Ethnoeconomical, Ethnomedical, and Phytochemical Study of *Argania spinosa* (L.) Skeels: A Review.

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ABSTRACT. Populations of Morocco South-western part traditionally use the fruits of *Argania spinosa* (L.) Skeels to prepare an edible oil whose obtention also furnishes, as side product, a cake used to feed the cattle and complements the forage furnished by the leaves of this same plant. Unfortunately, the wood of *Argania spinosa* is also used for fuel and deforestation is subsequently accelerated since populations are generally eager to replace argan groves by cultures of higher and immediate benefit. However, argan tree, that is particularly well adapted to grow in arid lands, has been proposed by several agencies to slow down the desert progress in northern Africa. In order to incite the South-western Morocco dwellers to reintroduce argan trees, a program aimed to increase the industrial value of *Argania spinosa*, and beginning by its phytochemical study, is currently carried out in Morocco. The results of these recent studies together with previous knowledge are summarised in this review.

KEYWORDS. Morocco, *Argania spinosa*, argan tree, argan oil, ethnopharmacology, phytochemistry, saponins

INTRODUCTION

Argan tree (Argania spinosa (L.) Skeels), of the family sapotaceae, is endemic in South-western Morocco where it grows over about 320,000 square miles.
For centuries, this slow growing and spiny tree, that may be either shrubby or up to seven or ten meters has played an essential ecological function in this part of Morocco. Indeed, it effectively protects the soil against heavy rain or wind-induced erosion and, furthermore, by shading all kind of cultures, maintains soil fertility. Additionally, because of its ability to survive

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to arid conditions, it has helped to speed down the desert progression. In addition to these important ecological aspects, argan trees also economically support indigenous populations (23) since, not only cereal crops or domestic agricultural productions grown in its shadow are generally essential for the native economy, but the fruits of argan trees furnish an edible and marketable oil that provides to the dwellers up to 25% of their daily lipid diet (14). The leaves of argan trees are also used as "hanging forage" for cattle (goats and sheep) and this forage is complemented by the energetic leftovers obtained after the oil preparation.

However, nowadays, the argan-grove is annually slowly decreasing in term of density and boundary as well. This is mainly a consequence of the over use of argan trees, for wood or forage production, by the native dwellers but has also recently been deeply accentuated by several consecutive unprecedented arid years.

In order to stop this disappearance a reimplantation program is currently being developed in Morocco which considers that, in any arid and highly populated lands, ecological and economic concerns cannot be separated. So, any method resulting in an increase of the argan tree derivative commercial value can be seen as a long term way to reinitialise an integrated domestic forestry. Indeed, growing trees producing domestic food, valuable derivatives and forage makes the populations more confident to spontaneously reinvest in this kind of culture.

Argan oil and preparations including argan oil have been used in the traditional Moroccan medicine for centuries to cure skin diseases. The use of argan oil, or any argan secondary metabolite in cosmetology could obviously boost the reimplantation of argan trees in south-western morocco. More recently, saponins have been proposed as protective agents against infective fungi (5). Since argan tree is highly resistant and rich in saponins, it could be considered as a source of valuable saponins. Prior to any cosmetic or phytoprotective application, the isolation and identification of the potentially biologically active components of argan trees or argan oil is prerequisite. This review is aimed to summarise the knowledge concerning the secondary metabolites isolated up to date from argan tree or argan oil.

ARGAN OIL

Argan tree fruits are nut-sized, round, ovoid or conical. Inside of a milky pulp covered by a thick peel, is an hard shelled seed (argan nut) that represents about one quarter of the fresh fruit weight. Argan nuts contain up to three oil-rich white kernels from which argan oil is extracted in 30 to 55% yield depending on the extraction method.

Extraction of the argan oil:

Traditional method:

Traditionally, argan oil is extracted by women. The ripe-fruit pulp and peel are carefully discarded, then argan nuts are broken with stones and the kernels are air-dried in clay containers and roasted by mild heating. Roasted kernels are cooled then ground affording a brownish dough. This latter is finally hand-mixed with mild water for several minutes. To extract the oil, the dough is hand-pressed until it got solid and the obtained brownish emulsion is decanted, furnishing, after several minutes, a limpid oil with an hazelnut taste. The extraction residue or "press-cake" is dark-brown to black and generally still contains up to 10% of oil. It is very palatable to cattle.

This hand-made extraction technique is very slow and around ten hours are necessary to get one litre of oil. This technique barely affords more than 30% of an oil that badly preserves due

to the water added during the extraction process. Traditionally, the oil is extracted when necessary and salt is added for its preservation.

Press-extraction:

Recently, mechanical presses have been introduced to extract argan oil. Using this technique, mixing of the dough and water is unnecessary and the dough can be directly pressed. All other steps remaining unchanged, the oil is obtained in about 43% yield (calculated from the kernels) and only two hours are needed to get one litre of oil that preserves correctly.

