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HIGHLY OXYGENATED GUAIANOLIDES FROM *OTANTHUS MARITIMUS*

J JAKUPOVIC, R BOEKER, M GRENZ, L. PAREDES, F BOHLMANN and A SEIF EL-DIN*

Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F R G , *Pharmacognosy Department, Faculty of Pharmacy, Alexandria University, Alexandria, Egypt

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Key Word Index—*Otanthus maritimus*; *Pentzia albida*, Compositae, sesquiterpene lactones, guaianolides; seco-guaianolide, monoterpenes

Abstract—The reinvestigation of the aerial parts of *Otanthus maritimus* afforded in addition to five known guaianolides 33 new ones, a seco-guaianolide and three monoterpene diols The structures were elucidated by high field NMR spectroscopy and chemical transformations. The aerial parts of *Pentzia albida* gave a further guaianolide closely related to one of the types from *Otanthus*.

INTRODUCTION

The monotypic genus *Otanthus* is widespread in the coastal areas of the Mediterranean. *O. maritimus* (L) Hoffm et Link (Arabic name, Gaadeh) is used by the bedouins for treating asthmatic bronchitis. It has been studied chemically by different groups The roots contained acetylenes and highly unsaturated amides [1] while from the aerial parts several widespread terpenoids were reported [2, 3] Furthermore a guaianolide [4] and flavone glycoside [5] were isolated. A reinvestigation of the aerial parts afforded a highly complex mixture of oxygenated guaianolides The results are discussed in this paper

RESULTS AND DISCUSSION

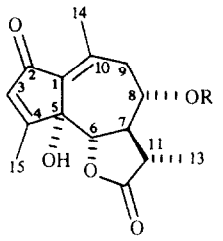
The polar fraction of an extract of the aerial parts of *O. maritimus* afforded a complex mixture of sesquiterpene lactones. Finally in addition to artabin [6] the guaianolides **1a–d**, **2a–d**, **3a–d**, **4a–d**, **5a–d**, **6a–d**, **7a–e** and **8a–d**, the seco-guaianolide **10**, the monoterpene diols **11a/b** and **12** as well as the known ionone derivatives romalea allene [7] and vomifoliol [8], undeca-2*E*,4*E*-diene-8,10-diynoic acid isobutylamide [1], lilolide and sesamin were found. A sample of the same species grown in the Botanical Garden Berlin gave tanaparthin-1α,4α-peroxide [9], **9a** and **9b–d** [10].

The ^{1}H NMR spectrum of **1a** (Table 1) showed that an angelate was present. Furthermore signals for two olefinic methyls at δ2.43 and 2 28 as well as for an olefinic proton (δ6 05) indicated the presence of a derivative of desacetyl matricarin As the H-6 signal was a doublet, a 5-hydroxy group was very likely. The down field shift of H-7 (δ3 11) and H-9α (δ3 25) required a 5α-orientation of the hydroxy group. The remaining signals could be assigned by spin decoupling The couplings of H-8 indicated the α-position of the angelate residue The ^{1}H NMR data of **1b–d** (Table 1) indicated the presence of the corresponding isobutyrate, isovalerate and methylbutyrate. The latter two esters could not be separated as in all the other cases where the same mixture of esters were present (**2c/d–9c/d**)

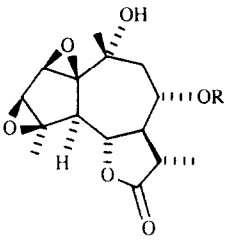
The ^{1}H NMR spectra of **2a–d** (Table 1) were close to that of artecanin [11] and those of **3a–d** to that of canin. However, the presence of 11β,13-dihydro derivatives followed from the replacement of the exomethylene signal by methyl doublets and a double quartet for H-11, its coupling indicating 11α-methyl compounds Furthermore the presence of 8α-acyloxy derivatives could be deduced from the threefold doublets around δ5.2 The nature of the ester groups followed from the typical signals One of the lactones, the methylbutyrate **3b** was isolated previously from the same species [4], but the stereochemistry has to be revised

The ^{1}H NMR spectra of **4a–4d** (Table 1) again showed that these lactones only differed in the nature of the ester groups In the spectrum of **4b** in deuteriomethanol all signals could be assigned by spin decoupling The low field pair of doublets with a 5 5 Hz coupling clearly indicated the presence of a guaianolide with a 2,3-double bond As no additional couplings were present no hydrogens were at C-1 and C-4 As followed from the molecular formula ($C_{19}H_{28}O_7$) most likely three hydroxy groups were present The similarity of the remaining signals with those of **3b** indicated an identical structure of the seven-membered ring The stereochemistry was determined by NOE difference spectroscopy Thus clear effects were observed between H-14, H-15 (5%), H-2 (5%), H-6 (10%), H-8 (6%) and H-9β (4%), between H-15, H-14 (5%), H-6 (12%) and H-3 (5%), between H-13 and H-7 (6%) as well as between H-8, H-11 (5%) and H-6 (6%). The ^{13}C NMR spectrum (Table 2) also supported the structure. The ^{1}H NMR spectrum of **4a** showed that the corresponding angelate was present while the unseparable mixture of **4c/d** was the isovalerate and the 2-methylbutyrate (Table 1) A 8-desacyloxy derivative has been isolated previously [12]. The ^{1}H NMR data are very close to those of **4a–d**

