Phytochemistry, Vol. 26, No. 10, pp. 2856–2857, 1987.
Printed in Great Britain.

0031–9422/87 \$3.00 + 0.00
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SESQUITERPENE LACTONES FROM *ACHILLEA MICRANTHA*

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(*Revised received* 31 *March* 1987)

Key Word Index—*Achillea micrantha*; Compositae; sesquiterpene lactones; germacranolides; eudesmanolides.

Abstract—The aerial parts of *Achillea micrantha* afforded the eudesmanolides santamarin, reynosin, dihydrosantamarin, dihydroerynosin and the germacranolides artemorin, gallicin, dihydroparthenolide as well as a new one, dihydroparthenolide bisepoxide. The structures were elucidated by spectroscopic data.

From the large genus *Achillea* (Compositae, Anthemideae) several sesquiterpene lactones were reported [1]. We now have studied *A. micrantha*. Careful separation by thin layer- and high pressure liquid chromatography of the polar fractions of the column chromatography of the extract of the aerial parts afforded dihydroparthenolide [2], santamarin [3], dihydrosantamarin [4], dihydroreynosin [3], reynosin [5], gallicin [6], artemorin [7] and a further lactone, molecular formula $C_{15}H_{20}O_4$. The ^1H NMR data (Table 1) indicated the presence of a further 11,13-dihydro derivative of a germacranolide as in addition to a doublet at δ1.05 two methyl singlets (δ1.09 and 1.06 s) were visible. Furthermore only one low field signal (3.46 *dd*, $J = 9$ and 9.5 Hz) was detectable indicating that the two signals around δ2.4 were due to epoxide protons. Spin decoupling agreed with this assumption. All signals could be assigned, only those of H-2 were multiplets. The couplings observed led to the structure and configuration 1. Accordingly, several signals were close to those of dihydroparthenolide.

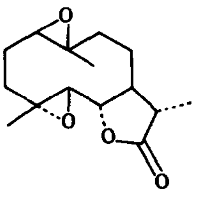

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Table 1. ^1H NMR spectral data of 1 [400 MHz, $CDCl_3$–C_6D_6 (1:1), TMS as internal standard]

Hydrogen		Hydrogen	
1	2.44 *dd*	8	1.45 *dddd*
2	1.90 *m*	8′	1.07 *dddd*
2′	1.19 *m*	9	2.08 *ddd*
3	1.95 *ddd*	9′	0.78 *ddd*
3′	1.05 *ddd*	11	1.84 *dq*
5	2.40 *d*	13	1.05 *d*
6	3.46 *dd*	14	1.06 *s*
7	1.32 *dddd*	15	1.09 *s*

J [Hz]: H-1, H-2_α = 1.5; H-1, H-2_β = 11; H-2_α, H-2_β = 15; H-3_α, H-3_β = 13; H-5, H-6 = 9; H-6, H-7 = 9.5; H-11, H-13 = 7.5; H-11, H-7 = 12; H-7_α, H-8_β = 8.5; H-8_α, H-9_β = 8; H-8_α, H-8_β = 16; H-9_α, H-9_β = 14; H-9_α, H-8_β = 12.

The lactones isolated from *A. micrantha* are somewhat unusual as most other *Achillea* species investigated so far have afforded guaianolides.

EXPERIMENTAL

The air dried aerial parts of *Achillea micrantha* M. B. (300 g) were collected in summer 1982 in Central of Elbrus mountains (Iran) (voucher deposited in the Herbarium of the Dept. of Botany, Shahid Beheshty University, Tehran) and extracted with $CHCl_3$. The resulting extracts after removal of saturated hydrocarbons by treatment with MeOH was first separated by CC (Sigel). Repeated TLC (Sigel, PF 254) of the polar fractions (ether) gave 30 mg dihydroparthenolide (further purified by TLC, Et_2O–petrol, 4:1), 35 mg santamarin, 45 mg dihydrosantamarin (further purified by TLC, $CHCl_3$–C_6H_6–Et_2O, 2:2:1), 25 mg reynosin, 37 mg dihydroreynosin, 40 mg gallicin, 32 mg 1 (Et_2O, further purified HPLC, CRP8, MeOH–H_2O, 7:3), 25 mg artemorin (further purified by TLC, Et_2O–CH_2Cl_2, 9:1). Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

