Arabian Journal of Chemistry (2013) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Flavonoids from Algerian propolis

Narimane Segueni [a], Amar Zellagui [a,b,*], Fairouz Moussaoui [a], Mesbah Lahouel [b], Salah Rhouati [a]

[a] *Laboratoire de produits naturel d'origine végétale et de synthèse organique, Département de chimie, Université Mentouri de Constantine, Route de Ain El-Bey, 25000 Constantine, Algeria*
[b] *Laboratoire de phytopharmacologie, Département de biologie, Université de Jijel, 18000 Jijel, Algeria*

Received 5 February 2011; accepted 24 May 2011

KEYWORDS

Propolis;
Algeria;
Flavones

Abstract The investigation of propolis collected from Jijel, located in the northern-east part from Algeria afforded five flavones: pectolinarigenin (**1**), pilosin (**2**), ladanein (**3**), Chrysin (**4**) and apigenin (**5**). The structures were elucidated by spectroscopic analysis, including mass spectrometry, 1D and 2D NMR.

1. Introduction

Propolis is a natural substance collected by bees from buds and exudates of plants and trees. Bees use this product to protect their hives from enemies. Propolis is used in folk medicines in many regions of the world (Ghisalberti, 1979). It has been reported to have various biological activities such as antibacterial, antiviral, anti-inflammatory and anticancer (Ammaros et al., 1994; Almeida and Menezes, 2002; Kimoto et al., 1998; Kujumgiev et al., 1999). Recent research has highlighted that propolis prevents such illnesses such as heart disease, diabetes and cancer (Burdock, 2000).

The chemical composition of propolis depends upon the vegetation of the collection site (Bankova et al., 2001; Marcucci, 1995). For example, Propolis from Europe contains many kinds of flavonoids and phenolic esters. In contrast, the major components in Brazilian propolis were terpenoids and prenylated derivatives of *p*-coumaric acids (Marcucci and Bankova, 1999; Tazawa et al., 1999).

In previous studies we have demonstrated that Algerian propolis prevents hepatic toxicity of some cancer therapy (Lahouel et al., 2004). Hence, it is worthy of consideration to carry out a chemical study dealing with the chemical composition of Algerian propolis collected from Jijel.

2. Experimental

2.1. Material

Propolis was collected from the north-east of Algeria (Jijel) in 2006 by scraping the "bee glue" of walls, frames and entrance of the hive.

* Corresponding author at: Laboratoire de phytopharmacologie, Département de biologie, Université de Jijel, 18000 Jijel, Algeria. Tel.: +213 772465125; fax: +213 213 81 88 62.
E-mail address: zellaguia@yahoo.com (A. Zellagui).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

1878-5352 © 2011 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.arabjc.2011.05.013

3. Extraction and isolation

Propolis (500 g) was extracted with CH_2Cl_2:MeOH (1:1). The extract was concentrated to dryness, the residue was then extracted with MeOH:H_2O (70:30 v/v) and concentrated under reduced pressure. The extract (70:30 v/v) was dissolved in boiling water, stored in the cold and filtered after 24 h. The filtrate was extracted successively with EtOAc to yield (2.7 g) and *n*-BuOH to yield (8.3 g).

Two-dimensional paper chromatography using 15% AcOH and BAW (*n*-BuOH:AcOH:H_2O 4:1:5 upper phase) as solvents shows that the MeOH–CH_2Cl_2 and EtOAc extracts contain different compounds representing flavonoids and phenolic acids.

The CH_2Cl_2:MeOH (1:1) extract (10 g) was fractionated by silica gel CC eluted with *n*-hexane, followed by a gradient of *n*-hexane–CH_2Cl_2 up to 100% CH_2Cl_2 and CH_2Cl_2–MeOH up to 15% MeOH, 28 fractions were collected and analyzed by TLC. Fractions 13, 14 and 15 were concentrated and yellow precipitates were obtained. Recrystallisation of fraction 13 in $CHCl_3$ yielded a mixture of compounds **1** and **2** as yellow crystals (Fig. 1). Due to the small quantity of the mixture, we have not attempted to separate both compounds in order to avoid any loss of material. However, NMR data were discernable since they furnished different intensities of the signals for both compounds. Recrystallisation of fractions 14 and 15 in MeOH yielded compounds **3** and **4** (Fig. 1).

EtOAc extract was subjected to column chromatography on silica gel eluting with a gradient of CH_2Cl_2–MeOH with increasing polarity; 47 fractions were collected and analyzed by TLC. Fraction 5 was separated on thin layer chromatography using CH_2Cl_2:EtOAc (9:1) as an eluting system to offer compound **5** (Fig. 1). Purification was carried out using MeOH over Sephadex LH20. Compounds **1** and **2** were identified by spectroscopic techniques (UV–visible, ^{1}H NMR, ^{13}C NMR, Dept, COSY, HMQC and HMBC), while compound **3** and **4** were identified by UV–visible, ^{1}H NMR and ^{13}C NMR. Compound **5** was identified by UV–visible and ^{1}H NMR and compared with the reported data (Livinenko et al., 1969; Maisashvili et al., 2009).

