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SHORT REPORTS

ON THE PUNGENT PRINCIPLE OF *MATRICARIA PUBESCENS*

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Key Word Index—*Matricaria pubescens*; Compositae–Anthemideae; pungent principle; unsaturated aliphatic acid amides; ^{13}C NMR.

Abstract—The pungent principle of the aerial parts and roots of *Matricaria pubescens* has shown to be the known thienyl-hexadien-isobutylamide. The structure was confirmed by ^{13}C NMR analysis. In addition, the roots afforded small amounts of decadien-isobutylamide, and the aerial parts afforded large amounts of herniarin. The chemosystematic significance of amide accumulation within the tribe Anthemideae is briefly discussed.

The aerial parts and roots of the North African annual *Matricaria pubescens* (Desf.) Schultz Bip[†] have a somewhat pungent taste and produce a characteristic tingling sensation on the tongue and lips. This effect is well known for some unsaturated aliphatic acid amides which have been shown to occur in the Piperaceae, Aristolochiaceae, Rutaceae and Compositae. Accordingly, the methanol (aerial parts) and petrol/ether extracts (roots) of *M. pubescens*, collected in South Morocco, afforded large amounts of the thiophene-isobutylamide (**1**), which has been previously isolated from *Argyranthemum* (= *Chrysanthemum*) *frutescens* (L.) Schultz Bip. [1]. Later, compound **1** was also found in *A. gracile* Schultz Bip. [2], *A. broussonetii* (Pers.) C. J. Humphries and *A. pinnatifidum* (L.f.) Lowe [H. Greger, unpublished results], and has already attracted attention in the leaves of *A. foeniculaceum* (Willd.) Webb ex Schultz Bip. (as *Chrysanthemum anethifolium* Brouss.) because of its pungent and numbing properties [3].

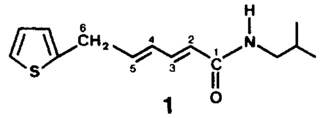
In the course of our current screening programme for new chemical characters in the tribe Anthemideae, it became apparent that the accumulation of amides with olefinic and acetylenic patterns represents a typical biogenetic trend of the genus *Achillea* [4–8]. Moreover, amides have also been shown to occur in *Leucocyclus* [5], *Anacyclus* [9–11], *Otanthus* [11], *Chamaemelum* [12] and *Cladanthus* [11]. With regard to the restricted distribution of amides within the Compositae, this common biogenetic capacity suggests a close connection with *Achillea* [13]. In contrast to *M. pubescens* and the *Argyranthemum* species, which uniformly accumulate the thiophene-amide (**1**) as the main component in the aerial parts as well as in the roots, these genera contain many different amides, mainly in the underground parts. Although to date no obvious morphological similarities are known between the annual *M. pubescens* and the shrubby species of *Argyranthemum*, this common chemical feature deserves special systematic and/or ecological attention.

Besides the dominating amide **1**, the lipid fraction of *M. pubescens* additionally contains large amounts of the coumarin herniarin (**3**) in the aerial parts and small amounts of decadien-isobutylamide (**2**) in the roots. Both compounds have been identified by comparison of ^{1}H NMR, MS, IR and UV data with authentic samples.

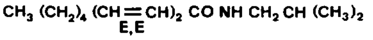
The structure of the thienyl-hexadienamide **1** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. All proton resonances in the olefinic region—not resolved in refs. [1, 3]—were unambiguously assigned by double-resonance experiments (see Experimental). The assignments of the ^{13}C NMR chemical shifts are based on the multiplicities and on literature data of comparable 2*E*,4*E*-dienamides [14] and 2-substituted thiophenes [15, 16].

EXPERIMENTAL

Matricaria pubescens was collected near Tafraoute, Antiatlas, South Morocco (H. Greger, 4 April 1983). Voucher specimens have been deposited at the Herbarium of the Institute of Botany,

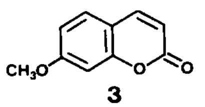


1



$$CH_3(CH_2)_4\underset{E,E}{(CH{=}CH)_2}CONHCH_2CH(CH_3)_2$$

2



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[†] On the basis of fruit characters, *M. pubescens* neither fits in with the current generic concept of *Matricaria* nor with those of the genera *Cotula* and *Chlamydophora*. A generic revision is at present underway at the Botanical Institute, University of Vienna.

University of Vienna (WU).

Air-dried, ground aerial parts (flower heads, leaves and stems) were extracted twice with MeOH for several days at room temp. and the solvent was removed by evapn at red. pres. The combined residue was partitioned between $CHCl_3$ and H_2O and the conc. $CHCl_3$ fraction was separated by TLC on 1 mm thick layers of silica gel using Et_2O–petrol (3:2) as solvent. The roots were cut into small pieces and extracted, in turn, with petrol–Et_2O (2:1) and Et_2O for several days at room temp. The combined conc. extract was separated as mentioned above.

123 g aerial parts afforded 105 mg **3** and 85 mg **1**. 4 g roots afforded traces ($<$ 1 mg) of **2** and 3 mg **1**.

(2E,4E)-6-(2-*Thienyl*)-2,4-*hexadien-isobutylamide* (**1**). Colourless crystals from Et_2O, mp 104–105°; ^1H NMR ($CDCl_3$, 250 MHz): δ7.25 (*dd*, 1H, H3, $J = 15$ and 8 Hz), 7.17 (*d*, 1H, thienyl H5, $J = 5$ Hz), 6.95 (*dd*, 1H, thienyl H4, $J = 5$ and 3.5 Hz), 6.81 (*d*, 1H, thienyl H3, $J = 3.5$ Hz), 6.20–6.25 (*m* with pseudo AB pattern, H4 and H5, olefinic *trans*-coupling *ca* 14 Hz), 5.84 (*d*, 1H, H2, $J = 15$ Hz), 5.58 (*br t*, 1H, –NH–, $W_{1/2} = 18$ Hz), 3.69 (pseudo *d*, 2H, $CH_2$6, $J = 4.5$ Hz), 3.18 (*dd*, 2H, $-NH-C\underline{H}_2-CH<$, $J = 6.5$ and 7 Hz), 1.81 (nonett, 1H, $-CH_2-C\underline{H}Me_2$, $J = 7$ Hz), 0.93 (*d*, 6H, 2Me, $J = 6.5$ Hz). Assignments in the olefinic region are based on decoupling experiments by irradiation at 7.2 (H3 + thienyl H5), 6.95 (thienyl H4), 6.81 (thienyl H3), 6.23 (H4 + H5), 5.84 (H2) and 3.69 ($CH_2$6). ^{13}C NMR ($CDCl_3$, 360 MHz): δ166.1 (C1), 141.7 (thienyl C2), 140.2 (C3), 139.1 (C5), 129.6 (C4), 127.0 (thienyl C4), 125.0 (thienyl C3), 124.0 (thienyl C5), 123.5 (C2), 47.0 ($N-CH_2-$), 33.1 (C6), 28.6 (isobutyl $-CH<$), 20.1 (2 × isobutyl Me). (Multiplicities were checked by means of DEPT.)

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