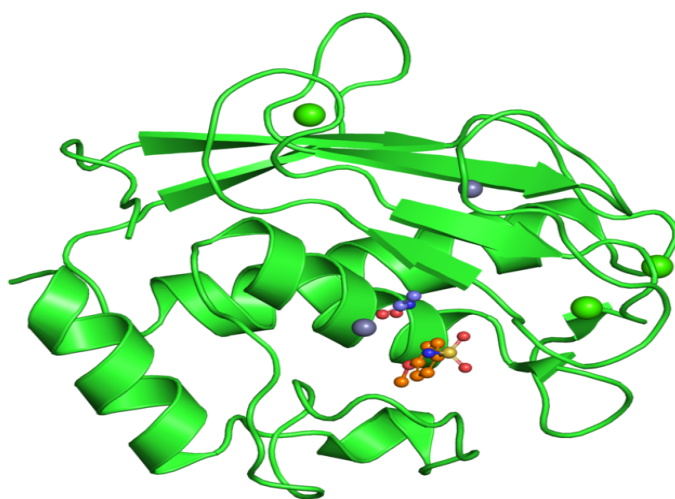
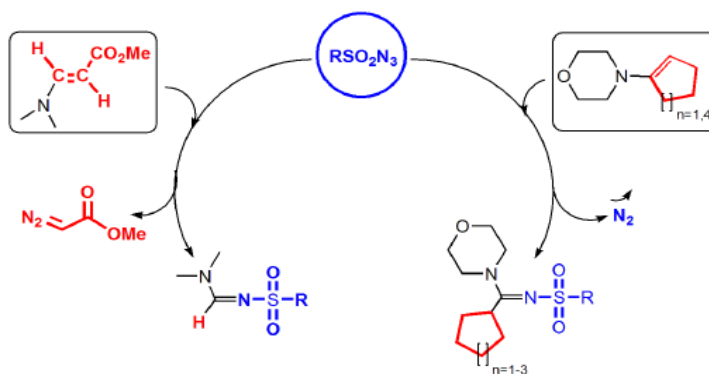


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organic chemistry research and her retirement
from Oran 1 University (Algeria)

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Special issue dedicated to Professor *Douniazad El Abed*
on the occasion of her retirement from Oran 1 University (Algeria),
in recognition of her significant contributions to organic chemistry research

Phytochemical diversity in the endemic medicinal specie *Warionia saharae*

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Abstract. Algerian Sahara constitutes an important reservoir of many plants which have been used in the local traditional ethnopharmacopeae. This review focuses on diverse secondary metabolites isolated from the endemic medicinal plant *Warionia saharae* (Asteraceae family). Sesquiterpene lactones, guaianolide-type sesquiterpene lactones, eudesmane type sesquiterpene, dimeric sesquiterpene lactones, dehydroleucodin, flavonoids as well as volatile compounds from essential oils, have shown to be the most common secondary metabolites, suggest that this endemic specie could be source of new bioactive compounds.

Key Words. Ethnopharmacopeae; Bioactive compounds; Endemic; Asteraceae; Sesquiterpene; flavonoids; Sahara

1. INTRODUCTION

Plants have formed the basis of Traditional Medicine (TM) systems since ancient civilizations (Ayurveda, Arabian, Chinese and Kempo) and continue to provide mankind with new remedies for disease treatment, such as, the oldest known medicinal systems of the world: Actually, 50% of all the drugs in clinical use in the world are derived from natural products and in which higher plants contribute to no less than 25% [1-3].

Algeria is known by its large area, diversified climate and biodiversity flora about 3139 species with 1000 medicinal species, 700 endemic, 315 rather scarce, 590 scarce species, 730 very scarce, 35 extremely scarce and 226 species are threatened with extinction. Algerian Sahara has a potential medicinal flora very rich and diversified with a very pronounced endemism especially Different regions of Algerian Sahara are characterized by a high socio-cultural mixture and traditional therapeutics is mostly based on the contributions of several ethnics (Arab, Amazight,

Cheleuh, Mozabit and Toureg). Therefore, this mixture of cultures offers a wealth of knowledge in uses of plants by the population in health care [1, 4, 5].

