Antiadenoviral	Antiaggregant
Anticancer	Anticarcinogenic	Antiedemic
Antiflu	Antigonatotropic	Antihemolytic
Antihepatotoxic	Antiherpetic	Antihypercholesterolemic
Antiinflammatory	Antimutagenic	Antinitrosamic
Antiophidic	Antioxidant	Antiperoxidant
Antiprostaglandin	Antiradicular	Antiseptic
Antispasmodic	Antistomatic	Antisunburn
Antithiamin	Antithyroid	Antitumor
Antiulcerogenic	Antivaccinia	Antiviral
Bactericide	CNS-Active	Cancer-Preventive
Carcinogenic	Cholagogue	Choleretic
Clastogenic	Cocarcinogenic	Collagen-Sparing
Cytoptotective	Cytotoxic	DNA-Active
Diuretic	Fungicid	Hepatoprotective
Hepatotropic	Histamine-Inhibitor	Immunostimulant
Leucotriene-Inhibitor	Lipoxigenase-Inhibitor	Lyase-Inhibitor
Metal-chelator	Ornithine decarboxylase-In	Prooxidant
Prostaglandigenic	Sedative	Spasmolytic
Sunscreen	Tumorigenic	Viricide, Vulnerary

N

3.4. KNOWN BIOLOGICAL ACTIVITIES ATTRIBUTED TO TANNIN, A MODEL OF POLYMERIC PHENOLIC COMPOUND FOUND IN COFFEE

This aromatic compound, is a model of polymeric and polyphenolic structure. Both condensed and hydrolyzable tannins exist in coffee plant, but it was demonstrated that in coffee pulp, tannins were mostly condensed and consisted primarily of proanthocyanidins (Ramirez-Martinez and Clifford, 2000). Information on calculation of the content of tannins in coffee is sometimes contradictory. The data regarding concentration of hydrolysable tannins (gallotannins and ellagitannins), condensed tannins or both, depends on the drying method and the extraction method. For example, the amounts of condensed tannins were calculated in our laboratory with three storage techniques of coffee pulp :

1. fresh-frozen and crushed,
2. frozen after storage and crushed in N_2, and
3. lyophilized before crushing.

These coffee pulps were both extracted with methanol:H_2O (80:20) and quantified with the method of Swain and Hillis (1959), also known as the ferrous-butanol-HCl method (autodepolymerisation of proanthocyanidins). The results were given as equivalent of mimosa tannin powder and results were respectively 2,000; 6,000 and 11,200 ppm (fresh weight) of condensed tannins .

This gives a 5 times ratio between technique 1 and technique 3. With these samples 100g f.w. (fresh weight) represented 21g d.w (dry weight), which gives 9,500; 28,600 and 53,300 ppm (d.w.) of condensed tannins respectively. Total tannins were previously reported between 18,000 and 86,000 ppm in coffee pulp and condensed tannins (as flavonoids) between 28,000 and 40,000 ppm (cf. Table 2). Our results are comparable with previous reports, and show that lyophilization permits high tannins recovery.

Total tannins were previously reported between 18,000 and 86,000 ppm in coffee pulp (Table 2) and condensed tannins (as flavonoids) between 28,000 and 40,000 ppm

As with CGA and caffeic acid, tannin was reported to exhibit various physiological and biological activities. To our knowledge, up to 33 biological activities were attributed to tannin (as a generic name). They are listed below, but still remain, as previously, to be unambiguously demonstrated (Table 6).

N

Table 6. Compilation of 33 reported biological activities of tannin (adapted from Duke 1992a)

Biological activity	Biological activity	Biological activity
Anthelminthic	Anti tumor promoter	Anti HIV
Anticancer	Anticariogenic	Antidiarrheic
Antidysenteric	Antihepatotoxic	Antihypertensive
Antilipolytic	Antimutagenic	Antinephritic
Antiophidic	Antioxidant	Antiradicular
Antirenitic	Antitumor	Antiulcer
Antiviral	Bactericide	Cancer preventive
Chelator	Cyclooxygenase inhibitor	Glucosyl transferase inhibitor
Hepatoprotective	Lipoxygenase inhibitor	MAO inhibitor
Ornithine decarboxylase inhibitor	Psychotropic	Viricide
Xanthine oxidase inhibitor	Carcinogenic	Immunosuppressant

4. Conclusion

In this paper, we provide evidence that high biotechnological potential exists with various identified polyphenolic compounds found in liquid by-product like OMW or with solid by-product like coffee pulp. The large lists of examples of phenolic compounds from olive and coffee plant species opens researchpossibilities on other agroindustrial by-products specifically rich in such polyphenolics. Chlorogenic acid, caffeic acid and tannin represent three examples of bioactive compounds identified in olive and coffee by-products. These three compounds along with a few other compounds which are listed, could be valuable as food additive, cosmetic food or nutrient for human health.

