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Phenols and Polyphenols from *Argania spinosa*

Z. Charrouf and D. Guillaume
Laboratoire de Chimie Des Plantes et de Synthèse Organique et Bioorganique,
Département de Chimie, Faculté des Sciences, Université Mohamed V-Agdal,
Avenue Ibn Batouta, BP1014, Rabat, Morocco
FRE2715, 51 Rue Cognacq Jay, 51100 Reims, France

Abstract: *Argania spinosa* is a tree specifically growing in Morocco. Its seeds contain two or three oleaginous kernels that are crushed to afford argan oil, an oil of high dietetic value. Cardioprotective argan oil properties have been associated with the presence of various (poly)phenols within the oil. In addition to tocopherols, caffeic acid, oleuropein, vanillic acid, tyrosol and catechol are the main phenols identified so far from argan oil. Resorcinol (-)-epicatechin and (+)-catechin are the main polyphenols. The full (poly)phenol composition of argan oil and of the different parts of the tree, is presently reviewed together with the recent development of argan (poly)phenols as cosmetic ingredients.

Key words: *Argania spinosa*, argan oil, phenol, Morocco

INTRODUCTION

Argan tree (*Argania spinosa*, L. Skeels) of the family Sapotaceae is exclusively endemic in Morocco. The tree grows on the west side of the High Atlas mountains, primarily within the provinces of Agadir, Essaouira, Taroudant and Tiznit. Argan tree is the only species of its family to grow in a subtropical zone and Argan is considered to be a Tertiary relic species.

Nowadays, the argan grove covers 3197 square miles of a mainly arid or semi-arid soil. For the population living in this part of Morocco, argan tree represents an invaluable economic resource (Charrouf *et al*., 2002). Indeed, each part of the tree is used and most of the rural activities are organized around the tree or its productions. Argan tree wood is used for carpentry or as fuel, its leaves and fruits are used to feed cattle (mainly goats and camels), advantage is taken from its shadow to grow family-size vegetable or cereal production; finally and most importantly, the oil prepared from its fruit is used as food and in traditional medicine as well. On a larger scale, because of its deep root system, its ability to support long period of drought and its longevity (more than 200 years), argan tree is frequently the ultimate warrior when the desert is encroaching on the land. Moroccan officials estimate that the argan grove is the single source of wealth for three million people, 2.2 millions of which being rural. The agro-economy induced by the argan grove generates more than 20 millions of days of work, one third of which being dedicated to the preparation of argan oil, an activity exclusively accomplished by women in the Berber society. Nevertheless, despite its obvious usefulness, the argan grove is steadily decreasing in terms of density and surface covered (2 to 3 square miles disappear each year). Among the culprits responsible for this decline are: the over-use of the wood, a series of unprecedented arid years and the replacement of argan trees by exogenous but quickly lucrative species. Consequently, ecology and economy matters cannot be dissociated and a program aimed at promoting the economical value of argan tree is currently developed in Morocco with the strong support of

Corresponding Author: Z. Charrouf, Laboratoire de Chimie des Plantes, Département de Chimie, Faculté des Sciences, Université Mohamed V-Agdal, Ave Ibn Batouta, BP1014, Rabat, Morocco
Tel: (+212) 376 828 48 Fax: (+212) 377 132 79

governmental and several non-governmental organizations. The core of this program is the phytochemical study of the argan tree together with the implementation of cooperatives producing an argan oil of high and reproducible microbiologic and physico-chemical quality. The first part of this program has led to the investigation of the phenol content of argan tree and argan oil. This review summarizes the recent results obtained in this specific field.

RESULTS AND DISCUSSION

Argan oil is the best known production of argan tree. Its specific unsaturated fatty acid content provides to the oil cardioprotective properties that are extremely valued in developed societies. Whereas argan oil has been considered as a tourist attraction for long time, improvements made to its production quality have dramatically boosted its market share and argan oil is now widely sold across Western Europe, North America and Japan. Argan oil is marketed either as a culinary oil and for cosmetic purposes. In both case, argan oil is obtained by crushing the argan fruit kernel however, the alimentary oil is prepared from slightly roasted kernels whereas the cosmetic oil is obtained from crude kernels (argan oil used by the cosmetic industry is extracted from crushed crude kernels with organic solvents). The roasting step gives to the oil its unique hazelnut flavor (For a detailed oil extraction procedure (Charrouf *et al*., 2002).