The flora of the Algerian Sahara includes more than 960 species to be organized following different types of habitats or landscapes. Furthermore, Ozenda noted that Asteraceae, Fabaceae and Poaceae are everywhere dominant families in the flora of Sahara. This Asteraceae family represent 13,8%, 11,2% and 7,9% of the total flora respectively in Sptentrional Sahara, Central Sahara and Meridional Sahara [6].

Among this flora, species from Asteraceae family have been widely used in the Algerian Sahara ethnopharmacopea for the treatment of various diseases as a medicinal plant such as: *Warionia saharae* [2, 5].

2. THERAPEUTIC POTENTIAL OF THE ENDEMIC SPECIE *WARIONIA SAHARAE*

Species of Asteraceae (Compositae) family have been and are still used as medicinal plants, particularly in folk medicine as stomachic, for treating diarrhea, gastrointestinal tracts, as antiinflammatory, antidiabetic, for skin diseases, insecticides and used as a food. Several studies demonstrated the antimicrobial, antiparasitic, antiviral, anti-inflammatory, antioxidant, antitumor capacities and molluscicidal activities of Asteraceae species which contained a diversity of chemical compounds especially flavonoids, flavones glycosides, phenolic derivatives, diterpenoids sesquiterpene lactones, polyacetylenic fatty acids, triterpenoid saponin and pyrrolizidine alkaloids [7]. It's well known that in Saharan traditional pharmacopeae, the knowledge about plants were transmitted only orally from generation to generation. Unfortunately, this medical heritage is still unknown, underexploited and only few studies have been conducted on phytochemistry and the bioactivities assessment of local medicinal plants [1,3]

In the Sahara, the specie *W. saharae* (Asteraceae family) is considered to have medicinal properties mainly by its essential oils. Decoction of dried leaves is used as antirrheumatic, anti-inflammatory and against gastrointestinal tracts, icter and epileptic crisis. In addition, the local women anoint themselves with the perfume of the leaves, and believe that the supernatural powers attributed to the plant make them more seductive [1, 2, 8].



Kingdom: Plantae
 Division: Angiosperm
 Class: Eudicots
 Subclass: Asterids
 Order: Asterales
 Family: Asteraceae
 Subfamily: Cichorioideae
 Tribe: Cichorieae
 Sub-tribe: Warioniinae
 Genus: Warionia
 Specie: *Warionia saharae*
 Vernacular name: *Efessas, Kabar lemaiz, Abessas, Afezded*
 N° POSL Herbarium: CA 02/07

Figure 1. The medicinal plant *Warionia saharae* - Algeria Sahara

Botanically, the genus *Warionia*, with its only one species *W. saharae*, an endemic to the northwestern edge of the Sahara desert (Figure 1), may be found in several localities on dry shale in Algeria and Morocco. The aromatic specie was reported for the first time in the region of Beni Ounif (SW Algeria) by J. P. Adrien Warion (1837-1880), a French military physician and botanist who made extensive collections while stationed in North Africa. The generic name of this plant is derived from its last name. *W. saharae* grows on slopes of the Saharian Atlas (western Algeria) and in desert areas on basic and siliceous rocks from 3 to 500 m. The flowering season has been recorded from April to June [6, 9-11].