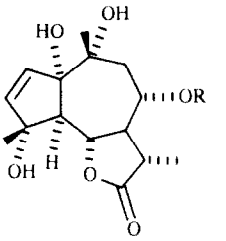
In the mass spectrum of **5b** the highest very weak ion corresponds to $C_{19}H_{27}O_7Cl$ and high resolution of *m/z* 366 showed that this fragment was due to $C_{19}H_{26}O_7$. Accordingly, **5b** most likely was a chlorohydrin. Again the ^{1}H NMR spectrum (Table 1) was in part close to that



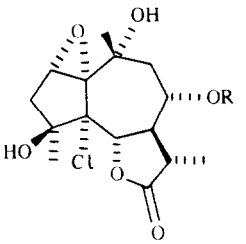
1 a-d



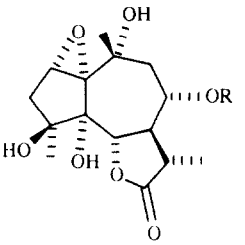
2 a-d
3 a-d (bis α-epoxide)



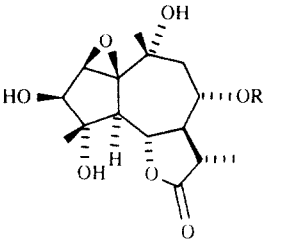
4 a-d



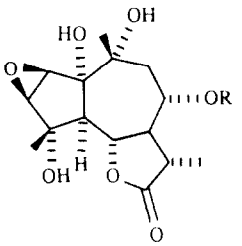
5 a-d



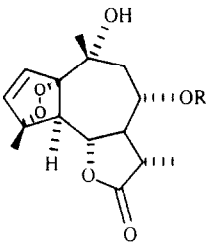
6 a-d



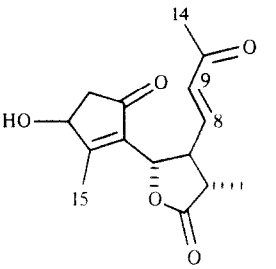
7 a-f



8 a-d



9 a-d



10

1a-9a R = Ang, **1b-9b** R = *t*Bu, **1c-9c** R = *t*Val, **1d-9d** R = MeBu, **7e** R = Prop
7f 8-desacyloxy-11,13-dehydro, **7g** R = Ang, 3-OAc, **7h** R = Ang, 10-OAc, **7i** R = Ang, 3,10-OAc

of **3b**. However, the H-3 signal was replaced by two signals at δ2 14 (*d*) and 1.69 (*dd*) and the H-2 signal was slightly shifted down field (δ3 48) The latter showed only a small coupling with H-3′ (3 Hz) This is typical for epoxy protons All data therefore agreed with the structure **5b** The stereochemistry could not be deduced from the data This, however, was possible by NOE difference spectroscopy Clear effects were observed between H-14, H-6 (10%), H-8 (6%) and H-2 (6%), between H-6, H-14 (5%) and H-8 (3%) as well as between H-13 and H-7 (10%) while no effect between H-15 and H-6 was obtained

The ^{1}H NMR spectra of **5a** and **5c/d** (Table 1) showed that again the corresponding angelate, isovalerate and methylbutyrate were present

The ^{1}H NMR spectrum of **6b** (Table 1) was very close to that of **5b** Small changes, especially a down field shift of the H-7 signal indicated that the corresponding 5α-hydroxy derivative was present This was supported by W-couplings of H-14 with H-9α and 10-OH, most likely due to a fixed conformation by a hydrogen bond between 5α- and 10α-hydroxy (OH δ2 49 *br s*). As the chemical shifts and the couplings were nearly identical in the case of **5b** and **6b** the stereochemistry surely also was the same The spectrum of **6a** and **6c/d** (Table 1) indicated that the corresponding angelate, isovalerate and methylbutyrate also were present

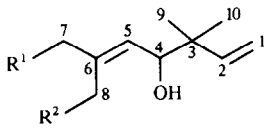
The ^{1}H NMR spectra of **7a–e** (Table 3) again showed that these lactones only differed in the nature of the ester groups In the spectrum of the angelate **7a** all signals could be assigned by spin decoupling As followed from the molecular formula ($C_{20}H_{28}O_8$) an epoxytriol angel-

Table 1 ^{1}H NMR spectral data of **1a/b**, **2a/b**, **3a/b**, **4a/b**, **5a/b** and **6a/b** (400 MHz, $CDCl_3$, δ-values*)

