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REFERENCES

1. Seaman, C. F. (1982) *Bot. Rev.* **48**, 121.
2. Ogura, M., Cordell, G. A. and Farnsworth, N. R. (1978) *Phytochemistry* **17**, 957.
3. Romo de Vivar, A. and Jimenez, H. (1965) *Tetrahedron* **21**, 17141.
4. Shafizadeh, F., Bhadane, N. R., Morries, S. M., Kelsey, R. G. and Khanna, S. N. (1971) *Phytochemistry* **10**, 2745.
5. Yoshioka, H., Renold, W., Fischer, N. H., Higo, A. and Mabry, T. J. (1970) *Phytochemistry* **9**, 823.
6. Gonzales, A. G., Bermejo, J., Mansilla, H., Massanet, G. M., Cabrera, I., Amarao, J. M. and Galindo, A. (1977) *Phytochemistry* **16**, 1836.
7. Kelsey, R. G. and Shafizadeh, F. (1979) *Phytochemistry* **18**, 1591.

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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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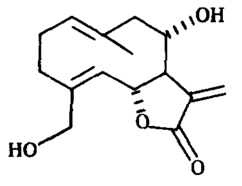

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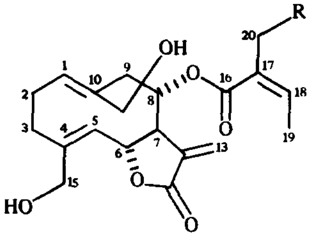

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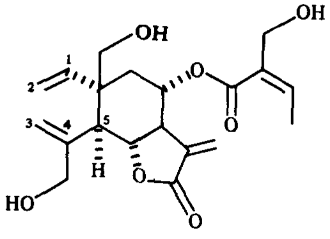
3 R = OH



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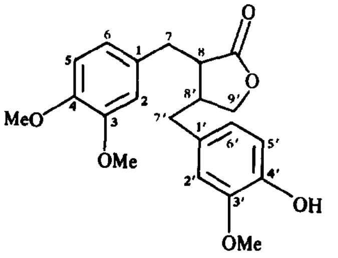

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Table 1. ^{1}H NMR spectral data of compounds 2–4 (400 MHz, $CDCl_3$, TMS as internal standard)

H	2	3	4
1	5.14 *br dd*	5.15 *dd*	5.72 *dd*
2	2.52 *m*	2.55 *m*	5.12 *d*
2′	2.35 *m*	2.34 *m*	5.00 *d*
3	2.65 *ddd*	2.65 *ddd*	5.50 *br s*
3′	2.21 *ddd*	2.21 *ddd*	5.21 *br s*
5	4.93 *d*	4.91 *br d*	2.66 *d*
6	5.18 *dd*	5.19 *dd*	4.81 *dd*
7	3.16 *dddd*	3.15 *dddd*	2.89 *dddd*
8	5.48 *ddd*	5.61 *ddd*	5.69 *ddd*
9	2.73 *dd*	2.78 *dd*	1.72 *dd*
9′	2.58 *dd*	2.60 *br d*	2.46 *dd*
13	6.33 *d*	6.21 *d*	6.15 *d*
13′	5.83 *d*	5.80 *d*	5.67 *d*
14	4.30 *br d*	4.30 *br d*	3.68 *br d*
14′	3.96 *br d*	3.91 *br d*	3.95 *br d*
15	4.39 *br d*	4.39 *br d*	4.15 *br s*
15′	4.03 *br d*	4.02 *br d*	
OCOR	6.17 *qq*	6.45 *br q*	6.46 *q*
	2.00 *dq*	2.08 *d*	2.10 *br d*
	1.93 *dq*	4.33 *br d*	4.28 *br s*
		4.23 *br d*	

J[Hz]: Compounds 2 and 3: 1,2α = 4; 1,2β = 2α,2β 2β = 2β,3α = 3α,3β = 13; 5,6 = 9; 6,7 = 11; 7,8 = 11; 7,13 = 7,13′ = 3; 8,9β = 5; 9α,9β = 13; 14,14′ = 12; 15,15′ = 14; OCOR: 3,4 = 7; 5,5 = 12; compound 4: 1,2c = 10.5; 1,2t = 17.5; 5,6 = 6,7 = 7,8 = 11; 8,9α = 7,13 = 7,13′ = 3; 8,9β = 4; 9α,9β = 13; 14,14′ = 13; OCOR: 3,4 = 7; 3,5 = 4,5 = 1.

EXPERIMENTAL

The air-dried aerial parts (120 g, collected 80 km N of Tehran, Iran, voucher deposited in the Herbarium of the Dept of Botany, Shahid Beheshty University, Tehran) were extracted at room temp. with MeOH–Et_2O–petrol, 1:1:1. After evapn the residue was treated with MeOH to remove long chain saturated compounds. The extract obtained was separated by CC (silica gel). The polar fractions (Et_2O to Et_2O–MeOH, 9:1) were separated first by TLC (silica gel, PF 254) and then by HPLC (MeOH–H_2O, 7:3, always RP 8, *ca* 100 bar, flow rate 3 ml/min.). The CC fraction obtained with Et_2O gave 18 mg 5, 20 mg 2 (R_t 6 min.) and 10 mg 1. The CC fraction obtained with Et_2O–MeOH, 9:1, were separated by TLC (Et_2O) and further by HPLC (MeOh–H_2O, 6:4) affording 12 mg 3 (R_t 5.5 min.) and 6 mg 4 (R_t 6.2 min.). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

Jurinelloide (2). Colourless oil; IR $\nu_{max}^{CHCL_3}$, cm^{-1}: 3580 (OH), 1770 (γ-lactone), 1715 ($C=CCO_2R$); CIMS *m/z* (rel. int.): 363 $[M+1]^+$ (6), 263 $[363-RCOOH]^+$ (11), 100 $[RCOOH+1]^+$ (100), 83 $[100-H_2O]^+$ (92); $[\alpha]_D + 135$ ($CHCl_3$; *c* 0.2).

