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FLAVONOLS OF *PULICARIA ARABICA*

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Key Word Index—*Pulicaria arabica*; Inuleae; Compositae; quercetin glycosides; quercetagetin methyl ethers.

Abstract—Three quercetagetin methyl ethers, quercetin 3-glucoside, quercetin 3-glucuronide and a sulphated flavonoid were identified in leaves and flowers of *Pulicaria arabica*.

INTRODUCTION

Pulicaria is in the tribe Inuleae, family Compositae. The Compositae is rich with flavonoids [1], particularly highly methylated ethers [2–5]. *Pulicaria dysenterica* Gaertner flowers are reported to contain quercetagetin 3,7,4′-trimethyl ether as well as kaempferol 3-glucoside [6]. Furthermore, the presence of a sulphated 6-hydroxyflavone was detected in *P. burchardii* Hutch [1].

RESULTS AND DISCUSSION

In the present report the flavonoids of *Pulicaria arabica* (L.) Cass. were studied. Three quercetagetin methyl ethers were isolated and identified along with quercetin 3-glucoside, quercetin 3-glucuronide and traces of a sulphated flavonoid (which appears to be a 6-substituted flavonoid). All flavonoids were detected in the leaves as well as the flowers. Quercetin 3-glucoside and 3-glucuronide were identified through standard methods of identification and comparison with authentic samples.

The three quercetagetin methyl ethers were identified as quercetagetin 3,7-dimethyl ether, 3,5,7-trimethyl ether and 3,5,7,3′-tetramethyl ether. The two latter methyl ethers are not previously reported as natural products.

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Table 1. Chromatographic properties, UV and MS data of quercetagetin methyl ethers of *Pulicaria arabica*

	Quercetagetin-3,7-dimethyl ether	Quercetagetin-3,5,7-trimethyl ether	Quercetagetin-3,5,7,3′-tetramethyl ether
R_f values*			
BAW	0.57	0.57	0.65
50% HOAc	0.45	0.53	0.64
PhOH	0.70	0.83	0.86
TLC	0.45	0.54	0.64
Colour			
UV	d.purple	fluorescent white	fluorescent white
$+NH_3$	greenish purple	yellow	yellow
UV data			
MeOH	238, 257, 281, 348	255,† 273, 337	256,† 272, 338
NaOMe	270, 396	258, 296,† 376	257, 289, 383
$AlCl_3$	278, 302,† 346,† 433	264, 307,† 362	270, 342
$AlCl_3$–HCl	242, 267, 294, 380	254,† 274, 303,† 340	272, 338
NaOAc	258, 282, 352, 396†	256, 274,† 350, 376†	256,† 272, 353, 382†
NaOAc–H_3BO_3	266, 284, 363	256,† 349	256,† 272, 342
MS data			
M^+	346 (85)	—	374 (100)
M − 1	345 (100)	—	373 (80)
M − 43 (–Me–CO)	303 (20)	—	331 (32)
B_2^+	137 (59)	—	151 (80)
$B_2^+ - 28$ (–CO)	109 (45)	—	123 (71)

*BAW = *n*-BuOH–HOAc–H_2O (4:1:5). PhOH = PhOH–H_2O (4:1). TLC = C_6H_6–pyridine–formic acid (36:9:5) Si gel.

†Shoulder.

Quercetagetin 3,7-dimethyl ether. This compound on demethylation with pyridinium hydrochloride gave rise to quercetagetin. After 5 min from the commencement of the reaction, an intermediate was observed which showed chromatographic properties of a 7-methyl ether. (R_f values of quercetagetin and its 7-methyl ether in BAW: 30, 37; 50% HOAc: 16, 22; PhOH: 10, 20 respectively.) The mass spectrum gave a molecular ion at $m/z = 346$, consistent with a hexaoxygenated flavonoid with two *O*-methyl groups, and a comparable peak at 345 for the expected loss of a proton from the 6-hydroxyl group [7]. The B-ring ion B_2^+ (m/z 137) indicated a free 3',4'-oxygenated pattern. UV spectral data (Table 1) indicated that this compound was 3-*O*-substituted (Band I at 348 nm and bathochromic shift with $AlCl_3$–HCl only 32 nm) and possessed a 3',4'-*ortho*-dihydroxyl system (hypsochromic shift of 53 nm in Band I between $AlCl_3$ and $AlCl_3$–HCl and a 15-nm Band I bathochromic shift in NaOAc–H_3BO_3) and that it lacked a free 7-hydroxyl group (no Band II NaOAc bathchromic shift, and absence of a Band III (*ca* 325 nm) absorption in NaOMe). These data are identical for that recorded in the literature for quercetagetin 3,7-dimethyl ether [8].

Quercetagetin 3,5,7-trimethyl ether. This compound on standing overnight in Et_2O–dry $AlCl_3$ at room temperature gave rise to quercetagetin 3,7-dimethyl ether. Complete demethylation with pyridinium hydrochloride afforded quercetagetin. UV spectral data (Table 1) indicated that this compound was substituted at positions 3 and 5 (no bathochromic shift of Band I with $AlCl_3$–HCl), possessed a 3'4'-*ortho*-dihydroxyl system (hypsochromic shift of 22 nm in Band I between $AlCl_3$ and $AlCl_3$–HCl and a 12 nm Band I bathochromic shift in NaOAc–H_3BO_3) and that it lacked a free 7-hydroxyl group (no Band II NaOAc bathochromic shift, and absence of a Band III absorption in NaOMe).

Quercetagetin 3,5,7,3'-tetramethyl ether. This compound gave quercetagetin on demethylation with pyridinium hydrochloride. The mass spectrum gave a molecular ion at $m/z = 374$, consistent with a hexaoxygenated flavonoid with four *O*-methyl groups, and a comparable peak at 373 for the expected loss of a proton from the 6-hydroxyl group [7]. The B-ring ion B_2^+ (m/z 151) indicated that either 3' or 4' was substituted. UV spectral data (Table 1) indicated that this compound was substituted at positions 3 and 5 (no bathochromic shift of Band I with $AlCl_3$–HCl), is substituted in either 3' or 4' (no shifts of Band I $AlCl_3$–HCl or NaOAc–H_3BO_3), lacked a free 7-hydroxyl group (no Band II NaOAc bathochromic shift, and absence of a Band III absorption in NaOMe) and possessed a 4'-hydroxyl group (Band I NaOMe bathochromic shift of 45 nm and increase in intensity compared with Band I in MeOH).

EXPERIMENTAL

Material. Pulicaria arabica (L.) Cass. was collected 1 km west of Koum-Ushim, Fayoum. The plant was identified by Professor M. N. El-Hadidi, Department of Botany, Cairo University. Voucher specimens are deposited at the Herbarium, NRC.

Methods. Air-dried leaves and flowers were extracted with 70% EtOH. Fractionation was carried out using elution techniques on PC. Identification was carried out according to standard methods [9, 10].

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