In terms of bioactivity, the endemic specie *W. saharae* revealed very interesting pharmacological and biological activities. We summarize in table 1 the main activities observed for extracts or essential oil from the aerial part of *W. saharae*, we have already reported the detail of the study in our previous works [2]

Table 1. Biological activities of the medicinal plant *Warionia saharae*

Origin	Nature of crude from aerial parts	Activity	Ref
Algeria	Organic extracts	Anti nosocomial	[12]
Algeria	Organic extracts	Molluscicidal against <i>Lymnaea acuminata</i>	[13]
Algeria	Essential oils	Antimicrobial	[14]
Algeria	Organic extracts	Antioxidant	[14, 15]
Morocco	Essential oils	Inhibitory against <i>Alternaria sp</i>	[16]
Morocco	Essential oils, Ethanolic extract	Antibacterial, Antioxidant, Anti-inflammatory	[17, 18]
Morocco	Isolated Guaianolide type sesquiterpene lactones	Cytotoxic, anti-inflammatory	[19, 20]

3. MOLECULAR DIVERSITY OF THE ENDEMIC SPECIE *WARIONIA SAHARAE*

Natural products and their derivatives identified or isolated from plants represent more than 50% of all pharmaceuticals drugs used in the world. It is also a fact that one quarter of all medicinal prescriptions are formulations based on substances resulting from plants or plant derived synthetic analogs. The isolation and structural identification of bioactive compounds is one of the most important areas of research in phytochemistry. It is important to note that the determination of molecular structure of the bioactive compounds may enable production of synthetic synthon, incorporation of pharmacomodulation and rationalization of mechanism of action [1, 21, 22].

Chromatographic techniques such as: CC; TLC; GC; CCC; CE; HPTLC; HPLC; HPCPC; FCPC....were applied for isolation and purification of biologically active compounds from plants. Actually novel analytical methods represented by hyphenation techniques were developed with combination or coupling of two or more analytical techniques using an appropriate interface. Most common link between chromatography techniques with an online spectroscopic (GC-MS; GC-MS-

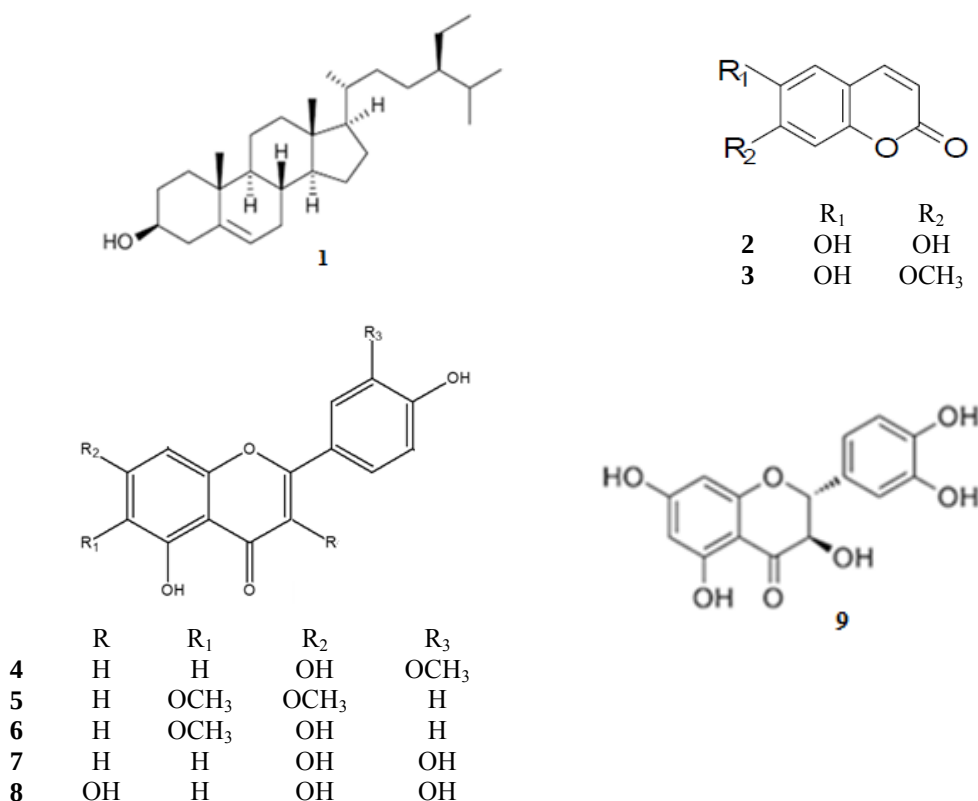
MS; LC-MS; LC-MS-MS; SPE-LC-MS; LC-PDA-MS; LC-HMRS; HPLC-NMR; LC-NMR-MS...) [23, 24].