Solvent-extraction:

For industrial (19) or laboratory purposes, argan oil can be extracted from ground kernels using any volatile lipophilic solvent. After evaporation of this latter, and one or two cycles of extraction, the oil is obtained in 50 to 55% yield (8). However, this type of extraction furnishes an oil with unsatisfactory organoleptic properties compared to the traditional or press extraction. This technique is exclusively reserved to prepare argan oil for cosmetic purposes.

Traditional use of argan oil:

The main traditional use of argan oil is by far for nutritional purposes. Natives either directly eat the oil on toasts, generally for breakfast, or use it for frying.

As cosmetic, the oil is traditionally indicated to cure all kind of pimples on the skin and more particularly juvenile acne and chicken pox pustules. It is also recommended to reduce dry skin problems and slow down the appearance of wrinkles. It is also used in rhumatology. For these indications, the oil is used as a skin lotion and applied on the area to be cured. In addition, and as olive oil, argan oil is also used by mouth and is traditionally prescribed as hepatoprotective agent, or in case of hypercholesterolemia or atherosclerosis.

Analytical study of argan oil:

Physico chemical data:

Physico chemical properties of argan oil obtained by traditional and industrial methods have been reported. Values are listed Table 1.

Table 1: Chemical composition of argan oil obtained by traditional and solvent extraction.

	Traditional extraction (4)	Solvent extraction (8)
massic volume (g/mL)	-	0.9
refraction index	1.463	1.468
acidity index	1.3	1.0
iodine index	96.1-96.7	98.1
saponification index	190.9-193.8	195.2
unsaponifiable	1.03	1.0

Fatty acids:

Glycerides (including 95% of triglycerides) constitute 99% of the oil. Unsaturated fatty acids are the major components (together oleic and linoleic acids constitute 80% of the fatty acids) and linolenic acid is only present as traces. Values are listed Table 2.

Table 2: Fatty acid composition of argan oil (%)

acid	Traditional extraction (3,4, 20)	Extraction by solvent (7, 16)
myristic	0.2	0-0.2
pentadecanoic	-	0-0.1
palmitic	11.7-14.3	13.5-13.9
palmitoleic	-	0-0.2
heptadecanoic	-	0-0.1
stearic	5-5.9	5.6
oleic	46.4-48.1	45.2-46.9
linoleic	31.5-34.9	31.6-34.6
linolenic	0-0.6	0-0.1
nonadecenoic	-	0-0.1
arachidic	-	0-0.4
gadoleic	-	0-0.5
behenic	-	0-0.1

Triglycerides:

The triglyceride fraction has been recently more specifically studied (22). Its fatty acid composition, determined by HPLC, is almost identical to this of the crude oil. The major triglycerides include three oleic acid residues (O, O, O), two linoleic and one oleic (L, L, O), one palmitic, one oleic and one linoleic (P, O, L), two oleic and one linoleic (O, O, L) or one palmitic and two oleic (P, O, O).

Stereospecific analysis determined in 1992 (22) (Table 3) by use of Brockerhoff's method (6) shows that saturated fatty acids (palmitic or stearic) generally substitute the glycerol extremities (Sn-1 and Sn-3) while linoleic acid generally esterifies the glycerol secondary alcohol (Sn-2). Oleic acid can be equally find at any of this three positions.

Table 3: Fatty acid distribution at the three positions of glycerol (%) (16, 22).

Acid	Sn-1	Sn-2	Sn-3
palmitic	54.0	9.4	36.6
stearic	19.4	1.7	78.9
oleic	33.3	39.7	27.0
linoleic	29.5	40.0	30.5

Unsaponifiable:

The unsaponifiable fraction composition has been reported in 1984 (17). It contains carotene (37%), tocopherol (8%), triterpene alcohols (20%), sterols (20%) and xantophylles (5%). Provitamine A as trans β-carotene seems absent (14).

Tocopherols:
Argan oil is about twice as rich in tocopherol as olive oil (620 mg/kg vs. 320 mg/kg). The main tocopherol is by far α-tocopherol (69%) whose eutrophic activity of well known, β and γ-tocopherol are found in roughly equal proportions (16% and 13% respectively), δ-tocopherol is a much minor component (2%). β, γ and δ-Tocopherol are anti-oxidative agents and are probably responsible for the oil good conservation.

Sterols:
Four sterol have been found in argan oil. The two major are named spinasterol and schottenol (44 and 48% respectively), the two minor (stigmasta-8,22-dien-3β-ol (22-*E*, 24-*S*) and stigmasta-7,24-28-dien-3β-ol (24-Z)) have been both isolated in 4% yield. Interestingly, no Δ-5 sterols, that are however frequently encountered in vegetable oil, have been isolated so far.

Triterpene alcohols:
Several triterpene alcohols have been isolated from the unsaponifiable fraction of argan oil. The three major have been identified as : butyrospermol (18.1%), tirucallol (27.9%), and β-amyrine (27.3), the four minor have been identified as lupeol (7.1%), 24-methylene cycloartanol (4.5%), citrostadienol (3.9%), and cycloeucalenol (less than 5%).