1β,10β-Epoxydihydroparthenolide (1). Colourless gum, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 1775 (γ-lactone); MS *m/z* (rel. int.): 266.152 $[M]^+$ (4) ($C_{15}H_{22}O_4$), 237 $[M - CHO]^+$ (5), 219 $[237 - H_2O]^+$ (6), 57 (100); $[\alpha]_D^{24°} = -23$ ($CHCl_3$; *c* 0.1).

Acknowledgements—A. Rustaiyan thanks the Ministry of Culture and Higher Education of Iran for financial support and Prof. Dr F. Bohlmann, Technical University of Berlin for giving the opportunity to work in his Institute and for helpful discussions.

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Phytochemistry, Vol. 26, No. 10, pp. 2857–2859, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

SESQUITERPENE LACTONES FROM *JURINELLA MOSCHUS*

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(*Received* 3 *February* 1987)

Key Word Index—*Jurinella moschus*; Compositae; sesquiterpene lactones; germacranolides; elemanolide; arctigenin.

Abstract—The aerial parts of *Jurinella moschus* afforded the lignane arctigenin, four sesquiterpene lactones, the germacranolides salonitenolide and two new ones as well as a new elemanolide. The structures were elucidated by high field ^{1}H NMR spectroscopy.

The small genus *Jurinella* (Compositae, Cynareae, Carduinae), which is distributed over SW Asia, has hitherto not been a subject for chemical study. The investigation of the aerial parts of *J. moschus* (Halb.) Bobrov afforded salonitenolide (**1**) [1] and arctigenin (**5**) [2] as well as three new sesquiterpene lactones, the germacranolides **2**, named jurinelloide, and **3** as well as the elemanolide **4**, named 20-hydroxyelemajurinelloide.

The ^{1}H NMR spectra of **1** and **5** were identical with those of authentic material. As the NMR data of the latter have not been reported in the literature we have added them in the Experimental.

The ^{1}H NMR spectrum of **3** (Table 1) was close to that of jurineolide [3] with broadened partly overlapped signals. Acetylation afforded a triacetate. Spin decoupling allowed the assignment of all signals and the resulting sequences were only in agreement with the proposed structure as allylic and homoallylic couplings allowed the connection of interrupted sequences. The stereochemistry at C-6, C-7 and C-8 followed from the observed couplings and the position of the side chain acetoxy group was deduced from the signals of the ester residue.

The ^{1}H NMR spectrum of **2** (Table 1) only differed from that of **3** by the signals of the ester residue which clearly indicated the presence of an angelate. The ^{1}H NMR data of **4** (Table 1) indicated the presence of an elemanolide by the typical signals of the vinyl groups. Most signals were close to those of the corresponding 14-desoxyelemanolide which has been isolated from *Centaurea phrygia* [4]. The presence of a 14-hydroxy group followed from a pair of doublets at δ3.95 and 3.68 while a signal for a methyl singlet was missing. Again the signals could be assigned by spin decoupling and the stereochemistry followed from the couplings. Obviously **4**, which we have named 20-hydroxyelemajurinelloide, was derived from **3** by a Cope rearrangement. As in similar cases the question whether **4** was an artifact cannot be answered with certainty.

The chemistry of this *Jurinella* species is close to that of the closely related genus *Jurinea* where highly oxygenated germacranolides are common [3, 5]. However, these lactones are also present in many *Centaurea* species. Therefore the chemotaxonomic relevance is limited.

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