H	1a	1b	2a	2b†	3a	3b†	4a	4b†‡	5a	5b†	6a	6b†
2	—	—	3.60 *br s*	3 61 *br s*	3 46 *d*	3 45 *d*	5.96 *d*	5 84 *d*	3 86 *d*	3 84 *d*	3 77 *d*	3 75 *d*
3	6.05 *dq*	6 05 *dq*	3 28 *br s*	3 28 *br s*	3 29 *d*	3 28 *d*	5 91 *d*	5 81 *d*	2 15 *d* 1 73 *dd*	2 14 *d* 1 69 *dd*	2 19 *d* 1 76 *dd*	2 19 *d* 1 76 *dd*
5	—	—	2 80 *d*	2.78 *d*	2 58 *d*	2.56 *d*	2 61 *d*	2 46 *d*	—	—	—	—
6	3 98 *dd*	3 96 *dd*	4.27 *t*	4.23 *t*	4 18 *dd*	4 15 *dd*	4 39 *dd*	4 61 *dd*	4 92 *d*	4 87 *d*	4.85 *d*	4 81 *d*
7	3 11 *q*	3 10 *q*	2 83 *q*	2 82 *q*	3 08 *q*	3 03 *q*	2.58 *q*	2 51 *q*	2 33 *q*	2 31 *q*	2.57 *m*	2 58 *m*
8	4 97 *ddd*	4 81 *ddd*	5 29 *ddd*	5 17 *ddd*	5.25 *ddd*	5 11 *ddd*	5 16 *ddd*	5 04 *ddd*	5 37 *dt*	5 19 *dt*	5.29 *ddd*	5 13 *ddd*
9α	3 25 *dd*	3 18 *dd*	2 38 *m*	2 36 *m*	2 18 *dd*	2 15 *dd*	2 42 *t*	2 43 *t*	2 03 *dd*	1 95 *dd*	2 00 *t*	1 97 *t*
9β	2 25 *dd*	2 16 *dd*	2 15 *m*	2 14 *m*	2 10 *dd*	2 07 *dd*	1 92 *dd*	1 78 *dd*	2 32 *dd*	2 26 *dd*	2 16 *dd*	2 15 *dd*
11	2 53 *dq*	2 52 *dq*	2 55 *dq*	2 49 *dq*	2 52 *dq*	2 48 *dq*	2 58 *m*	2 63 *dq*	2 71 *dq*	2.64 *dq*	2 56 *m*	2 56 *m*
13	1 38 *d*	1 38 *d*	1 28 *d*	1 33 *d*	1 30 *d*	1 32 *d*	1 36 *d*	1 30 *d*	1 33 *d*	1.35 *d*	1 34 *d*	1 33 *d*
14	2 43 *s*	2 42 *s*	1 12 *s*	1 13 *s*	1 16 *s*	1 12 *s*	1 19 *s*	1 15 *s*	1.56 *s*	1 53 *s*	1 57 *s*	1 54 *s*
15	2 28 *d*	2 28 *d*	1 53 *s*	1 52 *s*	1 54 *s*	1 52 *s*	1 44 *s*	1 37 *s*	1.58 *s*		1 60 *s*	1 59 *s*

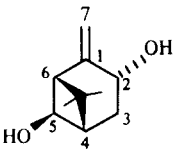
*OAng 6 15–6 21 *qq*, 2 04–1 99 *dq*, 1 92–1 89 *dq*, OMeBu· 2 43–2 49 *tq*, 0 94–0 91 *t*, 1 21–1.18 *d*, OiVal 2 18–2 22 *d*, 1 00–0 97 *d*, OiBu. 2 58–2 55 *qq*, 1 20 *d*, OProp 2 40 ABM_3, 1 20 *t*, †Isovalerates and methylbutyrates nearly identical signals, ‡D_3COD

J[Hz] Compounds **1a–d** 3,15 = 1 5, 6,7 = 7,8 = 7,11 = 8,9 = 11, 8,9′ = 2, 11,13 = 7, 9,9′ = 15, compounds **2a–d** 5,6 = 6,7 = 7,8 = 10, 7,11 = 12, 8,9 = 8,9′ = 7, 11,13 = 7, compounds **3a–d** 2,3 = 1, 5,6 = 11, 6,7 = 10, 7,8 = 10, 7,11 = 11, 8,9 = 4, 8,9′ = 5, 9,9′ = 15, compounds **4a–d** 2,3 = 5 5, 5,6 = 11, 6,7 = 7,8 = 7,11 ~ 10; 8,9 = 9,9′ = 11; 8,9′ = 4; 11,13 = 7, compounds **5a–d** and **6a–d** 2,3′ = 3; 3,3′ = 16 5, 6,7 = 10, 7,8 = 7,11 = 8,9′ = 11, 8,9 = 3 5, 9,9′ = 13, 11,13 = 7

