chemistry at C-3, C-6 and C-7, however, could not be determined.

EXPERIMENTAL

The air-dried aerial parts (1 kg) collected from the 'Abha' region, Saudi Arabia, in Nov. 1981 were extracted continuously with petrol (bp 60–80°). The concentrates on standing in a refrigerator afforded a solid which was separated first by CC (Si gel) and further by TLC (Si gel). The fractions obtained with C_6H_6–EtOH (19:1) afforded 1 g **1**, 100 mg **2** (mp and ^{1}H NMR spectra of **1** and **2** identical with those of authentic material) and 7 mg **3**, colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3500 (O_2H), 1695, 1635 (C=CC=O); MS m/z (rel. int.): 268.167 $[M]^+$ (0.5) ($C_{15}H_{24}O_4$), 235 $[M-O_2H]^+$ (3), 234 $[M-H_2O_2]^+$ (6), 129 $[C_6H_9O_3$ (**5**)$]^+$ (13), 111 $[C_7H_{11}O$ (**6**)$]^+$ (100). To 7 mg **3** in 1 ml $CDCl_3$ 10 mg triphenylphosphine was added. After 15 min, TLC (Et_2O–petrol, 1:1) afforded 6 mg **4**, colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1695, 1675, 1630 (C=CCO); MS m/z (rel. int.): 252.173 $[M]^+$ (2.3) ($C_{15}H_{24}O_3$), 237 $[M-Me]^+$ (15), 234 $[M-H_2O]^+$ (20), 216 $[234-H_2O]^+$ (5), 193 $[M-C_3H_7O]^+$ (11), 166 $[234-Me_2CO]^+$ (24), 142 $[MeCH=C(OH)CH=CHC(Me)_2OH$, McLafferty$]^+$ (23), 113 $[HO(Me)_2CCH=CHCO]^+$ (100), 111 $[$**6**$]^+$ (98);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{\begin{array}{cccc} 589 & 578 & 546 & 436\,\text{nm} \end{array}}{\begin{array}{cccc} +49 & +53 & +62 & +130 \end{array}} \ (CHCl_3;\ c\ 0.6).$$

Acknowledgement—We thank Professor Dr. A. Migahad, King Saud University, Riyadh, for identification of the plant material.

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PSEUDOGUAIANOLIDES AND GUAIANOLIDES FROM *HELENIUM PUBERULUM**

FERDINAND BOHLMANN, ELENA TSANKOVA† and JASMIN JAKUPOVIC

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany; †Institute for Organic Chemistry and Centre of Phytochemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria

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Key Word Index—*Helenium puberulum*; Compositae; sesquiterpene lactones; pseudoguaianolides; guaianolides.

Abstract—The aerial parts of *Helenium puberulum* afforded three new sesquiterpene lactones, two pseudoguaianolides and 2α-acetoxyhelenium lactone. The structures were elucidated by ^{1}H NMR spectroscopy. The stereochemistry of helenium lactone was determined by NOE measurements.

A reinvestigation [1] of the polar fractions of the aerial parts of *Helenium puberulum* (tribe Heliantheae, subtribe Gaillardiinae) [2] afforded helenium lactone (**1**) [3], helenalin (**3**) [4], mexicanin I (**4**) [5] and three further lactones, the guaianolide **2**, the 2α-acetoxy derivative of **1** and the pseudoguaianolides, **5** and **7**. The ^{1}H NMR spectrum of **2** was close to that of **1**. As, however, the stereochemistry of helenium lactone was not established, we studied the relative stereochemistry of **1** by NOE in deuteriobenzene which showed close *cis*-relationships of H-8 with H-1 and H-7, and vice versa, and of H-6α with H-7 and H-13′. Therefore, with the small coupling $J_{7,13}$ an 8,12-*cis*-lactone was present and H-1 was α-orientated. Though the NOE of H-5 could not be observed, as the corresponding signal was an overlapped multiplet, the coupling $J_{5,6\beta}$ clearly indicated that H-5 was also α-orientated. The chemical shift of H-15 agreed with a β-methyl group at C-4. Accordingly, the stereochemistry of helenium lactone was most likely as shown by structure **1**. The ^{1}H NMR spectral data of **2** differed from those of **1**, mainly by the additional lowfield signal at δ 5.25. Spin decoupling showed that this three-fold doublet had to be assigned to H-2β, if a model was considered. In agreement with this orientation, the H-1 signal was slightly shifted downfield. An H-1β epimer of **2**, pleniradin acetate, its configuration being established by X-ray analysis [6], showed typically different ^{1}H NMR signals [6]. In particular, the chemical shifts of H-1 and H-7 differed strongly.

