BYPRODUCTS FROM AGRICULTURE AND FISHERIES

CHAPTER 5: APPLICATION OF PLANT BYPRODUCTSTS IN COSMETICS

5.1. Introduction

An essential part of our diet is represented by vegetables and fruits and for decades their undeniable worth has been extensively studied. Other than primary metabolites (e.g., lipids, saccharides, and amino acids), the plants manufacture a majority range of "secondary" metabolites, which have a vital role in the protection of plants against both abiotic and biotic stresses (Barbulova et al., 2014). Furthermore, various types of interactions with the environment and with other organisms that lodge the same environmental habitat have been medicated by the secondary metabolites (Oksman-Caldentey & Inze, 2004). As fragrances, preservatives, dyes, pharmaceuticals, and flavors, they have been of great interest for centuries: consumption of vegetables and fruits has been indicated by the epidemiological researches which shows the great benefits of health, such as certain types of cancer as well as reduced risk for stroke and coronary heart disease. The effects of secondary metabolites and dietary fibers are the main protective action, mainly flavonoids, and carotenoids with powerful antioxidant activity. The most copious carotenoid, beta-carotene, was proficient in neutralizing the free radicals contained in red and orange fruits such as tomatoes and growing the cellular antioxidant defenses. The most vital examples of mixtures with therapeutic activity among the flavonoids are epicatechins, catechins, procyanidins, and flavanols, present in grapes and apples, that subsidize to preserve the heart health; the flavanones, the foremost flavonoid type in citrus fruits; the anthocyanidins, mostly present in red grapes, berries, cherries, that enhance the brain functions and rise the antioxidant defenses (Kris-Etherton et al., 2004; Djilas et al., 2009).



Figure 5.1. Image showing different plant-basedcosmetics

[Source: https://seybeautenaturelle.com/]

Thanks to all these features and to the wide range campaign to encourage the benefits of fresh green products, in the last decades, the consumption of vegetables and fruit have enhanced substantially and the residues and wastes, are now estimated to be around 800,000 tons per year of fresh matter globally, produced by agro-food industries, without taking into account the processing of food (Ayala-Zavala et al., 2004). Today, valorization strategies and basic waste management techniques are used for the processing of the agricultural waste as the production of fertilizers and composts, animal feed as well as anaerobically digestion to biogas. Environment-friendly and efficient recycling and utilization of this waste are becoming more and more critical since this kind of processing is linked with the high costs of transport, storage and drying (Tuck et al., 2012). 10~60% of the raw materials are generated by the agricultural processing industries as solid waste and it was it has been proved that in some scenarios the waste by-product was even more useful than the main products (Goñi et al., 2011). Vegetable and fruit processing industries produce waste materials which have been illustrated in Table 6.1 expressed as percentages, which we wish to call "by-products" to emphasize their large potentialities to be recycled as appreciated products for industry. Seeds, leaves, skins, stems, unstable pulp and wastewaters are the by-products which in some scenarios represent more than 40% of total food (such as the cases of asparagus, papaya, artichoke, pineapple, citrus fruits, mango) and are normally discarded.

It is a known fact that by-products of food are very rich in minerals, dietary fiber sugars, organic acids, bioactive compounds, as carotenoids and polyphenols, analogously to their edible counterparts. Their attracting composition along with the increasing interest in searching natural constituents as a substitute to synthetic substances has found that the by-products of food are the economically beneficial source for the synthesis of high-value compounds in various fields of industry which include Pharmaceutics, Food, Cosmetics and Nutraceutics (Schieber et al., 2001). This review covers some examples among the most significant application of agricultural by-products of food in Cosmetics, and argue their performance as safety and efficacy.

