Industrial Crops and Products 88 (2016) 91–95

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Chemical composition of medicinal plant *Atractylis serratuloides*

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ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form 17 February 2016
Accepted 20 February 2016
Available online 5 March 2016

Keywords:
Asteraceae
Atractylis serratuloides
NMR
Polyphenol
Triterpenoids

ABSTRACT

Phytochemical investigation of the roots of *Atractylis serratuloides* Sieber ex Cass. (Asteraceae) led to the isolation of nine compounds **1–9** including eight triterpenoids and one phenolic compound. Their structures were established on the basis of physical and spectroscopic analysis, including 1D and 2D NMR (^{1}H, ^{13}C, COSY, HSQC, and HMBC), mass spectrometry ESI, and by comparison with those published in the literature. Triterpenoids are typical compounds of *Atractylis* genus and could be useful as characteristic markers in chemotaxonomic research. In addition, isolated triterpenoids have previously showed many biological activities and might explain the use of *A. serratuloides* in traditional medicine.

1. Introduction

The Asteraceae (Compositae) family is one of the most important botanical families of vascular plants containing approximately 24,000 species and 1600 genera (Bremer, 1994). The species of this family are herbaceous plants, shrubs and trees spread throughout the world, growing in sunlit places, in temperate and subtropical regions. *Atractylis* genus of the family Asteraceae (Quezel and Santa, 1963), is widely known for its uses in folk medicine in Mediterranean basin. Indeed, *Atractylis* plants have been utilized as medicinal herbs against circulatory disorders, snake-bite poisoning, intestinal parasites, and for their diuretic effects. However, the species *Atractylis serratuloides* is used in North Africa against gallstone disease, circulatory disorders and to treat hepatitis (Daniele et al., 2005; El Rhaffari and Zaid, 2002). The species *A. serratuloides* Sieber ex Cass. belonging to the *Atractylis* L. genus is a perennial plant, 20–30 cm long, with carmine color flowers and yellow thorns (Ozenda, 1991; Quezel and Santa, 1963). *Atractylis* species have been the subject of few phytochemical investigations which allowed mainly the isolation and characterization of diterpenes, triterpenes and flavonoids (Calmes et al., 1994; Chaboud et al., 1988; Melek et al., 1992; Sadek et al., 1998). Recently, two new flavonoid glycosides named Atraflavoside A and Atraflavoside B and three new triterpenoid saponins have been isolated from *Atractylis flava* (Chabani et al., 2013, 2016). Triterpenoids are known as products displaying various pharmacological activities including analgesic, anti-ulcerative, antimicrobial, anti-inflammatory, antitumor, insecticidal and anti-feedant activities (James and Dubery, 2009; Ríos, 2010; Ríos et al., 2012; Shan et al., 2013). Therefore, triterpenoids are interesting for industrial medicinal chemistry in terms of discovering structures with diverse biological properties. This paper deals with the isolation and identification of nine secondary metabolites including eight triterpenoids and one phenolic compound from the roots of *A. serratuloides*. Structures of the isolated compounds **1–9** (Fig. 1) were determined using spectroscopic analysis, including 1D and 2D NMR, mass spectrometry ESI, and by comparison with literature data. It is very interesting to indicate that triterpenoids are typical compounds of *Atractylis* genus and could be useful as characteristic markers in chemotaxonomic research. Furthermore, the major isolated triterpenoids have previously exhibited many biological activities and might explain the relationship between the chemical composition of *A. serratuloides* and its reported uses in folk medicine. To the best of our knowledge, no phytochemical studies have been performed previously on *A. serratuloides*.

2. Material and methods

2.1. General

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Advance spectrometer in $CDCl_3$, and CD_3OD. 2D NMR experiments (COSY, HSQC, and HMBC) were

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http://dx.doi.org/10.1016/j.indcrop.2016.02.048
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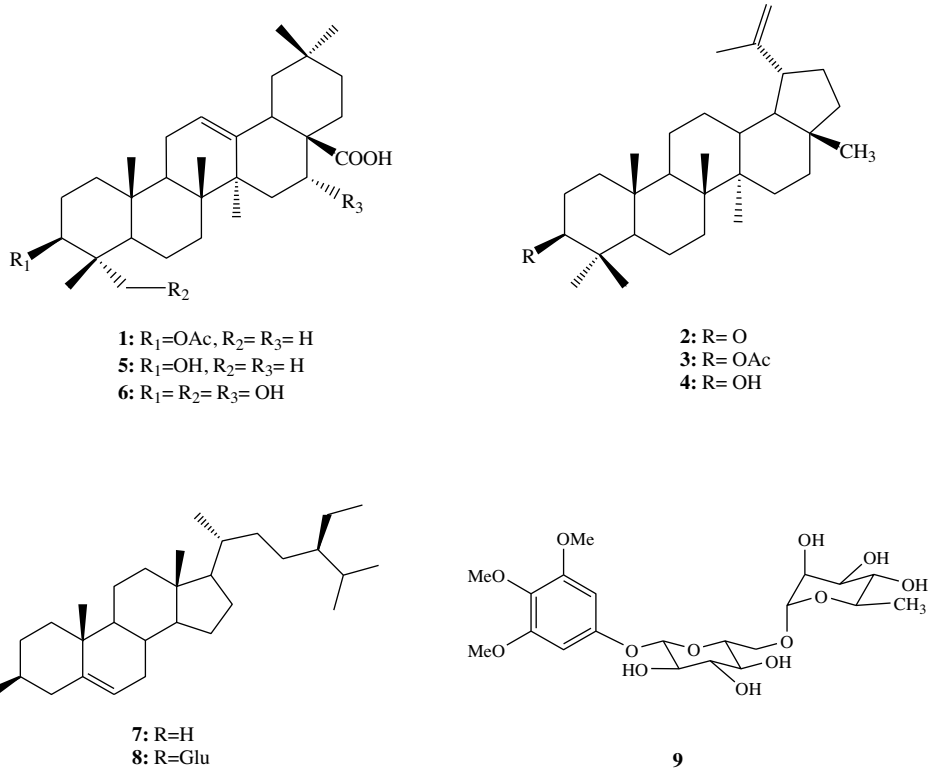