The (poly)phenol content of various parts of argan tree and of argan oil has been studied together with the influence of the roasting step on the (poly)phenol composition (Table 1).

Argan Oil Phenols

Argan oil phenol content is low. However, because of the flavor and pharmacological activities of some of these compounds, their impact on the taste and/or biological properties of argan oil can be important. The difficulty associated with the study of argan oil phenolic fraction is the removal of the huge quantity of fatty acid and the collect of minor quantity of (poly)phenols. Preliminary work (Chimi *et al*., 1988) indicated a polyphenol level of 56.3 ppm in argan oil. Caffeic acid and oleuropein were the only two phenol derivatives unambiguously identified during this study.

A more detailed phytochemical analysis of the phenolic components of argan oil was repeated later (Khallouki *et al*., 2003). Though several phenolic derivatives were detected, the structure of only seven of them was successfully achieved by GC-MS analysis of the methanolic extract. Those are: vanillic acid, tyrosol, ferulic acid, syringic acid, p-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid and vanillin. Since ferulic acid was identified after acid hydrolysis of the methanolic extract, the hypothesis of its natural occurrence as an heteroside cannot be discarded.

Such possibility is strongly reinforced by a more recent analysis performed using GC-MS spectroscopy and in which the presence of all previously identified compounds but ferulic acid was confirmed (Rojas *et al*., 2005). In addition to this list, catechol, resorcinol and 4-hydroxy benzyl alcohol were identified in alimentary argan oil together with (-)-epicatechin and (+)-catechin in cosmetic oil.

Of the upmost importance is also the presence of tocopherols (vitamin E) in argan oil. Tocopherols constitute an important class of compounds because of their strong antioxidant and vitamin activity. Total level of tocopherols in argan oil is between 630 and 750 mg kg^{-1} (Hilali *et al*., 2005). Such level is four times higher than that found in olive oil and two times higher than that found in hazelnut oil. γ-Tocopherol is by far the main tocopherol found in argan oil (between 580 and 700 mg kg^{-1}), α-and δ-tocopherols are present in roughly equal quantities (between 45 and 60 mg kg^{-1}). β-Tocopherol is almost absent in argan oil (Hilali *et al*., 2005). Since γ-tocopherol is generally considered as being the tocopherol with the greatest antioxidant activity, it is likely that it participates for a large part to the oil pharmacological properties.

Table 1: Phenol and diphenol derivatives and their occurrence in argan parts or preparation

Phenol	Press cake	Oil	Leaves	Fruit pulp
Caffeic acid		+		
Oleuropein		+		
Vanillic acid	+	+		
Tyrosol	+	+		
Ferulic acid		+		
Syringic acid	+	+		
p-Hydroxybenzoic acid	+	+		+
Vanillin	+			
Catechol	+	+		
4-Hydroxy benzyl alcohol	+	+		
α-Tocopherol		+		
β-Tocopherol		±		
γ-Tocopherol		+		
δ-Tocopherol		+		
Vanillyl alcohol	+			
4-Hydroxy-3-methoxyphenethyl alcohol	+			
Methyl 3,4-benzoate	+			
Polyphenol				
Resorcinol	+	+		
(-)-Epicatechin	+	+		+
(+)-Catechin	+	+		+
3,4-Dihydroxybenzyl alcohol	+			
Hydrotyrosol	+			
Protocatechuic acid	+			+
Quercetin			+	
Myricitin			+	
Quercetrin			+	
Myricitrin			+	
Hyperoside			+	+
Myricitine-3-O-galactoside			+	
Gallic acid				+
Isorhoifolin				+
Procyanidin				+
Hesperidin				+
Isoquercetin				+
Rutin				+
Quercetine-O-pentose				+
Naringenin-7-O-glucoside				+
Rhamnetin-O-rutinoside				+
Luteolin				+
Naringenin				+

Roasting of argan kernels necessary for alimentary argan oil preparation does not seem to dramatically affect the tocopherol content of argan oil, only α-tocopherol levels being slightly decreased.