Plant	By-Products	Edible Part
Agave	40% (rind and pith)	60%
Citrus fruits	66% (peel)	44%
Pineapple	52% (core, peels, top, pulp)	48%
Apple	11% (pulp and seed core)	89%
Artichoke	60% (outer bracts, receptacles and stems)	40%
Cactus cladodes	20% (spines, glochids and peel)	80%
Carrot	30%-40% (pomace)	60%-70%

Table 5-1. By-product quantities generated from some fruit and vegetable processing industries

Banana	Up to 30% (peel)	70%
Asparagus	Up to 40%–50% (spear)	50%-60%
Mango	42% (seeds, peels, unusable pulp)	58%
Tomato	3%–7% (peel and seeds)	93%-97%
Рарауа	47% (seeds, peels, unusable pulp)	53%
Passion fruit	75% (rind and seeds)	25%
Potato	15%-40% (peel)	60%-85%
Mandarin	16% (peels)	84%

5.2. Citrus Fruit Processing By-Products

One of the world's main fruit crops are citrus plants (genus *Citrus* in family *Rutaceae*), also recognized as *agrumes*, with global popularity and availability contributing to the human diet. One of the sources of dietary fibers are fresh citrus fruits connected with lowered circulating cholesterol and gastrointestinal disease prevention; they are rich in vitamin B, C vitamins (pantothenic acid, niacin, folate, pyridoxine, riboflavin, and thiamin) and phytochemicals i.e., limonoids, flavonoids, and carotenoids (Liu et al., 2012; Kim et al., 2013). In human health development, the biological ingredients are of vital importance because of their ability to be changed to vitamin A (for instance the β -cryptoxanthin), antioxidant properties, and to shelter from numerous chronic diseases. About one-third of the citrus fruits are utilized after processing worldwide although many citrus fruits, such as grapefruits, tangerines, and oranges can be eaten fresh, and lemon/orange juice production is considered for nearly 85% of total processed intake.



Figure 5.2. Cosmetic products produced from citrous fruits

[Source: https://manofmany.com/fashion/mens-fragrances/15-best-fresh-citrus-fruity-colognes]

High quality and high value of agricultural waste are generated by citrus processing, and most of the waste is in the shape of press cakes, that due to costs for transport and handling are pricy to dispose of. A study was carried out into the anti-melanogenic impacts of ethanol extracts of the press cakes of *Citrus unshiu*, to give value to this waste, the fruit peel was widely used to treat atopic and severe dermatitis or in the conventional medicine as digestive, which were mainly grown in Jeju Island in Korea (Kim et al., 2008).

From natural sources, the development of novel whitening phytochemicals has become a very common trend. The color of human eyes, hair and skin are determined by the end product of melanogenesis known as Melanin and although it has some limitations such as accumulation and overproduction in the skin may cause aesthetic problems and skin disorders and problems like dark spots and hyperpigmentation due to its photoprotective role in absorbing free radicals in the cells and shielding from UV light (Balkrishnan et al., 2006; Costin & Hearing, 2007).

The transcription factor MITF (Microphthalmia-associated transcription factor and the activity of the main enzyme, tyrosinase determine the production of Melanin; hence, reduced melanin content in the skin would be caused by the expression or a down-regulation tyrosinase activity. Moreover, for melanin synthesis, tyrosinase-related protein TRP-2 and TRP-1 are also vital and are regulated by MITF (Yen et al., 2012).

Using ethanol as solvent, citrus press cakes composed of *C. unshiu* fruit peels were extracted its capacity to inhibit protein expression profile of TRP-2 and TRP-1 and MITF, tyrosinase activity and melanin content in murine B16F10 melanocytes was tested. It was determined that the cellular melanin content was significantly reduced by the treatment with citrus press cake extracts, through the transcription factors TRP-2 and TRP-1 and inhibition of the tyrosinase activity in a dose-dependent manner. Based on the Western blot examination (analytical method, used to notice precise proteins in a sample), in a dose-dependent manner, the upstream transcription factor MITF was also down-regulated. These results recommended that this kind of by-products of food was an auspicious applicant for treating skin pigmentation disorders, which should be complemented with further *in vivo* valuation of the biological activity of citrus press cake extracts (Sabio et al., 200; Papaioannou & Karabelas, 2012).

Citrus by-products, besides the ethanol extracts, are the significant basis of essential oils (Pavithra et al., 2009). Because of their strong antioxidant, antimicrobial and anti-inflammatory features, essential oils acquired from plants are well known and have a large number of suitable applications which include use as preservatives against spoilage, food additives, cosmeceuticals and pharmaceuticals (Baik et al., 2008). Hence, the study was done into the potential utilization of an essential oil using hydro-distillation obtained from *C. unshiu* peel wastes, as an anti-microbial and anti-inflammatory agent in Cosmetics (Yang et al., 2009). The existence of six main compounds was revealed in the chemical analysis of this

