# FLAVONOID GLYCOSIDES OF ARTEMISIA MONOSPERMA AND A. HERBA-ALBA

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Key Word Index-Artemisia monosperma; A. herba-alba; Compositae; flavone and flavonol glycosides.

Abstract—Ten flavonoid glycosides were isolated and identified from Artemisia monosperma: vicenin-2, lucenin-2, acacetin 7-glucoside, acacetin 7-rutinoside, the 3-glucosides and 3-rutinosides of quercetin and patuletin, and the 5-glucosides of quercetin and isorhamnetin. From Artemisia herba-alba eight flavonoid glycosides were isolated and identified: isovitexin, vicenin-2, schaftoside, isoschaftoside and the 3-glucosides and 3-rutinosides of quercetin and patuletin.

## INTRODUCTION

Artemisia L. belongs to the tribe Anthemideae of the Compositae. This genus has received increasing interest in its chemistry, especially with regards to sesquiterpene lactones [1] and flavonoids [2]. The flavonoids of Artemisia show a large structural variation, ranging from common flavones and flavonols to highly methylated flavonoids [2–5]. The present study is an investigation of the flavonoids of A. monosperma Del. and A. herba-alba Asso.

## **RESULTS AND DISCUSSION**

From the leaves and stems of Artemisia monosperma and A. herba-alba, 13 flavonoid glycosides based on quercetin, isorhamnetin, patuletin and acacetin were characterized. Five C-glycosides were also isolated. The distribution of the glycosides in both plants is outlined in Table 1 (see Experimental for details of the characterization).

Quercetin and isorhamnetin are common to the tribe Anthemideae, with glycosylation occurring mainly in

|                          | Presence and relative quantity* in |               | <i>R<sub>f</sub></i> s (×100)† |                  |      |      |
|--------------------------|------------------------------------|---------------|--------------------------------|------------------|------|------|
|                          | A. monosperma                      | A. herba-alba | BAW                            | H <sub>2</sub> O | HOAc | PhOH |
| Quercetin 3-glucoside    | +                                  | +             | 47                             | 12               | 45   | 49   |
| Quercetin 3-rutinoside   | ++                                 | +             | 32                             | 30               | 60   | 42   |
| Quercetin 5-glucoside    | ++                                 | _             | 20                             | 1                | 9    | 32   |
| Isorhamnetin 5-glucoside | + +                                | -             | 27                             | 2                | 12   | 72   |
| Patuletin 3-glucoside    | +                                  | +             | 40                             | 13               | 46   | 60   |
| Patuletin 3-rutinoside   | +++                                | +++           | 26                             | 36               | 62   | 54   |
| Acacetin 7-glucoside     | +                                  | -             | 35                             | 11               | 44   | 81   |
| Acacetin 7-rutinoside    | +                                  | _             | 17                             | 54               | 79   | 73   |
| Isovitexin               | _                                  | +             | 50                             | 18               | 56   | 79   |
| Vicenin-2                | +                                  | tr            | 14                             | 30               | 58   | 51   |
| Lucenin-2                | +                                  | _             | 8                              | 15               | 46   | 33   |
| Schaftoside              | -                                  | +)            | 20                             | 20               | ()+  |      |
| Isoschaftoside           | -                                  | +}            | 20                             | 28               | 02‡  | 00   |
| Methylated aglycones     | ++                                 | ++            |                                |                  |      |      |

Table 1. Flavonoid glycosides of Artemisia monosperma and A. herba-alba

\* + + + = major, + = strong, + = weak, tr = trace, - = absent.

 $\dagger$  BAW, *n*-Butanol-HOAc-H<sub>2</sub>O (4:1:5); H<sub>2</sub>O, water; HOAc, 15% acetic acid; PhOH, phenol-water (4:1).

15% acetic acid on cellulose TLC: schaftoside = 48, isoschaftoside = 35.

position 3 [2, 6]. Glycosylation in position 5 is apparent in Leucanthemum and Cotula species [2, 7]. Greger [2] pointed out that 5-glycosylation represents the major flavonol glycosides in all Leucanthemum species and the allied genera Coleostephus, Plagius and closely Leucanthemopsis. It was further pointed out [2] that this chemical feature might also provide an excellent systematic criterion for the generic delimitation of the Leucanthemum-Chrysanthemum-Tanacetum complex. Heywood and Humphries [8] indicated that Artemisia does show some transition to Tanacetum, and the presence of 5-glycosylation in A. monosperma is thus noteworthy. The presence of patuletin (quercetagetin 6-methyl ether) in both species examined is not unexpected, in view of the fact that it has been reported in several genera of the Anthemideae [2, 9].