In terms of phytochemical investigation of the endemic specie *Warionia saharae*, we noted little studies, especially focused on the analysis of components of the essential oils. Other investigations on the aerial part of this species, reported the presence of sesquiterpene lactones with guaianolide skeleton type and flavonoids derivatives. Since the first study on the chemical composition of *W. saharae* essential oils from the leaves conducted in 1985 [25], several works were done on the characterisation of the essential oils from the specie collected in different region (Algeria and Morocco) as indicated in the table 2. In addition to the study on essential oils, a Moroccan team has explored the chemical composition of the hexanic extract of leaves and found that the major components of the extract were hexadecanoic acid (17.8%), ethenyl-oxy-1-octadecane (9.5%), tridecene (7.3 %), eicosene-9 (6.7%), octadecanoic acid (6,7 %), (E)-2-decenol, (6.7%), eicosene-3 (5.1 %) and eicosane (4.5%) [26].

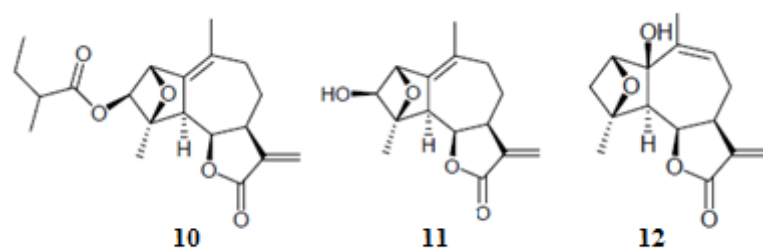
Table 2. Chemical composition of essential oils from *Warionia saharae*

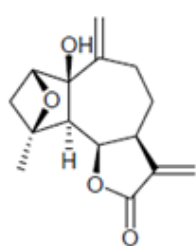
Origin	Chemical composition of EOs (major constituent)	Ref (Date)
Morocco	Eudesmol (42.25%), linalool (8.63%), nerolidol (17.26%).	[25] (1985)
Morocco	Eudesmol (52.7%), nerolidol; (17.4%), linalool (5.1%), guaiol (2.4%), terpinen-4-ol (1.4%), 1,8-cineol (1.2%).	[27] (2007)
Algeria	Cadinene (27.93%), guaiane (6.27%)	[14] (2010)
Morocco	Eudesmol (38.12%), nerolidol (25.95%)	[17] (2012)
Morocco	Eudesmol (23.74%), nerolidol (17.95%), linalool (16.79%), 1,8-cineole (6.12%)	[28] (2012)
Morocco	Eudesmol (34.9%), nerolidol (23%), linalool (15.2%), camphor (5.3%), terpineol(3.4%).	[16] (2013)
Algeria	Eudesmol (32.87%), isomenthol (6.27%), terpinyl butyrate (5.51%), trans-nerolidol (5.31%), linalool (4.99%), terpinen-4-ol (3.55%) and caryophyllane (3.36%)	[29] (2015)

In 2012, Benyache team while exploring the aqueous-EtOH extract of the aerial part of *W. saharae* collected during the flowering phase in the south-west of Algeria, they identified ten compounds including: β - sitosterol **1** as a major component, Esculetin **2**, Scopoletin **3**, Chrysoeriol **4**, Cirsimaritin **5**, Hispidulin **6**, Luteolin **7**, Quercetin **8**, and the chiral flavonoid Taxifolin **9** [30]