oil (containing up to 94.5% of the total oil composition): and α -terpinolene (0.56%), α -pinene (1.02%), β -myrcene (1.59%), cymene (4.02%), γ -terpinene (6.80%), limonene (80.5%). The oil due to its monoterpene composition displayed a strong antibacterial activity, which inhibits the respiration process damaged the cellular integrity of the microbial cells. It was displayed that nitric oxide (NO) synthesis can be down-regulated by the oil. NO is synthesized in many animal tissues and cells and is an endogenous free radical species produced by nitric oxide synthase (NOS), and also the inflammatory process is activated by the oils in the tissues. NO synthesis can be induced in numerous cells, after exposure to stress inducers, i.e., bacterial lipopolysaccharide (LPS), triggering a transduction cascade causing inflammation and tissue damage (Muracami, 2009). *C. until* the oil, produced a strong inhibition of NO production extracted from the press-cakes, when tested on LPS-treated RAW264.7 cell line (macrophages of the immune system), recommending that it could be beneficial anti-inflammatory component to be used in cosmetic formulas (Zuorro et al., 2014; Yilmaz et al., 2016).

5.3. Tomato and Olive Processing By-Products

The olive oil production farms and the tomato processing industries are the two most significant processes which produce valuable products exported worldwide, these are mostly located in the Mediterranean areas.

Approximately 160 million tons of the fresh tomatoes are produced annually on a global scale and about 40 million tons of tomatoes are processed as tomato products: chopped or whole, unpeeled or unpeeled tomatoes, tomato paste (Strati & Oreopoulou, 2014; Barbulova et al., 2015). A large number of fascinating by-products are produced by the tomato processing, seeds, and pulps, also known as "tomato pomace", peels, which are significantly rich in the antioxidant compounds: a compound recognized for its part in the prevention of disease, known as lycopene is of particular importance and is in high demand from cosmetic, pharmaceutical and food industries (Borguini & Torres, 2009).

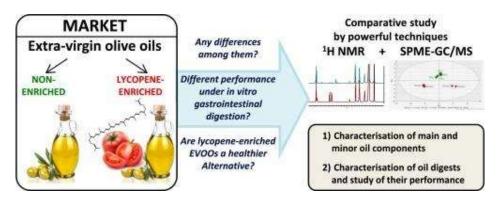


Figure 5.3. Extra-virgin oils are produced from tomato and olives

[Source: https://www.sciencedirect.com/science/article/abs/pii/S0963996920300120]

Chemical synthesis or standardized tomato fruit extraction are the common sources of commercially accessible lycopene, but due to complicated extraction procedures, the product is normally expensive. Comparative to a pulp, the by-products have the peel fraction of tomato contains up to five-time additional lycopene, but the processing and storage of this material is an issue because of its susceptibility to microbial spoilage and high moisture level. The extractability of lycopene is extremely low by traditional food-grade organic solvents, such as ethyl acetate, ethanol, and hexane, at least under this situation that usually reserves the activity of the carotenoids *in vivo* (Zuorro & Lavecchia, 2010; Papaioannou & Karabelas, 2012). It was determined with pectinolytic enzyme preparation, an enzymatic pre-treatment of tomato peels, suggestively increased the level of lycopene recovery, together with the use of surfactant-assisted extraction. Moreover, for recovery of the lipophilic lycopene, the utilization of organic solvents, was evaded making the procedure of its extraction ecologically friendly, guaranteeing direct lycopene usage in cosmetics and food industries.

Olive (*Olea Europea*) oil is also a significant part of the Mediterranean diet, besides tomatoes connected with enhanced health status in consideration with reduced occurrence of coronary heart diseases. In an extensive variety of cosmetic products, it has been used as a vital ingredient like body and face creams, shampoos, soaps, lotions because of the existence of phenolic compounds and monounsaturated fatty acids. The aqueous phase of the olives predominantly contains these compounds and in epithelial and endothelial platelets, cells, neurons, neoplastic cells and cells of the immune system, they exert diverse biological activities (Cicerale et al., 2009).