20-*Hydroxyjurinelloide* (3). Colourless oil; IR $\nu_{max}^{CHCL_3}$, cm^{-1}: 3580 (OH), 1765 (-lactone), 1720 ($C=CCO_2R$); CIMS *m/z* (rel. int.): 379 $[M+1]^+$ (3), 361 $[379-H_2O]^+$ (2), 263 $[379-RCO_2H]^+$ (44), 117 $[RCO_2H+1]^+$ (100), 99 $[117-H_2O]^+$ (44); $[\alpha]_D$ +24 ($CHCl_3$; *c* 0.6). 5 mg 3 were acetylated with Ac_2O (2 hr, 70°) affording the triacetate, colourless oil, ^{1}H NMR spectrum ($CDCl_3$) the same as that of 3, except OAc: 2.14, 2.11 and 2.06 *s*, and a 0.5 ppm down field shift of H-14, H-15 and H-20.

20-*Hydroxyelemajurinelloide* (4). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3580 (OH), 1765 (-lactone), 1720 ($C=CCO_2R$); CIMS *m/z* (rel. int.): 379 $[M+1]^+$ (4), 361 $[379-H_2O]^+$ (5), 263 $[379-RCO_2H]^+$ (100), 117 $[RCO_2H+1]^+$ (65), 99 $[117-H_2O]^+$ (62); $[\alpha]_D$ +38 ($CHCl_3$; *c* 0.2).

Arctigenin (5).Colourless crystals, mp 102°; ^{1}H NMR ($CDCl_3$): 6.64 (*d*, H-2), 6.82 (*d*, H-6), 6.60 (*dd*, H-7), 2.96 and 2.91 (*dd*, H-8), 2.57 (*ddd*, H-2′), 6.46 (*d*, H-5′), 6.74 (*d*, H-6′), 6.55 (*dd*, H-7′), 2.64 and 2.53 (*dd*, H-8′), 2.49 (*ddd*, H-9′), 3.89 (*dd*, OMe), 3.86, 3.82, 3.81 (*s*, OH), 5.52 (*br s*); (J [Hz]: 2, 6 = 2′,6′ = 2; 5, 6 = 5′, 6′ = 8; $7_1, 7_2$ = 14; 7,8 = 4; 8,8′ = 7; $7_1'$, $7_2'$ = 13; 7′,8′ = 6; 8′,9′ = 7; $9_1'$,$9_2'$ = 9).

Acknowledgements—We thank Prof. Dr F. Bohlmann and Dr J. Jakupovic, Technical University of Berlin, for their help during structure elucidation.

REFERENCES

1. Suchy, M., Samek, Z., Herout, V. and Sorm, F. (1967) *Coll. Czech. Chem. Commun.* **32**, 2016.
2. Haworth, R. D. and Kelly, W. (1937) *J. Chem. Soc.* 384.
3. Suchy, M. Dolejs, L., Herout V., Sorm. F., Snatzke, G. and Himmelreich, J. (1969) *Coll. Czech. Chem. Commun.* **34**, 507.
4. Tsankova, E. and Ognyanov, I. (1985) *Planta Med.* 465.
5. Drozdz, B., Samek, Z., Holub, M. and Herout, V. (1977) *Coll. Czech. Chem. Commun.* **38**, 727.

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2-DEOXYCHAMAEDROXIDE, A NEO-CLERODANE DITERPENOID FROM *TEUCRIUM DIVARICATUM*

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(*Received* 16 *March* 1987)

Key Word Index—*Teucrium divaricatum*; Labiatae; neo-clerodane diterpenoids.

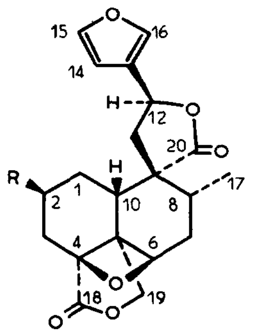
Abstract—A new neo-clerodane diterpenoid, 2-deoxychamaedroxide, has been isolated from the aerial parts of *Teucrium divaricatum* subsp. *canescens*. Also identified were the previously known diterpenoids teuflin, teucrin H_2, teuflidin, teucrins A, F and G, 6β-hydroxy-teuscordin, montanin D and dihydroteugin. The structure of 2-deoxychamaedroxide, (12*S*)-4β,6β; 15,16-diepoxy-neo-clerodane-13(16),14-diene-18,19; 20,12-diolide, was established mainly by spectroscopic means.

INTRODUCTION

In continuation of our studies on neo-clerodane diterpenoids from *Teucrium* species [1, 2], we have now investigated *T. divaricatum* Sieber *ex* Boiss. subsp. *canescens* (Celak.) Holmboe. From the aerial parts of this plant we have isolated 10 neo-clerodane diterpenoids, nine of which are the already known teuflin [3], teucrin H_2 [4], teuflidin [5], teucrins A [6, 7], F and G [8, 9], 6β-hydroxyteuscordin [10], montanin D [11] and dihydroteugin [7, 12], and the tenth is a new substance, 2-deoxychamaedroxide (1), whose structure has now been established.

RESULTS AND DISCUSSION

2-Deoxychamaedroxide (1) had a molecular formula $C_{20}H_{22}O_6$ and its IR spectrum was devoid of hydroxyl absorptions and was consistent with the presence of a furan ring (3140, 1505, 875 cm^{-1}) and γ-lactone groups (broad and strong absorption at 1770 cm^{-1}).



1 R= H

2 R= OH

3 R= OAc