C-Glycosides are known to occur in the Compositae [10], but not as frequently as other flavonoids. Little is reported on C-glycosides of Artemisia; thus only isovitexin, vicenin-2 and an isomer of the latter were isolated from Artemisia transiliensis [11]. In the present study vicenin-2 (6,8-di-C-glucosylapigenin) and lucenin-2 (6,8di-C-glucosylluteolin) were detected in A. monosperma, isovitexin while (6-C-glucosylapigenin), vicenin-2, schaftoside (6-C-glucosyl-8-C-arabinosylapigenin) and (6-C-arabinosyl-8-C-glucosylapigenin) isoschaftoside were detected in A. herba-alba. A number of methylated flavonoids were also detected, and their structures are presently under investigation and will be published elsewhere.

A total of 30 samples of *A. monosperma* were examined with a geographical distribution ranging from the Libyan Desert to Rafah (in the northeast of Sinai) and two samples from Saudi Arabia. All showed identical flavonoid patterns, with patuletin 3-rutinoside forming the major component. A slight variation in the concentrations of some secondary flavonoids was observed in some samples. This is most probably due to different environmental conditions.

#### **EXPERIMENTAL**

Material. Fresh material of Artemisia monosperma Del. was collected from the Cairo-Alexandria desert road, 100 km from Cairo during March. A. herba-alba was collected from Sinai, 10 km south of Nekhl, during June. Samples were authenticated by Professor Dr. L. Boulos, NRC, and voucher specimens have been deposited at the herbarium, NRC. Thirty herbarium samples of A. monosperma were examined, and their locations are as follows (CAI sheet No. in parentheses): (1) NE of Maghra Oasis, 8/11/1966, Osborn and Helmy (026161). (2) Maghra Oasis, NE of Qattara Depression, 18/11/1968, Zahran and Girgis (026231). (3) Between El-Alamein and Qattara, 25/11/1976, Osborn (026219). (4) Burg El-Arab, 5/4/1976, Täckholm and Brydolf (026135). (5) El-Amiria, 10/4/1971, Ibrahim et al. (026206) (6) 10 km S. of Alexandria on agricultural road, 8/1/1977, Zahran (026217) (7) 75 km from Alexandria on desert road to Cairo, 5/4/1976, El-Hadıdı et al. (026133). (8) 90 km, Cairo-Alexandria road, 7/3/1978, Merxmuller et al. (026206). (9) N. of Wadı El-Natroun, 11/10/1962, V. Täckholm et al. (026127). (10) Wadı El-Natroun, 2/2/1968, Romee (026201). (11) Wadı El-Natroun, 27/2/1959, Ghabbour (026125). (12) 12 km from Giza, Giza-Bahriya road, 10/4/1980, Abdel-Ghani. (13) Wadi Dowaiqa, E of Cairo, 3/12/1926, G. Täckholm (026204). (14) Wadı Anqabiya, Suez road, 16/3/1956, El-Hadidi and El-Batanony (026146). (15) Wadı Anqubiya, Suez road, 16/3/1956,

Imam (026148). (16) Wadı Katamiya, Suez road, 11/3/1960, V. Täckholm et al. (026117). (17) Cairo-Suez road, 12/1/1978, Kassas et al. (026213). (18) Cairo-Suez road, 29/6/1973, Nabil et al. (026222). (19) Near Bir Gindali, S. of Suez road, 28/10/1960, V. Täckholm et al. (026193). (20) Wadi Etheili, Cairo-Suez road, 8/1/1960, V. Täckholm (026183). (21) El-Balousa, 70 km from Suez Canal, N. Sinai, 1/5/1976, V. Täckholm (026134). (22) El-Arish, Sinai, 20/3/1928, G. Tackholm (026154). (23) El-Arish, Sinai, 12/7/1955, Diab (026237). (24) Bir Lehfin, S. of El-Arish, 21/3/1928, G. Täckholm (026153). (25) Wadi El-Arish, 30/1/1929, J. R. Shabetai (026130). (26) Bir El-Meleha, Rafah, Sinai, G. Tackholm (026140). (27) Rafah, 11/11/1964, Boulos. (28) Sand dunes S. of Khan Yunis, 14/1/1955, Boulos (026257). (29) Near Riad, Saudi Arabia, March 1962, Khodeir (026258). (30) Wadı Hanifa, near Riad, Saudi Arabıa, March 1964, El-Naggar (026265).

