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Phytochemical constituents and chemosystematic significance of *Pulicaria jaubertii* E.Gamal-Eldin (Asteraceae)

Abdelsamed I. Elshamy[a,e], Tarik A. Mohamed[b], Mona M. Marzouk[c], Taha A. Hussien[d], Akemi Umeyama[e], Mohamed Elamir F. Hegazy[b,f], Thomas Efferth[f,*]

[a] Natural Compounds Chemistry Department, National Research Centre, 12622, 33 El Bohouth St., Dokki, Giza, Egypt
[b] Phytochemistry Department, National Research Centre, 12622, 33 El Bohouth St., Dokki, Giza, Egypt
[c] Phytochemistry and Plant Systematics Department, National Research Centre,33 El Bohouth St., 12622, Dokki, Giza, Egypt
[d] Pharmacognosy Department, Faculty of Pharmacy, Deraya university, Minia, Egypt
[e] Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima, 770-8514, Japan
[f] Department of Pharmaceutical Biology, Institute of Pharmacy and Biochemistry, University of Mainz, Staudinger Weg 5, 55128, Mainz, Germany

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ABSTRACT

The chemical characterization of methylene chloride/methanol (1:1) extract of the air-dried whole medicinal plant, *Pulicaria jaubertii* E. Gamal-Eldin, led to isolation and identification of two new hydroquinone compounds; 2-(2-acetoxy propyl), 5-methyl hydroquinone (**1**) and 2-(2-hydroxy propyl), 5-methyl hydroquinone-4-*O*-*β*-*D*-glucopyranoside (**2**), four known flavonols (**3**-**6**) and 7 known dihydroflavonols (**7**-**13**). The structures were established depending upon comprehensive analysis of the NMR, IR and HR/EI-MS data. Herein, compounds **6**, and **10-13** were isolated for the first time from this plant. The chemotaxonomic significance of the isolated flavonoids from *P. jaubertii* comparing with those reported from other *Pulicaria* species was also summarized.

1. Introduction

Pulicaria Gaertn. genus (Family Asteracaeae) that includes about 75 accepted species is a widely distributed around the Mediterranean from Asia to Africa and Europe (Williams et al., 2003; The Plant List, 2013). In traditional medicines; *Pulicaria jaubertii* E. Gamal-Eldin is one of *Pulicaria* species that used for treatment of inflammation, fever and as an insect repellent (Ragab and Raafat 2016). Recently; its alcoholic extract was reported to exhibit antioxidant and cytotoxic activities (Ragab and Raafat, 2016) and also reported for its antimicrobial, antifungal, antimalarial and insecticidal properties (Fawzy et al., 2013). The previous phytochemical studies on *Pulicaria* species (Family: Asteraceae) afforded sesquiterpenoids (Marco et al., 1992; Hegazy et al., 2015), diterpenoids (Das et al., 2005; Ahmad et al., 2006), triterpenes (Eshbakova and Saidkhodzhaev, 2001) and flavonoids (Christine et al., 2003; Hussein et al., 2017). Few researches have been carried out concerning the chemical constituents of *P. jaubertii* including volatile oils (Dubaie and El-Khulaidi, 1993), monoterpenes (Algabr et al., 2010) and flavonoids (Ragab & Raafat 2016; El-Ghaly et al., 2016). Herein; we reported isolation and identification of two new hydroquinones and 11 known flavonoids in addition to chemosystematic significance of this plant.

2. Results and discussion

2.1. Structure elucidation of the isolated compounds

In the present work, two new hydroquinone compounds along with 11 known flavonoids (Fig. 1) were identified from *P. jaubertii.* The structures were established depending upon comprehensive NMR, IR and HR-EI-MS experiments.