5. Abstract

Actual and future use of biotechnologies implies research focusing not only on agricultural production but also on the valorization of by-products generated by the agro industry. Micro-organisms are unique « cell factories » able to valorize agricultural by-products instead of only degrading them in depollution or methanisation processes. This paper gives two exemples of agricultural products and by-products that contain phenolic structures. Coffee pulp and olive mill wastewater (OMW) represent models of respectively solid and liquid by-products rich in polyphenolic compounds. Polyphenolics are homo- or hetero-cyclic aromatic compounds, where hydroxylic functions are

N

substituted to at least one of the cyclic carbonic structures. Hydroxylated phenols, flavonoids, anthocyans, tannins and lignins are polyphenolic compounds. Coffee pulp contains simple polyphenols including acid phenolics and caffeoyl derivatives, and polymeric polyphenols including tannins. OMW possess similar chemical structures with each by-product containing specific polyphenolic compounds. OMW is probably the agro-industrial liquid by-product exhibiting the highest carbon oxygen demand (COD), with values up to 200g of COD/litre. The difficulties encountered in treating such compounds often result from high concentration of pollutants and/or high toxicity to the microflora. Coffee (*Coffea arabica* L.) and olive (*Olea europeae* L.) release after processing a polyphenolic rich by-product where known biological activities are attributed to a large extent to these aromatics. Examples of three polyphenolic structures with high biotechnological potential, are given. Chlorogenic and caffeic acids as monoaromatic models and tannin as polyaromatic model of polyphenols, is described. These compounds are both found in coffee and olive plants. *Coffea arabica* is the plant which contains the highest concentration of chlorogenic acid, when compared with other plant species known to synthetise this compound. Up to 52 different names of biological activities are reported with chlorogenic acid. A tentatively exhaustive list of the various phenolic compounds which are detected and reported from olive and coffee is added in this paper, showing the large potential of valorisation of these two agro-industrial plants.

6. Aknowledgments

For olive results, the financial assistance from the EU DGXII-B in part of the project EC/ORSTOM/CBS, Contract CEE CI1*CT92-0104 is gratefully acknowledged. For coffee results, the financial assistance from the EU DGXII-B4 in part of the project BIOPULCA, Contract CEE IC18*CT97-0185 is gratefully acknowledged.

7. References

Baldioli M., Servili M., Perreti G., Montedoro G.F. (1996), Antioxidant activity of tocopherols and phenolic compounds of virgin olive oil. J.A.O.C.S., 73 (11): 1589-1593

Balice V., Cera O. (1984), Acidic phenolic fraction of the olive vegetation water determined by a chromatographic method. Grasas y Aceites, 35 (3): 178-180

Balyaya K.J., Clifford M.N. (1995), Individual chlorogenic acids and caffeine contents in commercial grades of wet and dry processed indian green Robusta coffee. J. Food Sci. Technol., 32(2), 104-108

Brauman A., Kane M.D., Labat M. Breznak A. (1992), Genesis of acetate and methane by gut bacteria of nutritionally diverse termites. Sciences, 257: 1384-1387

Bressani R., Estrada E. Jarquin R. (1972), Pulpa y pergamino de café. 1. Composicion quimica y contenido

N

de aminoacidos de la proteinadelapulpa. Turrialba, 22 (3): 299-304

Bressani R Elias, L.G. (1976), Utilizacion de desechos de café en alimentacion de animales y materia prima industrial. Exposicion Pecuria del Istmo Centroamericano. EXPICA 76, San Salvador, El Salvador, INCAP Doc., Guatemala, 25 pp