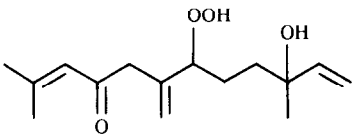


11a R^1 = H R^2 = OH

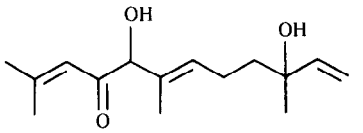
11b R^1 = OH R^2 = H



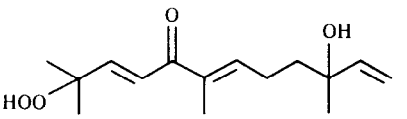
12



13a



13b



13c

Table 2 ^{13}C NMR spectral data of **4b**, **7a** and **7f** (100 6 MHz, $CDCl_3$, δ-values*)

C	4b†	7a‡	7f
1	90 2 *s*	72 9 *s*	73 3 *s*
2	135 2 *d*	64 2 *d*	64 4 *d*
3	140 7 *d*	64 4 *d*	64 7 *d*
4	83 5 *s*	83 1 *s*	72 2 *s*
5	52 8 *d*	57 3 *d*	57 9 *d*
6	75.0 *d*	76 5 *d*	79 9 *d*
7	43 9 *d*	41 5 *d*	45 1 *d*
8	66 1 *d*	72 2 *d*	23 6 *t*
9	41 2 *t*	43 2 *t*	35 1 *t*
10	79 3 *s*	71.5 *s*	83 4 *s*
11	50 6 *d*	51 6 *d*	139 3 *s*
12	177.7 *s*	177 2 *s*	169 4 *s*
13	16 5 *q*	15 9 *q*	119.9 *t*
14	24 4 *q*	22 2 *q*	22 1 *q*
15	23 3 *q*	26 9 *q*	26 5 *q*
OCOR	180 6 *s*	166 8 *s*	—
	19 6 *q*	126 9 *s*	
	19 1 *q*	140 3 *d*	
	35 4 *d*	15 1 *q*	
		20.6 *q*	

*Some signals may be interchangeable
†D_3COD
‡Singlets assigned by selective INEPT

ate was most likely as the ^{1}H NMR data indicated again the presence of a guaianolide with no double bonds. The signals of H-5–H-9, H-11, H-13 and H-14 were again close to those of **2a** As the couplings of H-8 differed a changed conformation was indicated. All data agreed with the presence of a triol formed by hydrolysis of **2a**. The relative position of the hydroxy groups and the configurations had to be established Acetylation afforded the monoacetates **7g** and **7h** and the diacetate **7i**. The ^{1}H NMR data of these derivatives (Table 3) indicated that again the conformations are partly changed. Inspection of models led to the conclusions that all data would agree with the triol **7a** where hydrogen bond between 10-OH and 8-OR was present. Accordingly, in the acetate **7h** the hydrogen bond was missing. This assumption required in part the proposed configurations.

Table 3 ^{1}H NMR spectral data of **7a–i**, **8a–d**, **9a** and **10** (400 MHz, $CDCl_3$, δ-values*)

H	7a	7b†	7e	7f	7g	7h	7i	8a	8b†	9a	10
2	3 68 *s*	3 68 *s*	3 68 *s*	3 71 *s*	3 65 *s*	3 78 *br s*	3 67 *s*	3 33 *d*	3 32 *d*	6 32 *d*	2 82 *dd* 2 34 *dd*
3	4 06 *s*	4 06 *s*	4 07 *s*	4 08 *s*	5 03 *s*	4 07 *s*	4 92 *s*	3 31 *d*	3 31 *d*	6 25 *d*	4 72 *br d*
5	2 66 *d*	2 65 *d*	2 66 *d*	2 64 *d*	3 52 *d*	2 70 *d*	3 24 *d*	2 67 *d*	2 67 *d*	2 68 *d*	—
6	4 32 *dd*	4 30 *dd*	4 30 *dd*	4 35 *dd*	4 38 *dd*	4 34 *dd*	4 28 *dd*	4 49 *dd*	4 44 *dd*	3 76 *t*	4 98 *d*
7	3 12 *q*	3 06 *q*	3 07 *q*	3 43 *m*	2 59 *q*	2 83 *q*	2 91 *q*	2 81 *q*	2 80 *q*	2 95 *q*	3 74 *q*
8	5 26 *ddd*	5 16 *ddd*	5 19 *ddd*	2 33 *m* 1 61 *m*	5 24 *ddd*	5 23 *br dd*	5 22 *ddd*	5 42 *ddd*	5 24 *ddd*	5 14 *ddd*	6 61 *dd*
9	2 18 *dd*	2 15 *dd*	2 18 *dd*	2 05 *ddd*	2 17 *dd*	2 93 *dd*	2 98 *dd*	2 00 *m*	2 05 *m*	2 18 *dd*	6 11 *d*
9′	2 13 *dd*	2 05 *dd*	2 11 *dd*	1 86 *ddd*	2 06 *dd*	2 15 *dd*	2 16 *dd*			2 04 *dd*	
11	2 46 *dq*	2 44 *dq*	2 44 *dq*		2 54 *dq*	2 43 *dq*	2 44 *dq*	2 43 *dq*	2 43 *dq*	2 34 *dq*	2 63 *dq*
13	1 27 *d*	1 30 *d*	1 30 *d*	6 21 *d* 5 50 *d*	1 29 *d*	1 30 *d*	1 30 *d*	1 34 *d*	1 33 *d*	1 24 *d*	1 31 *d*
14	1 25 *s*	1 25 *s*	1 26 *s*	1 28 *s*	1 41 *s*	1 57 *s*	1 50 *s*	1 51 *s*	1 51 *s*	1 36 *s*	2 27 *s*
15	1 54 *s*	1 55 *s*	1 55 *s*	1 58 *s*	1 63 *s*	1 50 *s*	1 87 *s*	1 67 *s*	1 68 *s*	1 68 *s*	2 20 *br s*