Compound **1** was obtained as white amorphous powder with a negative optical rotation $[\alpha]_D^{25}$ − 5.1 (c 0.0041, $CHCl_3$). The molecular formula was deduced to be $C_{12}H_{16}O_4$ by a molecular HR-EI-MS ion peak at *m/z* 224.1040 (calculated: 224.1049). The IR spectrum of **1** indicated that the presence of hydroxyl (3361 cm^{-1}) and carbonyl (1741 cm^{-1}) groups. The ^1H and ^{13}C NMR data of **1** (Table 1) are closed to arbutin and ecdysanrosin A isolated from *Origanum majorana* (Erenler et al., 2016) and *Ecdysanthera rosea* (Zhu et al., 2010) exhibited 2,5-disubstituted hydroquinone skeleton. Two aromatic protons at δ_H 6.67 (brs) and δ_H 6.49 (brs) in addition to three methyls proton at δ_H 1.28 d (J = 5.0), δ_H 2.18 (brs) and δ_H 2.10 (brs) were observed by ^1H NMR spectra. Moreover, the ^1H NMR showed one aliphatic oxygenated methine at δ_H 4.84 d along with one aliphatic methylene at δ_H 2.52 dd (J = 10,15), 2.96 dd (J = 5,15),. The ^{13}C NMR spectra exhibited 12

* Corresponding author.
E-mail address: efferth@uni-mainz.de (T. Efferth).

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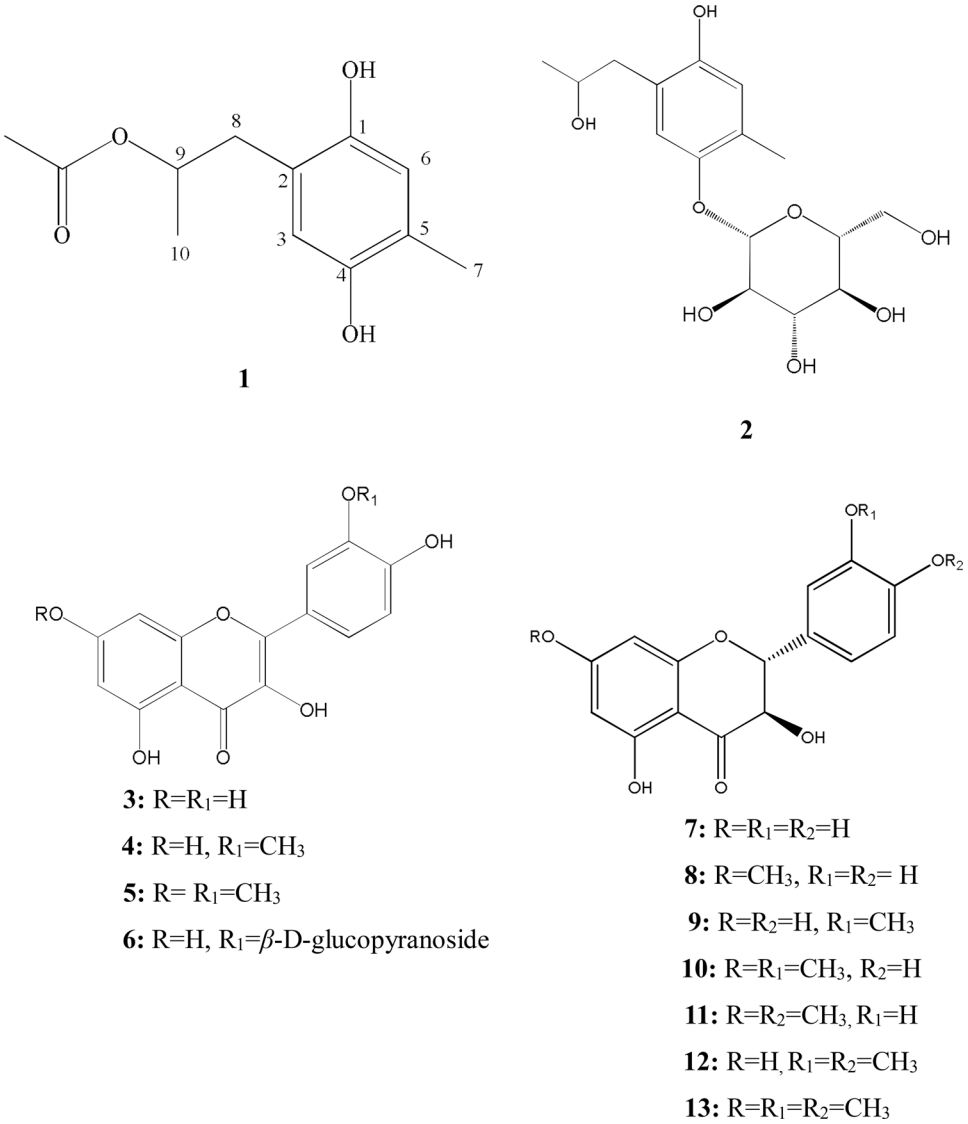

Fig. 1. Chemical structures of compounds isolated from *P. jaubertii*.