Fig. 1. Structures of the isolated compounds **1–9**.

performed using standard Bruker microprograms. Positive and negative ESI-MS mass spectra were recorded using a Bruker Esquire Ion trap. Column chromatography was carried out using Merck Kieselgel 60 (70–230 mesh), Merck Lobar Lichroprep RP-18 (40 × 63 μm), and Sephadex LH-20. Analytical TLC was carried out in silica gel plates (Merck Kieselgel 60 F_{254}) and RP-18 (Kieselgel 60 F_{254S}) plates.

2.2. Plant material

The plant *A. serratuloides* Sieber ex Cass. was collected on May 2011 in Biskra area (Algeria). The voucher specimen was identified by Prof. Bachir Oudjehih of Agronomic Institute of Batna under the number 624/LCCE.

2.3. Isolation of the compounds

The powder of the roots of plant *A. serratuloides* (1200 g) was macerated two times (12 L × 2, each 48 h) with EtOH—H_2O (70%) at room temperature. After filtration, the filtrate was concentrated under vacuum at room temperature to obtain (400 mL). The solution was submitted to liquid–liquid fractioning using solvents with increasing polarities (each solvent, 400 mL × 3). Filtration and evaporation of different solvents produced 34.5 g of petroleum ether, 8.2 g of CH_2Cl_2, 1.5 g of EtOAc and 10 g of *n*-butanol extracts.

The petroleum ether extract (8 g) was separated over a VLC chromatography (vacuum liquid chromatography) performed over silica gel (50 × 50 mm; fractions of 100 mL) using a gradient of petroleum ether-diethyl ether (100:0 to 0:100). Fractions having similar TLC profiles were pooled to give sixteen fractions. Fraction F_5 (830 mg) was purified over silica gel column eluting with petroleum ether–diethyl ether (100:0 to 50:50), to give eighteen sub-fractions. The sub-fraction $F_{5\text{-}10}$ (17.7 mg) was precipitated in ethanol to give compound **7** (2.4 mg). Preparative normal phase TLC of Sub-fraction $F_{5\text{-}12}$ (50.7 mg), developed with PE-EtOAc (85:15), afforded compound **1** (2.2 mg).

The CH_2Cl_2 extract (7 g) was subjected to vacuum liquid chromatography (VLC) performed over silica gel. The elution was performed successively using a gradient solvent system of hexane, hexane-EtOAc, EtOAc-MeOH with increasing amounts of the more polar solvent. Fractions having similar TLC profiles were pooled to afford eight fractions. The combined fractions F_3 and F_4 (605 mg) were submitted to silica gel CC eluting with hexane-EtOAc (100:0 to 50:50) to obtain eighteen sub-fractions. Compounds **2** (6 mg) and **3** (3.3 mg) were isolated from sub-fraction $F_{3\text{-}1}$ (36 mg), which was chromatographed over silica gel column, eluted with hexane–$CHCl_3$ (100:0 to 90:10). Sub-fractions $F_{3\text{-}6}$ and $F_{3\text{-}7}$ were combined and precipitated in acetone to afford compound **4** (2.6 mg). Fraction F_7 (800 mg) was precipitated in MeOH to furnish compound **8** (13.3 mg) and sub-fraction $F_{7\text{-}2}$. Compounds **5** (2.8 mg) and **6** (3.5 mg) were isolated from sub-fraction $F_{7\text{-}2}$ (550 mg), which was successively chromatographed over silica gel column, eluted with $CHCl_3$–MeOH (99:1, 97:3, 95:5: 90:10, 80:20, 70:30, 50:50) followed by Sephadex LH-20, eluting with $CHCl_3$–MeOH (50:50).

The *n*-BuOH extract (7 g) was subjected to reversed phase RP-18 vacuum liquid chromatography (VLC) using a gradient of solvents water/methanol (80:20 to 0:100) to give nine fractions. Fraction F_3 (430 mg) was separated on Sephadex LH-20 CC eluting with $CHCl_3$–MeOH (50:50), to give four sub-fractions. Sub-fraction $F_{3\text{-}3}$ (180.6 mg) was purified on silica gel CC eluting with $CHCl_3$–MeOH (100:0 to 80:20), to provide five sub-fractions. Preparative TLC on RP-18 of sub-fraction $F_{3\text{-}3\text{-}3}$ (15 mg), eluted with MeOH–water (30:70) yielded compound **9** (3.1 mg).

3. Results and discussion

This study allowed the isolation and characterization of nine compounds (**1–9**) from the roots of *A. serratuloides* (Fig. 1), which included 8 triterpenoids termed oleanolic acid acetate (**1**) (Zhu