

FLAVONOIDS IN FLOWER HEADS OF THREE *Achillea* SPECIES BELONGING TO *Achillea millefolium* GROUP

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Yarrow is a widespread plant used in folk medicine for preparation of herbal teas with antiphlogistic and spasmolytic activities [1]. In continuation of our study on Bulgarian *Achillea* species, we report the flavonoid composition of the flower heads of three species, belonging to the *Achillea millefolium* group – *A. asplenifolia* Vent., *A. collina* J. Becker ex Reichenb., and *A. distans* Waldst. & Kit. ex Willd. To the best of our knowledge only the flavonoid aglycones in the leaf exudates of the described above species have been studied so far [2, 3].

Plant material was collected during the flowering stage and voucher specimens were deposited in the Herbarium of the Institute of Botany, BAS, Bulgaria: *Achillea collina* (SOM CO 989, cultivated plant in the experimental field of the Institute of Botany, BAS near Sofia, July 2004), *Achillea asplenifolia* (SOM CO 1033, Bezden (Sofia), July 2004), and *Achillea distans* (SOM CO 1031, Stara planina (Beklemeto), July 2004).

Fresh flower heads were extracted exhaustively with CHCl₃ at room temperature. The CHCl₃ extract was defatted (precipitation with MeOH) and concentrated under vacuum, and the resulting gum was chromatographed (Sephadex LH-20, MeOH) to separate the flavonoids from the dominating terpenoid constituents. A portion of 50 mg of each flavonoid fraction was further subjected to preparative TLC (CHCl₃–acetone, 30:1, 2–4 developments) to give the individual compounds as follows: *A. collina*: artemetin (**1**) (1.6 mg) [4], casticin (**2**) (1.3 mg) [5], centaureidin (**3**) (7.4 mg) [5], quercetagenin 6,7,3',4'-tetramethyl ether (**4**) (1.0 mg) [6], 6-hydroxykaempferol 3,6,7,4'-tetramethyl ether (**5**) (1.0 mg) [7], santin (**6**) (4.0 mg) [5], pectolarigenin (**7**) (1.5 mg) [8], and diosmetin (**10**) (1.5 mg) [9]; *A. asplenifolia*: **1** (6.0 mg), **2** (1.7 mg), **3** (1.4 mg), **4** (1.1 mg), **5** (1.0 mg), and apigenin (**13**) (3.0 mg) [10]; *A. distans*: **3** (2.0 mg), **6** (1.5 mg), **7** (1.5 mg), ermanin (**8**) (1.0 mg) [11], acacetin (**9**) (1.3 mg) [10], mixture of **10** and chrysoeriol (**11**) (1.5 mg) [12], and luteolin (**12**) (1.5 mg) [10]. The flavonoids were identified by comparison of their UV [13], ¹H NMR, and MS data with those reported in the literature.

The flower heads of *A. collina* afforded quercetagenin derivatives **1–4**, compounds **5–7**, and **10**, among which centaureidin (**3**) and santin (**6**) were the main components. The flavonoids **3** and **10** were isolated for the first time from the investigated species.

A. asplenifolia produced predominantly quercetagenin derivatives **1–4**, among which artemetin (**1**) was the main component. It is worth noting that flavonoids **4**, **5**, and **13** were described for the first time in the investigated species.

The flavonoid profile of *A. distans* differed from the described above species by the presence of ermanin (**8**), acacetin (**9**), chrysoeriol (**11**), and luteolin (**12**). Flavonoids **9–11** were described for the first time in the studied species.

The obtained results for the flavonoid composition of *A. asplenifolia*, *A. collina*, and *A. distans* flower heads were in accordance with those reported for the leaf exudates [2, 3] by the accumulation of 6-methoxyflavonols and 6-methoxyflavones. However, polymethoxy derivatives proved to be the common constituents of the flower heads of *A. asplenifolia* and *A. collina*. In contrast, *A. distans* flower heads exhibited a more differentiated aglycone profile by accumulation of C-6 non-substituted flavonoids. It should be noted that quercetagenin 6,7,3',4'-tetramethyl ether (**4**), acacetin (**9**), diosmetin (**10**), and chrysoeriol (**11**) are reported for the first time in species of *A. millefolium* group.

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