Table 1
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) data of compounds **1** and **2.**

Compound (1) in $CDCl_3$			Compound (2) in CD_3OD		
No	δ_H (*J* in Hz)	δ_C, type	No	δ_H (*J* in Hz)	δ_C, type
1	—	148.5, C	1	—	150.2, C
2	—	121.0, C	2	—	123.3, C
3	6.49 brs	117.3, CH	3	6.81 brs	119.5, CH
4	—	147.1, C	4	—	148.8, C
5	—		5	—	126.9, C
6	6.67 brs	118.6, CH	6	6.46 brs	116.9, CH
7	2.18 brs	15.5, CH_3	7	2.11 brs	14.8, CH_3
8	2.52 dd (10, 15) 2.96 dd (5, 15)	37.5, CH_2	8	2.60 m	39.7, CH_2
9	4.84 dd (5, 10)	72.1, CH	9	3.92 m	67.8, CH
10	1.28 d (5)	19.1, CH_3	10	1.05 d (5)	21.6, CH3
Ac−C=O	—	171.9, C	1‘	4.63 d (7.7)	102.7, CH
Ac-CH3	2.10 brs	21.4, CH_3	2‘	3.36 m	73.7, CH
			3‘	3.28 m	76.8, CH
			4‘	3.24 m	70.1, CH
			5‘	3.35 m	76.5, CH
			6‘	3.61 m, 3.72 m	61.2, CH_2

carbon resonances that were divided depending upon DEPT experiment to 3 methyl groups at δ_C 15.5, δ_C 19.1 and δ_C 21.4 (Me of acetate group), one aliphatic methylene at δ_C 37.5, one aliphatic oxygenated methine at δ_C 72.1, two aromatic methines at δ_C 117.3 and δ_C 118.6 in addition to four quaternary carbons at δ_C 148.5, δ_C 121.0, δ_C 147.1, and δ_C 123.8. The characteristic protons and carbons signals of 2,5-disubstituted hydroquinone skeleton were assigned and confirmed depending upon HSQC and HMBC. The HMBC correlations (Fig. 2) of H-3 at δ_H 6.49 brs and aliphatic methylene C-8 at δ_C 37.5 (J^3) along with the correlations of H-8 at 2.52 and the aromatic carbons C-2 at δ_C 121.0 (J^2), C-1 at δ_C 148.5 (J^3) and the aliphatic oxygenated methine C-9 at δ_C 72.5 (J^2) confirmed the location of hydroxylated C-1 and the presence of alphatic chain in C-2. ^{1}H, ^{1}H COSY and HMBC correlations of H-9 at δ_H 4.84 dd (J = 5,10) and the methyl proton H-10 at δ_H 1.28 d, H-8 at δ_H 2.52 and the acetoxy carbonyl group at δ_C 171.9 (J^3) confirmed the 2-acetoxy propyl moiety. The 5-methyl substitution and hydroxylated C-4 was deduced by HMBC correlations of the methyl proton H-7 at δ_H 2.18 brs and C-1 at δ_C 148.5 (J^3) and C-6 at δ_C 118.6 (J^3). From the above mentioned, compound **1** was elucidated to be 2-(2-acetoxy propyl), 5-methyl hydroquinone (Fig. 1).

The HR-EI-MS of compound **2** exhibited a molecular ion peak at *m/z* 344.1479 calculated for molecular formula of $C_{16}H_{24}O_8$ (calculated: 344.1471). The IR spectrum of **2** indicated that the presence of hydroxyl (3372 cm^{-1}) groups. The ^{1}H and ^{13}C NMR data of **2** (Table 1) was very closed to compound **1** with slightly differences by presence of glucose anomeric proton at δ_H 4.62 d, δ_C 102.7, glucose moiety carbons [δ_C 61.5 (C-6‘), δ_C 70.1 (C-4‘),δ_C 73.7 (C-2‘),δ_C 76.5 (C-5‘), andδ_C 76.8