Preservation of argan oil:

When the water used in the case of traditional extraction is totally eliminated, the argan oil preserves quite well. It has been shown in 1994 that argan oil is less sensitive to oxidation than olive oil (12) and its stability has been attributed to the presence of tocopherols (620 mg/kg) and polyphenols such as caffeic acid and oleuropeine (13).

Nutritional, pharmacological and cosmetic value of argan oil:

Ingestion of argan oil by rats induces a change in the polyunsaturated fatty acids of the membranes similar to this observed with peanut oil (3). In addition, argan oil induces an increase of the antioxidant activity of the cell. This specific action has been attributed to the presence of vitamin E and could decrease the membrane susceptibility to peroxidation that could be at the origin of elderly processes (1).

PRESS CAKE

For the moment, and because of its high energetic value, the press cake is exclusively recycled as cattle food. The press cake is composed of glucides, proteins and saponins (11). Since this latter group of metabolites presents various and promising bioactive properties, the specific study of the saponins has been recently more particularly undertaken.

Chemical composition of the press cake:
It has been evaluated (15) that the press cake was composed of 26.3% of moisture, 3.6% of ash, 24.6% of nitrogen-containing derivatives, 18.9% of lipids, 26.6% of glucides including 17.6% of cellulose.

The aqueous-alcoholic extract:
After extraction with a mixture of water and alcohol, a sucrose-rich extract containing also 4% of triterpenoid saponins can be obtained (11).
The crude saponins were purified by reverse phase HPLC and identified using now well standardised methods (21) that generally combine a combination of chemical and spectroscopic methods. Seven saponins including five new couponds have been isolated from the aqueous-alcoholic extract and named arganine A-F (11), the last triterpenoid was Mi-saponin A already isolated from????. All these saponins are bidesmosidic and their aglycone is either protobassic acid (11) or 16-α hydroxyprotobassic acid (11), both belonging to the Δ-12 oleanane family. A few preliminary biological data have been obtained on these saponins (10); the crude mixture presents some promising molluscicide activity against *Biophalaria glabrata*, (the intermediate guest of *Shistosoma mansoni*) and also some fungicidal propetries against *Cladosporium cucumerinum* and *Polysticus versicolor*. No fungicidal activity againt *Candida albicans* or larvicidal activity againt *Aedes aegypti* were detected.

PULP

Chemical composition of the pulp:

The argan nut pulp is glucide-rich and is used, in dry or fresh form, to feed cattle in the argan grove. Its chemical composition has been determined but large differences have been observed may be reflecting the genetic variability of *Argania spinosa*.. The most recently determined chemical composition (18) of the pulp is listed table 3.

Table 3 : Chemical composition of the pulp (%)

moisture	20-50
ash	4.1
cellulose	12.9
nitrogen derivatives	5.9
lipids	6.0
glucides	18.5

The lipid fraction has been more particularly studied, it is composed of glycerides (33.3%), latex (63.4%) and an unsaponifiable fraction (3.3%) (18). This later fraction is composed of triterpenoids and sterols. The triterpenoids are erythrodiol (9), lupeol, α and β-amyrine, taraxasterol, ψ taraxasterol, betulinaldehyde and betuline (10). The sterols are very minor and are schottenol and spinasterol (10). The latex is constituted of cis and trans-polysoprene (86 and 14% respectively) (18).

LEAVES

Fresh leaves are used as "hanging forage" for sheep and goats. Leaf chemical composition has been studied by Chahboun (7). Lipids constitute 4.4% of the leaves. This lipid extract is constituted of 27% of unsaponifiable containing mainly mono and dihydroxylated triterpenes such as erythrodiol, lupeol, α and β-amyrine, taraxasterol, and ψ taraxasterol in addition, sterols such as spinasterol and scottenol have been also isolated together with tocopherol (up to 16%). Two flavonoids have also been isolated, these are quercetine and myricetine; two derivatives known to have fungicide and bactericide properties (2).

WOOD

Argan tree wood is traditionally used for fuel. Its phytochemical study has led to the identification of three novel saponins named arganine G, H, and J. In both cases, their aglycone is bayogenine, no biological data are available for these three compounds.

CONCLUSION

Argania spinosa is a tree that has played an essential function in the South-western moroccan micro-economy. By providing food for human beings and animals as well as fuel, it has played a key role for the native population of these regions for centuries. A second boost to the culture of this tree could come if one or several inductrial uses could be found and this is the reason of the current phytochemical study. Several secondary metabolites have been identified from *Argania spinosa* and some are very unique. However, their potential biological relevance in a cosmetic, pharmaceutical or phytoprotective field has not been determined yet whereas this step is necessary give a higher value to this tree that could be then easily presented to the South-western moroccan dwellers to stop the desert progression.

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Etude de la composition chimique de l'huile d'argan en fonction de son mode d'extraction

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