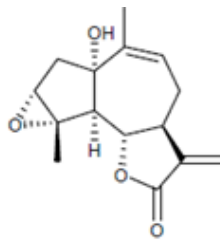


The most interesting work on the phytochemistry of *Warionia saharae* from Morocco dates back more than fifteen years ago, has been done by Sticher team [19, 20, 31]. Thus, bioactivity-guided fractionation of the MeOH-soluble part of the DCM extract led to the isolation of six new cytotoxic oxygenated guaianolides identified as: 6,7-cis-(**10**, **11** and **12**, **13**) 6,7-trans (**14** and **15**), -configured guaianolides [19]. Also, two other cytotoxic dimeric sesquiterpene lactones (**16** and **17**) were isolated [32]. In the first study, authors indicate that, all compounds showed significant cytotoxicity against the KB cancer cell line. The determined IC₅₀ values were 1.0 (**10**), 1.7 (**14**), 2.0 (**15**), 3.3 (**12**), 4.5 (**11**) and 5.5 (**13**) mg/mL, and the acylation of one of the free hydroxy groups resulted in a clear increase of activity [19]. The same team, in continuation of their exploration of methanol soluble part of the dichloromethane extract of the leaves of *W. saharae*, have isolated another compounds, new guaianolide-type sesquiterpene lactones and eudesmane type sesquiterpene respectively, **18**, **19** and **20**, in addition to sesquiterpene lactones **21**, **22**, **23**, together with the known guaiane-sesquiterpene dehydroleucodin **24** and flavone Hispidulin **6** [31].

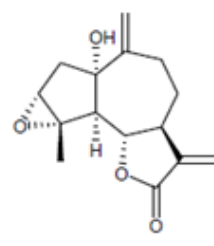




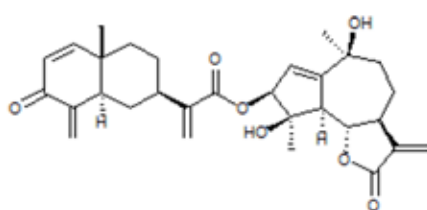
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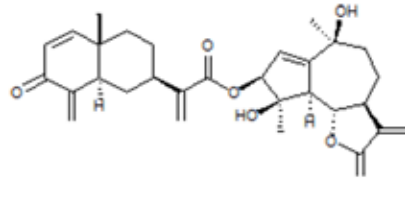
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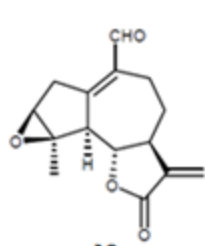
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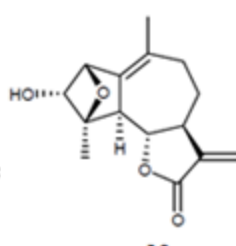
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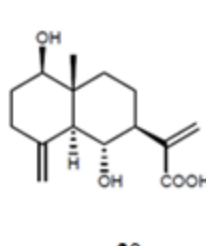
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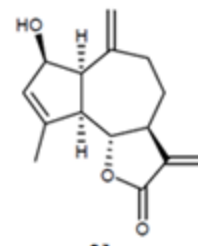
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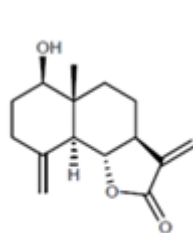
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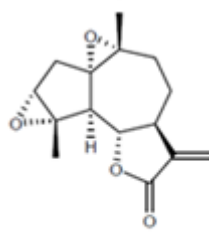
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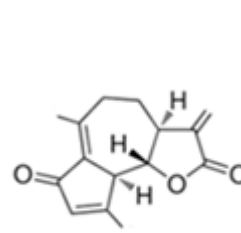
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5. CONCLUSION

. It is well known that studying species richness patterns at different scales is very important both for ecological, phytochemical and pharmacological explorations.

This review brought together phytochemical research carried out on the endemic medicinal specie: *Warionia saharae*. Based on the valuable information reported on the chemical diversity and bioactivity of compounds, it is concluded that this Saharan specie need to be better investigated. So, this endemic medicinal Saharan specie may be useful by scientists in the field of pharmacology and medicinal chemistry to develop new drug formulations to cure different kinds of illness.

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