Methods. Samples were extracted with 70% EtOH; extracts were evapd under red. pres. followed by CC on polyamide. Fractions were further fractionated using elution techniques. Pure compounds were investigated and their structures determined according to standard methods [12, 13]. Mild acid hydrolysis was carried out with 0.1 M HCl; enzymatic hydrolysis with  $\beta$ -glucosidase (Fluka) using an acetate buffer (pH 5); and  $H_2O_2$  oxidation according to the method of ref. [14]. The C-glycosides co-chromatographed with authentic samples of isovitexin, vicenin-2, lucenin-2, schaftoside and isoschaftoside, respectively. Vicenin-2, schaftoside and isoschaftoside showed identical R<sub>t</sub>s as their authentic samples on reversed-phase HPLC with a Lichrosorb RP18 (10  $\mu$ m) column [15]. The aglycones quercetin, isorhamnetin, patuletin and acacetin were identified through co-chromatography with authentic samples as well as UV spectrophotometry. Demethylation of patuletin and acacetin with pyridinium chloride gave quercetagetin and apigenin, respectively. MS data (m/z) and relative intensities for patuletin and acacetin were: patuletin:  $332 [M]^+$  (100),  $331 [M-1]^+$  (15),  $317 [M - 15]^+$  (20), 289  $[M - 43]^+$  (83), 137  $[B_2]^+$  (25); acacetin: 284  $[M]^+$  (100), 283  $[M-1]^+$  (10), 256  $[M-28]^+$  (9), 135  $[B_2]^+ (\bar{9}).$ 

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## APORPHINE ALKALOIDS FROM PHOEBE PITTIERI

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Key Word Index—Phoebe pittieri; Lauraceae; alkaloids; 1,2,3-trimethoxy-9,10-methylenedioxynoraporphine; 1,2,9-trimethoxy-10-hydroxynoraporphine (norlirioferine); norpurpureine; reticuline.

Abstract—The wood and bark of *Phoebe pittieri* afforded 1,2,3-trimethoxy-9,10-methylenedioxynoraporphine and 1,2,9-trimethoxy-10-hydroxynoraporphine (noraporphine), which are new alkaloids, and norpurpureine and reticuline, which have not been reported from this source before.

#### INTRODUCTION

Phoebe pittieri belongs to the Lauraceae which is well known as a rich source of isoquinoline alkaloids. A short review of previous work on the genus *Phoebe* has recently appeared [1]. Extracts of the wood and bark of *P. pittieri* were shown to have some antibacterial and antifungal properties (preliminary work done at our laboratory). This plant has not been studied previously and in this communication we report two new alkaloids, 1,2,3trimethoxy-9,10-methylenedioxynoraporphine (1) and 1,2,9-trimethoxy-10-hydroxynoraporphine (2) (norlirioferine), as well as the known alkaloids norpurpureine (3) and reticuline (4), which have not been reported from this source before

## **RESULTS AND DISCUSSION**

Compound 1,  $C_{20}H_{21}NO_5$ ,  $[M]^+$  355 had a methoxy group located at C-1 because according to the literature this is the one that appears further upfield in the <sup>1</sup>H NMR spectrum [2]. The methylenedioxy group was located at positions other than 9 and 10 because it appears as a singlet while if it is located at positions 9 and 10 it is usually split into two doublets because of the asymmetry of the twisted biphenyl system [2-4]. The <sup>1</sup>H NMR spectrum shows clearly two individual protons at  $\delta 6.70$ and 6.83 for protons at positions 8 and 11, respectively, as reported in the literature [3]. The <sup>13</sup>C NMR data for model compounds [3, 5-7] also support the proposed structure 1.

Compound 3 was identified as norpurpureine on the basis of published data (UV, <sup>1</sup>H NMR) for this compound [1, 4]. Norpurpureine has been isolated previously



- 1  $R^1 = R^2 = R^3 = OMe, R^4 = R^5 = O CH_2 O$ 2  $R^1 = R^2 = R^4 = OMe, R^3 = H, R^5 = OH$ 3  $R^1 = R^2 = R^3 = R^4 = R^5 = OMe$ 
  - MeO HO NMe