Argan Press Cake Polyphenols

The press cake is the name given to the residue obtained after crushing the argan kernels (roasted or not). The press cake is generally used as cattle food due to its high energetic value. Its polyphenol content was carried out to eventually discover molecules of high economic value. Indeed, increasing the production of argan oil has led to an overproduction of press cake and a special care is brought to increase the market value of argan oil byproducts. Press cake phenol content was found to be almost 40 times higher than that of argan oil (Rojas *et al*., 2005). Sixteen phenol derivatives were isolated from the press cake: catechol, resorcinol, 4-hydroxy benzyl alcohol, vanillin, tyrosol, p-hydroxybenzoic acid, vanillyl alcohol, 3,4-dihydroxy benzyl alcohol, 4-hydroxy-3-methoxyphenethyl alcohol, methyl 3,4-benzoate, vanillic acid, hydrotyrosol, protocatechuic acid, syringic acid, epicatechin and catechin.

Argan Leaf Polyphenols

Polyphenols from the leaves of *A. spinosa* belong to the flavonoid (17%) and catechic tannin (14%) family

In the flavonoid crude fraction, 16.5% are a mixture of quercetin, myricitin and their glycosides (quercetrin, myricitrin, hyperoside, myricitrin-3-O-galactoside). Myricitrin and myricitine derivatives are the major constituents of the mixture (20 mg g^{-1}), whereas quercetin derivatives represent 8 mg g^{-1} (Tahrouch *et al*., 2000; El Kabouss *et al*., 2001).

Argan Fruit Pulp Polyphenols

Early study had led to the identification of four phenolic compounds from argan fruit pulp (Chernane *et al*., 1999). Those are (+)-catechin (-)-epicatechin, rutin and p-hydroxybenzoic acid. Quercetin derivatives were also isolated but their structure remained unidentified. In a more recent study (Charrouf *et al*., 2007), the same plant part has been analyzed by LC-mass spectroscopy. Thirteen additional derivatives have been identified: gallic acid, protocatechuic acid, isorhoifolin, procyanidin, hesperidin, hyperoside, isoquercetin, quercetin-O-pentose, naringenin-7-O-glucoside, rhamnetin-O-rutinoside, quercetin, luteolin and naringenin

Use of Argan Polyphenols in Human Health

The crude phenolic extract from argan oil has recently been shown to inhibit low-density lipoprotein oxidation in Human (Berrougui *et al*., 2006). In the same study, the ability of this extract to enhance cholesterol efflux from human THP-1 macrophages has also been evidenced. These clinical results strongly sustain the high dietary value of argan oil and its ability to prevent cardiovascular diseases. Furthermore, the antiproliferative effect of argan oil tocopherols on human prostate cancer has recently been demonstrated (Drissi *et al*., 2006). However, so far, the most impressive industrial success achieved with argan tree polyphenols has been obtained in the cosmetic and dermopharmaceutical fields. Though numerous large cosmetic laboratories had included argan oil in several of their protective skin preparations for a long time, Laboratoires Serobiologiques has been the most active laboratory at discovering new outputs for argan tree secondary metabolites and acting to preserve the species (Stussi *et al*., 2005). Research in that domain was rewarded by the discovery of the antioxidant activity of the crude flavonoid fraction isolated from argan leaves. Furthermore, this extract was also shown to protect the skin against UV-light (Henry *et al*., 2002). Consequently, the properties of the flavonoids were further studied (Pauly *et al*., 2002; Henry *et al*., 2005) leading to the discovery of the anti acne properties of the flavonoid extract (Henry *et al*., 2004) and of their matrix metalloprotease (MMP) inhibitory properties (Kadir, 2006; Stussi *et al*., 2005). MMPs constitute a group of more than twenty enzymes responsible for the degradation of the extra cellular matrix. Collagenases and elastases are well known enzymes involved in the skin-aging process and belonging to the MMP group. These days, Laboratoires Serobiologiques is marketing arganyl®, an anti aging cream containing argan leaf flavonoids.

CONCLUSION

(Poly)Phenols of argan tree and oil have only been superficially explored so far. Crude (poly)phenol fractions have been frequently isolated from different parts of the tree but their exact composition is still unknown. The pharmacological properties already observed with these crude extracts evidence strong properties in the cardiovascular domain, but also promising results in the anticancer field. Together with the cosmetic properties, these activities fully justify a more detailed analysis of argan (poly)phenols.

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