*OCORs Table 1

†Isovalerates and methylbutyrates nearly identical signals

J[Hz] Compounds **7a–7i** 5,6 = 6,7 = 7,8 = 7,11 = 11, 8,9 = 5, 8,9′ = 3 5, 9,9′ = 16, 11,13 = 7 (compounds **7g–7i** 8,9 ~ 0 5, 8,9′ = 6 5, compound **7f** 7,13′ = 3 5, 7,13′ = 3, 8,9 = 8′,9′ = 6 5, 8′,9 = 3 5, 8,9′ = 9 5, 9 9′ = 14), compounds **8a–d** 2,3 = 3 5, 5,6 = 6,7 = 7,8 = = 7,11 ~ 11, 8,9 = 8,9′ = 11,13 = 7, compound **9a** 2,3 = 5 5, 5,6 = 6,7 = 7,8 = 7 11 ~ 11, 8 9 = 7, 8,9′ = 2 5, 9,9′ = 16 5, 11,13 = 7, compound **10** 2 2′ = 18, 2,3 = 6 2′,3 = 2 5, 6,7 = 9 5, 7 8 = 8 5, 7,11 = 11 5, 8 9 = 16 5 11,13 = 7

The whole stereochemistry was established by NOE difference spectroscopy in a chloroform–benzene mixture where also the hydroxy signals were visible Clear effects were obtained between H-3, 2-OH (10%), H-5 (4%) and H-15 (4%), between H-2, H-3 (15%) and H-14 (8%), between 4-OH, H-3 (10%) and H-5 (15%), between H-5 and H-7 (10%), between H-13 and H-7 (8%), between H-15 and H-6 (8%), between H-14 H-6 (4%), H-2 (10%) and H-9β (8%) as well as between H-8, H-6 (8%) and H-11 (12%) Also the ^{13}C NMR spectrum (Table 2) supported the structure Selective irradiation of H-14 and H-15 respectively allowed the assignment of the signals for C-10 and C-4 The chemical shift of the latter (δ83 1) excluded the presence of a 3,4-epoxide The ^{1}H NMR spectra of **7b–e** (Table 3) clearly indicated the presence of the corresponding isobutyrate, isovalerate, methylbutyrate and propionate The configuration of **7a** agrees with the expected one if **2a** was the precursor

A closely related guaianolide (**7f**) was isolated from *Pentzia albida* (DC) Huzel var *annua* (DC) Merx et Eberle together with artabin, tanaparthin-1α,4α-peroxide [7], nerolidol and the derivatives **13a–c** [12] The ^{1}H NMR spectrum of **7f** (Table 3) differed from that of **7a** by the absence of ester signals and the presence of exomethylene proton signals The low field signal for H-8 was replaced by a pair of multiplets at 2 33 and 1 61 and the H-9 signals were threefold doublets Thus **7f** was the 11,13-dehydro-8-deacyloxy derivative of **7a** Identical stereochemistry was established by the observed NOE's which were analogous with those of **7a** Also the ^{13}C NMR spectrum (Table 2) agreed with the structure

The ^{1}H NMR spectrum of **8b** (Table 3) was in part close to that of **4b** However, the signals of the olefinic protons were replaced by a AB quartet at 3 31, obviously due to epoxide protons Accordingly, the molecular formula was $C_{19}H_{28}O_8$ differing from that of **4b** by one oxygen As the chemical shift of H-5 was nearly the same as in the case of **4b** the presence of a 2,3β-epoxide was very likely The ^{1}H NMR spectra of **8a** and **8c/d** (Table 3) indicated that again also the corresponding angelate, isovalerate and methylbutyrate were present