The key phenolic compounds have powerful antioxidant activity both *in vitro* and *in vivo* including oleuropein and hydroxytyrosol and their derivatives, which provide extra-virgin olive oil its harsh taste. Regarding the oleuropein and its pharmacological activities, there are various studies including antiatherogenic, anti-inflammatory, antiviral, anti-cancer, antioxidant, hypolipidemic, antimicrobial, and hypoglycemic effect. Oleuropein and hydroxytyrosol along with the antioxidant compounds exiting in the olives, only a low percentage dissolves in the lipidic fraction of the olives because they are highly soluble in water (Visioli & Galli, 2002; Omar, 2010).

Most of the polyphenols vanish in the Oil Vegetation Waters (OVW), during the olive oil extraction procedure, which shows the fraction of the olives which is soluble in water, which are detached from the oil. International Olive Council gives some figures that the consumption of olive oil enhanced 78% between 1990 and 2010 worldwide (International Olive Council, 2011). Proportionally, the increase in the olive oil has increased the olive mill by-products, since the olive oil is on average less than 20% of the olive fruit, comprising OVW. For human health, the OVW has valuable features, including anti-inflammatory activity, and it shows for various biotechnological applications, a huge source of useful compounds including Cosmetics (Manach et al., 1998; Bitler et al., 2005).

Effects of hydroxytyrosol have been proved in recent studies on cytokines, inflammatory mediators and chemokines, and anti-inflammatory constituents were identified in aqueous olive extracts (Richard et al., 2011). High-Performance Liquid Chromatography (HPLC) is used for the fractioning of aqueous olive extracts and their effects on the production of inflammatory mediator's prostaglandin E2 (PGE2) and nitric oxide were investigated. It was determined that the production of PGE2 and NO was inhibited by the hydroxytyrosol, showing powerful anti-inflammatory activity and along with OVW decreases the secretion of chemokines (CXCL10/IP-10, CCL2/MCP-1) and cytokines (IL-1 α , IL-1 β , IL-6, IL-12, TNF- α). Furthermore, the valuable features of two fractions of OVW were investigated, OVW from *Olea Europea*, Carolea variety, in grouping with acacia fibers. The detoxifying effect, a strong anti-inflammatory effect, and antioxidant activity were monitored in on cultured skin cells, which suggested that fractions could be established as products for skincare, attained from OVW (Nasopoulou et al., 2014; Barbulova et al., 2015).

5.4. Valorization of By-Products Deriving from Pineapple and Grapevine

All the by-products and their derivatives, as already mentioned have some beneficial utilization, hence, concentration has been directed on how to attain greater value from them in consideration of efficiency. Grape mark extracts and pineapple rind and essential by-products are the examples of this type of valorization (Martín-Peláez et al., 2013; Yao et al., 2015).

A high quantity of by-products is produced from pineapple (*Ananas comosus*), which is the most processed tropical fruit. Being the rind and the core of the main ones, 25%–35% of the pineapple fruit is represented in these by-products (Reinhard & Rodriguez, 2009; WU et al., 2012). Compounds with high antioxidant activity are present in the pineapple rind and core, and concerning valorization in the cosmetics industry, they give them a huge potential. Presence of eight diverse carotenoids was determined by the use of ultra-high performance liquid chromatographic (UHPLC) technique (β -cryptoxanthin, zeaxanthin, lutein, β -carotene, violaxanthin, neoxanthin, α -carotene, and lycopene) and the result of Ultraviolet C (UV-C) radiations on these compounds and two vitamins (E and A) in the pineapple rind and core were assessed (Freitas et al., 2015).

One of the major sustainable sanitation methods of fruits is the ultra-violet radiation at a wavelength of 190–280 nm (UV-C), it is a relatively inexpensive and environmentally friendly method. It can promote the biosynthesis of vitamin C and carotenoids, can induce stress in the plant cells, and could provide additional benefits to the by-products (Gonzalez-Aguilar et al., 2010). Based on this, it was verified that L-ascorbic acid level in the whole fruit was lower compared with its level in the pineapple rind and it was also confirmed that L-ascorbic acid content in the rind is increased by the UV-C radiation. It was also confirmed that β -carotene was most abundant among the carotenoids, the carotenoid whose

concentration also enhanced in the rind after exposure of UV-C radiation has the maximum pro-vitamin A activity.