Clifford M.N., Kellard B., Birch G.G. (1989), Characterisation of caffeoylferuloyl-quinic acids by simultaneous isomerisation and transesterification with tetramethyl-ammonium hydroxide. Food Chem., 34: 81-88

Clifford M.N., Gonzàlez de Colmenares N., Ramirez-Martinez J.R., Aldana, J.O. (1993), Progress in the analysis of proantocianidins in freshly prepared coffee pulp. *15ème Coll. Scient. Intern. sur le Café*, ASIC, Paris, 884-886

Crawford D.L., Pometto A.L., Crawford R.L. (1983), Lignin degradation by *Streptomyces viridisporus* : Isolation and caracterisation of a new polymeric degradation intermediate. Appl. Environ. Microbiol., 45: 898-904

Duke J.A. (1992a), CRC Handbook of Phytochemical Constituents in GRAS Herbs and other Economic Plants. CRC Press, Boca Raton, Fl., 654 pp

Duke J.A. (1992b), CRC Handbook of Biologically Active Phytochemicals and Their Activities. CRC Press, Boca Raton, Fl., 183 pp

Ferry J.G., Wolfe R.S. (1976), Anaerobic degradation of benzoate to methane by a microbial consortium. Arch. Microbiol., 107, 33-40

Field J.A., Lettinga G. (1987), The methanogenic toxicity and anaerobic degradability of a hydrolysable tanin. Wat. Res., 20: 367-374

Labat M., Sayadi S., Gargouri A., Zorgani F., Jaoua M., Zekri S., Ellouz R. (1996), Procédé aérobie-anaérobie pour le traitement biologique des résidus liquides de l'industrie oléicole. In: "Journées Industrielles sur la Digestion Anaérobie", JIDA-96, Narbonne, 8 pp

Labat M., Sayadi S., Gargouri A., Garcia J.L. (1997), Development of biological process for treatment of olive mill waste water. Molecular studies of the ligninolytic system by *Phanerochaete chrysosporium. Final Progress Report* CEE DGXII-B, Contrat n° CI1-CT92-0104, feb. 1997, Marseille, 278 pp

Léger C.L. (1999), Co-produits de l'huilerie d'olive: les composés phénoliques et leurs propriétés biologiques. O.C.L., 6 (1), 60-63.

Molina M.R., De La Fuente G., Gudiel H. Bressani R. (1974), Pulpa y pergamino de café. 8. Estudios bàsicos sobre la deshydratacion de la pulpa de café. Turrialba, 24 (3) 280-284

Montedoro G.F., Servili M., Baldioli M., Selvaggini R., Miniati E. Macchioni A. (1993), Simple and hydrolyzable phenolic compounds in virgin olive oil. Note 3. Spectroscopic characteriz ation of the secoroidoid derivatives. J. Agric. Food Chem., 41: 2228-2234

Nefzaoui A. (1991), Valorisation des sous-produits de l'olivier. Options Méditerranéennes, 16: 101-108

Ramirez-Martinez J.R. (1988), Phenolic compounds in coffee pulp: quantitative determination by HPLC. J. Sci. Food Agric., 43: 135-144

Ramirez-Martinez J.R., Clifford M.N. (2000), Coffee pulp polyphenols: an overview, in T. Sera, C.R. Soccol, A. Pandey and S. Roussos (eds.) *Coffee Biotechnology and Quality*, Kluwer Academic Publishers, Dordrecht, pp 501-509

Ryan D., Robards K. (1998), Phenolic compounds in olives. Analyst, 123: 31-44

Salvemini F. (1985), Composizione chimica e valutazione biologica di un mangime ottenuto essicando tercamente le acque di vegetazione delle olive. Riv. Delle Sostanze Grasse, 112: 559-564

N

Swain T., Hillis W.E. (1959), The phenolic constituents of *Prunus domestica.* I.- The quantitative analysis of phenolic constituents. J. Sci. Food Agric., 10: 63-68

Zuluaga J., Bonilla, C., Quijano, R.M. (1975), Contribucion al estudio y utilizacion de la pulpa de café. 7th Intern. Col. Chim. Coffee, Hamburg, ASIC Ed, Paris, 233-242

Zuluaga J. (1981) Contribution à l'étude de la composition chimique de la pulpe de café (*Coffea arabica* L.). Thesis, Neuchatel Univ., Swiss, 93pp

N