3.1. Compound *1*, $C_{17}H_{14}O_6$; mp 210–211 °C

UV (λ_{max} in MeOH): gives bands at 321 and 267 nm for band I and II, addition of NaOH; 385, 329, 267 and $AlCl_3$: 338, 299; and HCl: 340, 299; and NaOAc: 331, 272; while H_3BO_3: 331, 272. Mass spectrum EI/MS *m/z* (**rel. int**): 314 $[M]^+$ (100), 299 [M-Me] (70), 271 [M-Me-CO] (76), 183 $[A_1+H]^+$ (10), 167 $[A_1-Me]^+$ (90), 133 $[B_1+H]^+$ (40).

^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ (ppm): δ 13.01 (1H, s, 5-OH), 10.67 (1H, s, 7-OH), 8 (2H, d, J = 8.9 Hz, H-2′ and H-6′), 7.08 (2H, d, J = 8.9 Hz, H-3′ and H-5′), 6.83 (1H, s, H-3), 6.59 (1H, s, H-8), 3.84 (3H, s, OMe), 3.75 (3H, s, OMe).

^{13}C NMR (75 MHz, DMSO-d_6), δ_c (ppm): 182.60 (C-4), 163.30 (C-2), 160.93 (C-4′), 15.23 (C-7), 152.15 (C-5), 151.9 (C-9), 131.29 (C-6), 128.75 (C-2′ and C-6′), 123.70 (C-1′), 11.48 (C-3′ and C-5′), 104.10 (C-10), 103.9 (C-3), 94.25 (C-8), 60.40 (6-OMe), 55.80 (4-OMe).

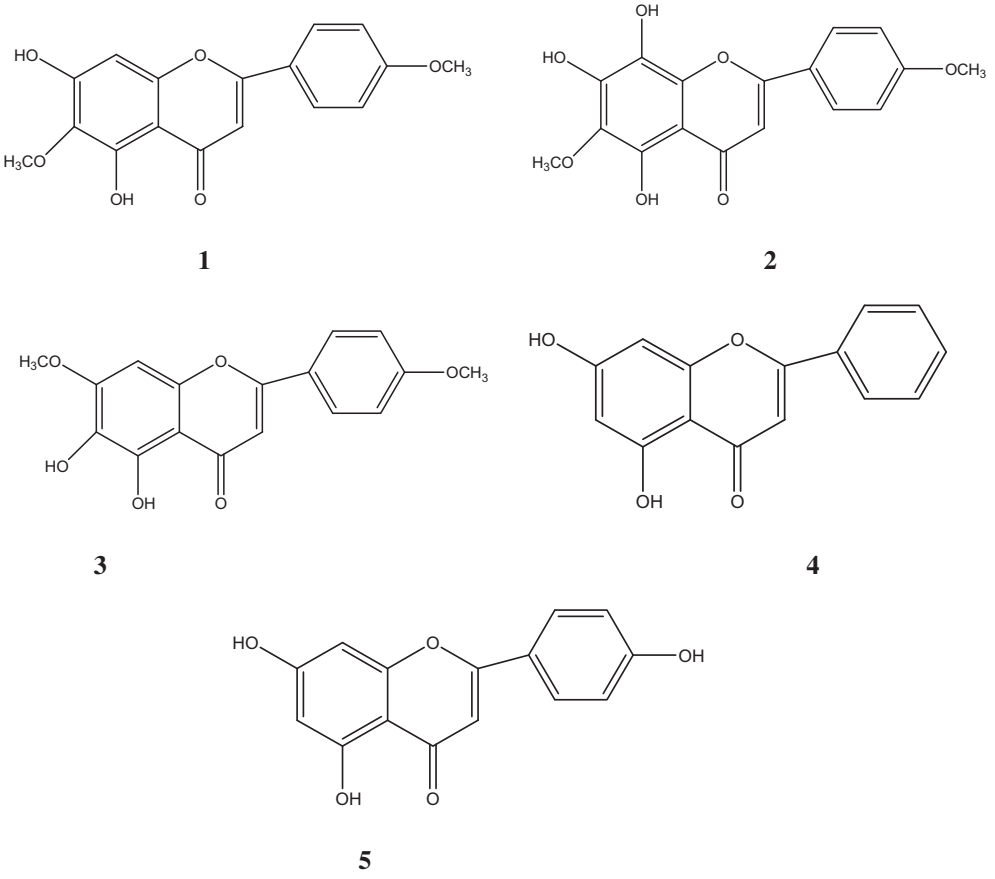

Figure 1 Chemical structures of compounds **1**–**5** from Algerian propolis.

Please cite this article in press as: Segueni, N. et al., Flavonoids from Algerian propolis. Arabian Journal of Chemistry (2013), http://dx.doi.org/10.1016/j.arabjc.2011.05.013