Figure 5.4. Different beauty produicts manufactured from grapevine and pineapple

[Source: https://i2.wp.com/ommorphiabeautybar.com/wp-content/uploads/2019/09/Caudalie-Skinare-2019-Launches-opener.jpg?fit=1149%2C1200]

High nutritional value, rich of beneficial compounds is also given to another specie Grapevine having compounds such as carotenoids, tannins, polyphenols, and vitamins. Pomace or grape marc accounts for around 15% of the crushed grapes, the solid by-product which contains, skins, seeds and pulp are leftover from the winemaking process (Caimari et al., 2013). Biotechnological processes utilize an industrial waste product represented as grape marc, uses are in the production of the Italian "Grappa", preparation of soil fertilizers, tartaric acid extraction and distillation of ethanol and purification of colorants (Carola et al., 2012). The grape marc is derived from white wine production which is obtained from Aglianico grapes (the most useful and the most esteemed variety of grapes in Campania region, Italy) and is richer in nutrients because no compound has yet been extracted by the winemaking process and it is unfermented. Furthermore, various types of lipophilic compounds are present in it, such as

ellagic acid, resveratrol, resveratrol, carotenoids, lycopene, and at the time of pressing these are not dissolved in the water-soluble juice, but an oil-soluble (liposoluble) solvent is used for extraction and attained extract can be utilized as an active component for skincare Cosmetics (Oliveira et al., 2004).

A new cosmetic component was developed based on this assumption, used for making white wine DOC (Controlled Designation of Origin), Sant' Agata dei Goti, Benevento, Italy composed of a liposoluble fraction of the unfermented Aglianico marc. Another liposoluble extract attained from *Vitis vinifera* cells (Aglianico cultivar) was mixed with the liposoluble marc extract (LME), developed as sterile liquid cultures (liposoluble cell extract, LCE) and on cultured skin cells, the attained mixture was tested. The effect of the combination of the LCE and LME was studied on proteasome activity in human keratinocytes (HaCaT) and Human Dermal Fibroblasts (HDF), mixed in a 1:10 ratio. Elimination of damaged and abnormal proteins is the responsibility of "Proteasome" by the proteolytic system and its activity is inhibited in the stressed cells by the generation of aggregated and highly oxidized proteins in the cytoplasm (Bulteau et al., 2002). In enhancing the detoxifying capacity of the cells, the tested mixture of LCE and LME provided strong effects by upregulating the proteasome activity by 61% in keratinocytes and 44% in fibroblasts. In boosting the hydrating potential, the role of LCE/LME has also been proven by the investigators by measuring the expression level of HAS 2 and by measuring the expression level of Collagen I and Collagen III in stimulating new collagen production APQ3 (Aquaporin 3) and (Hyaluronan Synthase 2) genes.

5.5. Coffee Processing By-Products

The coffee processing industry is another source of the huge number of disposable by-products. In various countries, these coffee plants (*Coffea robusta* and *Coffea Arabica*) are being produced, particularly in those localized in South Asia, equatorial Latin America, Africa, and India. The elevated degree of processing knowledge is required in coffee dispensation and by-products such as coffee husk and pulp are produced, which have limited application as livestock feed, fertilizer and compost (Murthy & Naidu, 2012). Contrary to this, quantities of unused green beans can be generated by the step of coffee berry selection and collection, because they cannot pass to the next processing step due to not sufficiently big and ripe or they have been mechanically damaged. These green beans are still considered a vital source of natural antioxidants, which have not yet been broken down by the roasting procedure (DeSA, 2013).

Hence, unroasted coffee beans were gathered, to have a valued ingredient, rich in bioactive anti-oxidant compounds, and using two natural elements carbon dioxide (CO_2) and pure water subjected to decaffeination, and extracted in ethanol. It was observed after the removal of ethanol that a jelly-like extract enhanced natural skin cell regeneration, reinforced the epidermal barrier and promoted an even skin tone for a radiant complexion. Furthermore, it also helped accelerated damaged skin repair, prevent

water loss, and lighten the skin by inhibiting melanin synthesis by decreasing the inflammatory process (Flanagan et al., 2014; Bessada et al., 2018).

Moreover, it helped prevent water loss, lighten the skin by inhibiting melanin synthesis and accelerated damaged skin repair, by decreasing the inflammatory process (Flanagan et al., 2014; Bessada et al., 2018).



Figure 5.5. Coffee-based beauty products

[Source: http://whatalookerbeauty.blogspot.com/2017/10/my-top-10-coffee-inspired-beauty.html]

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