The structure of **9a** could be easily deduced from its ^{1}H NMR spectrum which was very close to those of **9b–d** [10] The presence of the corresponding angelate followed from the typical signals The endoperoxides **9a–9d** surely are the precursors of the bis-epoxides **3a–3d** These lactones were not isolated from the material from the Botanical Garden Berlin However, only a small sample was investigated

The molecular formula of **10** ($C_{15}H_{18}O_5$) and the ^{1}H NMR spectrum (Table 3) indicated the presence of a seco-guaianolide The relative position of the oxygen functions followed from the results of spin decoupling and the chemical shifts Most likely a guaianolide with oxygen functions at C-3, C-4 and C-8 and a 1(10)double bond is a precursor of **10** which may be formed by oxidative degradation followed by elimination

The structures of **11a** and **11b** followed from the ^{1}H NMR spectra (Table 4) which were close to that of artemisia alcohol The relative position of the second hydroxy group followed from the shift differences of H-5, H-7 and H-8 The ^{1}H NMR spectrum of **12** (Table 4) was close to that of the epimeric diol [13] The changed configuration at C-5 followed from the absence of vicinal couplings

The isolation of a large variety of highly oxygenated guaianolides from *Otanthus maritimus* is of chemotaxonomic interest and indicates a relationship to *Artemisia* where in part very similar lactones are common The isolation of **7f** from a *Pentzia* species agrees with previous results which also may indicate a relation of this genus to *Artemisia*

EXPERIMENTAL

The air-dried aerial parts (8 kg, collected in May 1986 in sandy coasted strips, West of Alexandria, identified by Prof Dr

Table 4 ^{1}H NMR spectral data of **11a**, **11b** and **12** (400 MHz, $CDCl_3$, δ-values)

	11a	**11b**	**12**
1	{ 5.15 *dd* 5.10 *dd* (*t*)	{ 5.13 *dd* 5.09 *dd*	—
2	5.86 *dd*	5.89 *dd*	4.38 *br d*
3	—	—	{ 2.33 *ddd* 1.91 *br dd*
4	4.14 *d*	4.11 *d*	2.05 *ddd*
5	5.39 *br d*	5.47 *br d*	4.45 *s*
6	—	—	2.58 *d*
7	1.85 *d*	4.05 *br s*	{ 5.05 *br s* 4.87 *br s*
8	{ 4.27 *d* 4.05 *d*	1.73 *br s*	—
9	1.02 *s*	1.02 *s*	1.18 *s*
10	1.01 *s*	1.01 *s*	1.33 *s*

J[Hz] Compounds **11a** and **b** 1*t*,2 = 17, 1*c*,2 = 10, 1*t*,1*c* = 1, 4,5 = 9, 5,7 or 5,8 = 1.5, compound **12** 2,3 = 8, 3,4 = 3, 3′,4 = 3.5, 3,3′ = 14, 4,5 = 6

V. Tackholm, Cairo University) was extracted with Et_2O–petrol, 1:1. The extract obtained (375 g) was filtered over a silica gel column and the polar CC fractions (SiO_2, Et_2O and Et_2O–MeOH) were separated again by CC into four crude fractions (1 Et_2O–Petrol, 1:1, 2 Et_2O–Petrol, 3:1; 3 Et_2O and 4 Et_2O–MeOH, 9:1). One third of fraction 1 (0.3 g) was further separated by TLC (Et_2O–petrol, 3:1) into three bands (1/1–1/3). HPLC of 1/1 (MeOH–H_2O, 7:3, always RP 8, *ca* 100 bar) afforded 5 mg undeca-2,4-diene-8,10-diynoic acid isobutyl amide (R_t 9.0 min), 10 mg **8a** (R_t 10.8 min), 3 mg **8b** (R_t 10.3 min) and 8 mg **8c/d** (*ca* 2:3, R_t 11.5 min). HPLC of 1/2 (MeOH–H_2O, 3:1) afforded 15 mg **7a**, mp 232° (R_t 9.9 min), 5 mg **7b** (R_t 9.5 min), 10 mg **7c/d** (R_t 10.5 min). HPLC of 1/3 (MeOH–H_2O, 1:1) gave 4 mg **11a** (R_t 8.8 min), 8 mg **11b** (R_t 7.5 min), and 10 mg **12** (R_t 6.5 min). TLC (Et_2O–petrol, 3:1) and HPLC (MeOH–H_2O, 3:2) of 5% (100 mg) of SC 2 gave 15 mg artabsin, 8 mg lolioide, 10 mg sesamin, 5 mg **1a** (R_t 10.4 min), 5 mg **16** (R_t 10.0 min), 10 mg **1c/d** (R_t 11.0 min) and 5 mg **7e** (R_t 10.6 min). Repeated HPLC of 20% of SC 3 (300 mg) (MeOH–H_2O, 1:1) afforded 12 mg **3a** (R_t 4.8 min), 12 mg **3b** (R_t 5.2 min), 10 mg **3c/d** (R_t 5.6 min), 15 mg romalea allene (R_t 6.0 min), 12 mg vomifoliol (R_t 6.5 min), 7 mg **4a** (R_t 12.3 min), 9 mg **4c/d** (R_t 13.0 min), 5 mg **5b** (R_t 13.5 min), 3 mg **5a** (R_t 14.0 min), 5 mg **5c/d** (R_t 14.8 min),