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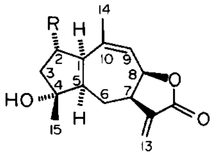
*Part 476 in the series "Naturally Occurring Terpene Derivatives". For Part 475 see Bohlmann, F., Brindöpke, G. and Vogel, W. (1982) *Justus Liebigs Ann. Chem.* 2041.

Table 1. ^1H NMR spectral data of compounds **1**, **2**, **5** and **7** (400 MHz, $CDCl_3$, TMS as int. standard)

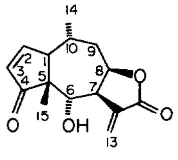
				7	
	1	**2**	**5**	(C_6D_6)	($CDCl_3$)
H-1	3.08 *m*	3.07 *m*	—	1.69 *br d*	—
H-2	*	5.25 *ddd*	4.87 *ddd*	2.79 *dd*	3.33 *dd*
H-3		2.30 *dd*	2.16 *dd*	3.24 *d*	3.47 *d*
H-3		1.86 *dd*	2.10 *ddd*		
H-4	—	—	5.35 *dd*	5.21 *s*	4.96 *s*
H-5	2.00 *m*	2.28 *ddd*	—	—	—
H-6α	1.99 *ddd*	2.00 *ddd*	3.60 *dd*	3.05 *br d*	3.55 *dd*
H-6β	1.35 *ddd*	1.33 *ddd*	—	—	—
H-7	3.08 *m*	3.10 *m*	3.50 *dddd*	2.57 *dddd*	3.38 *m*
H-8	5.24 *br d*	5.21 *br d*	4.81 *ddd*	4.00 *ddd*	4.76 *ddd*
H-9	5.27 *br s*	5.35 *br s*	1.85 *m*	*	*
H-9′			1.12 *m*		
H-10	—	—	2.02 *m*		
H-13	6.23 *d*	6.26 *d*	6.29 *d*	6.17 *d*	6.28 *d*
H-13′	5.53 *d*	5.54 *d*	5.63 *d*	5.08 *d*	5.66 *d*
H-14	1.73 *ddd*	1.79 *ddd*	0.93 *d*	0.80 *d*	1.20 *d*
H-15	1.17 *s*	1.14 *s*	0.75 *s*	0.90 *s*	1.04 *s*
OCOR	—	—	6.85 *br q*	6.94 *qq*	6.90 *qq*
			1.80 *br d*	1.45 *dq*	1.82 *dq*
			1.81 *br s*	1.40 *br s*	1.85 *dq*
OAc	—	2.07 *s*	2.02 *s*	—	—
OH	—	—	3.11 *d*	—	2.48 *d*

*Overlapped multiplets.

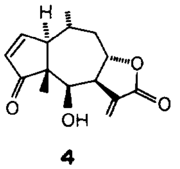
J (Hz): Compounds **1** and **2**: 5,6α = 3; 5,6β = 12; 6α,6β = 13.5; 6α,7 = 4.5; 6β,7 = 12; 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 1,14 = 8,14 = 9,14 = 1.5; (compound **2**: 1,2 = 2,3 = 2,3′ = 6.5; 3,3′ = 14); compound **5**: 1,2 = 2,3 = 9; 2,3′ = 3; 3,3′ = 15; 3,4 = 3′,4 = 9; 6,7 = 6, OH = 5; 7,8 = 7; 7,13 = 2.7; 7,13′ = 2.3; 8,9 = 9; 8,9′ = 2; 10,14 = 7; compound **7**: 1,2 = 1; 2,3 = 3; 6,7 = 6, OH = 5; 7,8 = 8,9′ = 8; 8,9 = 2; 7,13 = 2.5; 7,13′ = 2; 10,14 = 7.



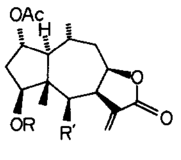
1 R = H
2 R = OAc



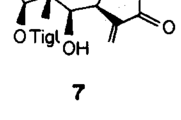
3



4



5 R = Tigl, R′ = OH
6 R = Ac, R′ = H



7

The ^1H NMR spectra of **5** and **7** (Table 1) showed that we were dealing with pseudoguaianolides. In particular, the results of spin decoupling and comparison of the ^1H NMR spectral data of **5** with those of similar helenanolides [7, 8] led to this conclusion. As the chemical shift of H-2 was identical in **5** and the related diacetate **6** [7], the relative position of the ester groups was clear, especially as **7** was also a 4-tigloyloxy derivative. The presence of an 8,12-*cis*-lactone followed from the chemical shifts of H-7 and H-8 if compared with the spectral data of the closely related 8-epimeric diacetates [7]. The β-orientation of the 6-hydroxy group was deduced from the chemical shift of H-13′; in known 6α-hydroxy derivatives a considerable downfield shift of H-13′ can be recognized. The ^1H NMR spectrum of **7** (Table 1) clearly showed that this lactone was a 2,3-epoxide. Inspection of a model showed that the coupling $J_{1,2}$ required an α-epoxide while the absence of the coupling $J_{3,4}$ agreed nicely with a 4β-tigloyloxy group as the angle H-3–H-4 was nearly 90°. The spectral data were close to those of autumnolide which, however, has a 6α-hydroxy group. The stereochemistry of the latter was established by X-ray analysis [9].