Table 5 Mass spectral data of the guaianolides, **11a/b** and **12**

1a 360.157 $[M]^+$ (6) ($C_{20}H_{24}O_6$), 260 $[M-RCO_2H]^+$ (9), 83 $[RCO]^+$ (100)

1b 348 $[M]^+$ (2.5), 260 $[M-RCO_2H]^+$ (8), 71 $[RCO]^+$ (100)

1c/d 362 $[M]^+$ (6), 260 $[M-RCO_2H]^+$ (10), 85 $[RCO]^+$ (44), 57 $[85-CO]^+$ (100)

2a 378 $[M]^+$ (0.2), 360 $[M-H_2O]^+$ (0.3), 278 $[M-RCO_2H]^+$ (0.7), 83 $[RCO]^+$ (100)

2b 366 $[M]^+$ (0.1), 358 $[M-H_2O]^+$ (0.2), 278 $[M-RCO_2H]^+$ (1), 71 $[RCO]^+$ (100)

2c/d 380 $[M]^+$ (0.2), 362 $[M-H_2O]^+$ (0.2), 278 $[M-RCO_2H]^+$ (1), 85 $[RCO]^+$ (45), 57 $[85-CO]^+$ (100)

3a 378 $[M]^+$ (0.1), 360 $[M-H_2O]^+$ (0.2), 318 $[360-C_2H_2O]^+$ (1.5), 278 $[M-RCO_2H]^+$ (1), 218 $[318-RCO_2H]^+$ (62), 83 $[RCO]^+$ (100)

3b 366.167 $[M]^+$ (0.1) ($C_{19}H_{26}O_7$), 348 $[M-H_2O]^+$ (0.2), 306 $[348-C_2H_2O]^+$ (4.5), 278 $[M-RCO_2H]^+$ (1), 218 $[306-RCO_2H]^+$ (48), 71 $[C_3H_7CO]^+$ (100)

3c/d 380 $[M]^+$ (0.1), 362 $[M-H_2O]^+$ (0.2), 320 $[362-C_2H_2O]^+$ (2.5), 278 $[M-RCO_2H]^+$ (1), 218 $[320-RCO_2H]^+$ (56), 85 $[RCO]^+$ (52), 57 $[85-CO]^+$ (100)

4a 362 $[M-H_2O]^+$ (0.3), 262 $[362-RCO_2H]^+$ (8), 83 $[RCO]^+$ (100)

4b 353.160 $[M-Me]^+$ (7) ($C_{18}H_{25}O_7$), 350 $[M-H_2O]^+$ (0.6), 332 $[350-H_2O]^+$ (1.5), 262 $[350-RCO_2H]^+$ (10), 167 $[C_9H_{11}O_3]^+$ (100), 71 $[C_3H_7CO]^+$ (96)

4c/d 364.189 $[M-H_2O]^+$ (0.5) ($C_{20}H_{28}O_6$), 262 $[364-RCO_2H]^+$ (7), 244 $[262-H_2O]^+$ (4), 85 $[RCO]^+$ (45), 57 $[85-CO]^+$ (100)

5a 378 $[M-HCl]^+$ (0.1) ($C_{20}H_{27}O_7$), 278 $[378-RCO_2H]^+$ (1.3), 260 $[278-H_2O]^+$ (5), 218 $[260-C_2H_2O]^+$ (56), 83 $[C_4H_7CO]^+$ (100)

5b 402 $[M]^+$ (0.3), 366.167 $[M-HCl]^+$ (0.8) ($C_{19}H_{26}O_7$), 348 $[366-H_2O]^+$ (1.3), 333 $[348-Me]^+$ (3), 306 $[348-C_2H_2O]^+$ (65), 218 $[306-RCO_2H]^+$ (74), 71 $[C_3H_7CO]^+$ (100)

5c/d 380 $[M-HCl]^+$ (0.1), 278 $[380-RCO_2H]^+$ (1), 85 $[RCO]^+$ (46), 57 $[85-CO]^+$ (100)

6a 378 $[M-H_2O]^+$ (0.1), 318 (2), 278 (1), 218 (42), 83 (100)

6b 366.167 $[M-H_2O]^+$ (0.5) ($C_{19}H_{26}O_7$), 348 $[366-H_2O]^+$ (1), 306 $[348-C_2H_2O]^+$ (7), 278 $[366-RCO_2H]^+$ (2), 218 $[306-RCO_2H]^+$ (66), 71 $[RCO]^+$ (100)

7a 396 $[M]^+$ (1) ($C_{20}H_{28}O_8$), 381 $[M-Me]^+$ (0.4), 363 $[381-H_2O]^+$ (2.5), 83 $[C_4H_7CO]^+$ (100)

7b 384.178 $[M]^+$ (1) ($C_{19}H_{28}O_8$), 71 $[C_3H_7CO]^+$ (100)

7c/d 398 $[M]^+$ (0.6) ($C_{20}H_{30}O_8$), 383 $[M-Me]^+$ (0.6), 85 $[C_4H_9CO]^+$ (68), 57 $[85-CO]^+$ (100)

7e 370.163 $[M]^+$ (0.6) ($C_{18}H_{26}O_8$), 296 $[M-RCO_2H]^+$ (1.3), 279 $[296-OH]^+$ (14), 261 $[279-H_2O]^+$ (7), 57 $[RCO]^+$ (100)

7f (CIMS) 297 $[M+1]^+$ (20), 269 $[297-H_2O]^+$ (19), 57 (100)

8a 394.162 $[M]^+$ (1.1) ($C_{20}H_{26}O_8$), 294 $[M-RCO_2H]^+$ (9), 167 (80), 83 $[RCO]^+$ (100), 55 $[83-CO]^+$ (60)

8b 382.178 $[M]^+$ (4) ($C_{19}H_{28}O_8$), 294 $[M-RCO_2H]^+$ (9), 167 (100), 71 $[RCO]^+$ (70)

8c/d 396.178 $[M]^+$ (1.7) ($C_{20}H_{28}O_8$), 294 $[M-RCO_2H]^+$ (10), 167 (82), 85 $[RCO]^+$ (60), 57 $[85-CO]^+$ (100)

9a 378.168 $[M]^+$ (0.5) ($C_{20}H_{26}O_7$), 346 $[M-O_2]^+$ (0.5), 278 $[M-RCO_2H]^+$ (6), 260 $[278-H_2O]^+$ (7), 111(58), 83 $[RCO]^+$ (80), 55 $[83-CO]^+$ (100)

9b 366.168 $[M]^+$ (2) ($C_{19}H_{26}O_7$), 334 $[M-O_2]^+$ (3), 278 $[M-RCO_2H]^+$ (8), 111 (100), 71 $[RCO]^+$ (88)

9c/d 380 $[M]^+$ (0.6) ($C_{20}H_{28}O_7$), 348 $[M-O_2]^+$ (0.3), 278 $[M-RCO_2H]^+$ (6.5), 85 $[RCO]^+$ (64), 57 $[85-CO]^+$ (100)

10 278.115 $[M]^+$ (10) ($C_{15}H_{18}O_5$), 260 $[M-H_2O]^+$ (10), 95 (100)

11a (CIMS) 171 $[M+1]^+$ (2), 153 $[171-H_2O]^+$ (86), 135 $[153-H_2O]^+$ (100)

11b 101 $[M-C_5H_9]^+$ (56), 83 $[101-H_2O]^+$ (80), 55 $[83-CO]^+$ (100)

15 mg **2b** (R_t 20 5 mın), 15 mg **2a** (R_t 21 0 mın), 8 mg **2c/d** (R_t 22 0 mın), 3 mg **6b** (R_t 23 0 mın), 3 mg **6a** (R_t 24 5 mın) and 2 mg **6c/d** (R_t 26 0 mın) HPLC of 5% of SC 4 (100 mg) (MeOH–H_2O, 1 1) gave 8 mg **4b** (R_t 8 0 mın) and 4 mg **10** (R_t 4 5 mın) 80 g aerial parts grown ın the Botanical Garden Berlın gave a polar SC fractıon which afforded by HPLC (MeOH–H_2O, 3 2) 6 mg **9b** (R_t 6 1 mın), 4 mg **9a** (R_t 8 2 mın), 6 mg **9c d** (R_t 8 8 mın) and 7 mg tanaparthın-1α,4α-peroxıde

The extract of the aerial parts of *Pentzia albida* (110 g, voucher M Muller 3704, collected at the Luderitz Bay) gave two crude SC fractıons (SC 1 and 2) TLC of SC 1 (Et_2O–petrol, 1 1) gave 30 mg nerolıdol and of SC 2 (Et_2O–MeOH, 9 1) 5 mg **13c**, 5 mg **13a**, 10 mg **13b**, 8 mg tanaparthın-1α,4α-peroxıde, 45 mg artabın and a mıxture which gave by HPLC (MeOH–H_2O, 7 3) 5 mg artabın and 5 mg **7f** (R_t 9 5 mın) Known compounds were ıdentıfied by comparıng the 400 MHz ^{1}H NMR spectra wıth those of authentıc materıal The mass spectral data of the new compounds are summarızed ın Table 5

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