EXPERIMENTAL

The fresh aerial parts (2.5 kg) grown from seeds, voucher 81/1512, were extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (SiO_2). The polar fractions were further separated by repeated TLC (Si gel). Known compounds were identified by high field ^{1}H NMR spectroscopy. Finally, 50 mg **1**, 6 mg **2**, 80 mg **3**, 150 mg **4**, 3 mg **5** and 10 mg **7** were obtained.

2α-Acetoxyhelenium lactone (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 246.126 $[M-HOAc]^+$ (9) ($C_{15}H_{18}O_3$), 55 $[C_4H_7]^+$ (100). CD (MeCN) $\Delta_{256}+0.3$.

4-O-*Tigloyl-6-epi-picrohelenin* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1725 ($C=CCO_2R$); MS *m/z* (rel. int.): 346.178 $[M-HOAc]^+$ (6), 306 $[M-HOTigl]^+$ (1), 246 $[306-HOAc]^+$ (6), 228 $[246-H_2O]^+$ (1.5), 218 $[246-CO]^+$ (6.5), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (84). CD (MeCN) Δ_{260} negative.

4-O-*Tigloyl-6-epi-autumnolide* (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone), 1730 ($C=CCO_2R$); MS *m/z* (rel. int.): 362.173 $[M]^+$ (2) ($C_{20}H_{26}O_6$), 262 $[M-HOTigl]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (73).

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THREE DITERPENES FROM THE RED ALGA *SPHAEROCOCCUS CORONOPIFOLIUS**

FRANCESCO CAFIERI, PATRIZIA CIMINIELLO, CIRO SANTACROCE and ERNESTO FATTORUSSO†

Istituto di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, I-80134 Napoli, Italy; †Istituto di Chimica Biorganica, Università di Napoli, Via L. Rodinò 22, I-80138 Napoli, Italy

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Key Word Index—*Sphaerococcus coronopifolius*; Rodophyta; diterpenes; presphaerene; bromosphaerenes A and B.

Abstract—Three new diterpenes, presphaerene and bromosphaerenes A and B, have been isolated from the chloroform extract of the red alga *Sphaerococcus coronopifolius* and their structures determined.

Seven diterpenes have been isolated previously from the red alga *Sphaerococcus coronopifolius* [1–7]. In connection with our investigation of this alga, we have now isolated three further tricyclic diterpenes which we have named presphaerene (**1**) and bromosphaerenes A (**2**) and B (**3**).

Compounds **2** and **3** are closely related to bromosphaerol (**4**) [2], while **1** possesses the same carbocyclic skeleton as presphaerol (**5**) [4, 5]. The chloroform extract of *S. coronopifolius* was chromatographed on a Si gel column. Selected fractions were further purified by rechromatography on prep. TLC (Si gel) to obtain three diterpenes. In order of polarity these were **1** (0.01 %), **2** (0.04 %) and **3** (0.02 %). The structure of **1** was assigned by comparison of its properties [$[\alpha]_D^{20}$ −46°; EIMS 70 eV, *m/z*: 270 $[M]^+$; UV λ_{max} nm: 271 and 279, ^{1}H NMR: δ6.94 (1H, *d*, $J = 5.7$ Hz), 7.06 (1H, *d*, $J = 5.7$ Hz), 7.02 (1H, *br s*), 3.26 (1H, *dd*, $J = 7$ and 11 Hz), 2.92 (1H, *m*), 2.32 (3H, *s*), 1.30 (3H, *d*, $J = 6.8$ Hz), 0.94 and 0.88 (3H each, *d*, $J = 7$ Hz) and 0.48 (3H, *s*)] with those of a sample prepared from presphaerol by selenium treatment at 270° for 36 hr as previously described [4, 5].

Structure **2** was assigned to bromosphaerene A on the basis of its physical and spectral properties [$[\alpha]_D^{20}$ − 143°; EIMS 70 eV, *m/z*: 428, 430, 432 $[M]^+$; mp 101 – 103°; ^{1}H NMR: δ0.88 and 0.97 (3H each, *d*'s, $J = 7.5$ Hz), 1.31 and 1.66 (3H each, *s*), 3.46 (1H, *m*), 3.65 (2H, AB system, $J = 10.5$ Hz), 4.11 (1H, *dd*, $J = 3.5$ and 12 Hz), 5.57 (2H, AB system, $J = 10$ Hz)], which were identical to those of a

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