Terpenoids from *Anthemis austriaca* Jacq.

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Z. Naturforsch. **59 c,** 161–165 (2004); received July 9/August 19, 2003

The aerial parts of *Anthemis austriaca* Jacq. afforded five new sesquiterpene lactones (two of which are dimeric guaianolides) and three new guaiane type sesquiterpene acids. In addition, seven known terpenoids were also found in the studied species. Their structures were elucidated by spectral methods.

Key words: Anthemis austriaca, Sesquiterpenoids, Dimeric Guaianolides

Introduction

In continuation of our chemical research on the genus *Anthemis*, we have studied Bulgarian *Anthemis austriaca* Jacq. (syn. *A. cotiformis* Velen.) (Fernandes, 1976). Two nerolidol derivatives (Bohlmann *et al.*, 1974) and only one sesquiterpene lactone xerantholide (Holub *et al.*, 1982) were the described constituents of the aerial parts of this species. In the present paper, we report the isolation of 15 compounds, eight of which are new natural products.

Experimental

Plant material

The plant material was collected in June 2002 near Sofia (Bulgaria). Voucher specimen (SOM Co 976) is deposited in the Herbarium of the Institute of Botany, Bulgarian Academy of Sciences.

Extraction and isolation

The air-dried aerial parts of *Anthemis austriaca* (340 g) were extracted exhaustively with MeOH at room temperature and the total extract (14 g) was worked up as reported previously (Ognyanov and Todorova, 1983) to give a crude lactone fraction (2 g). The latter was subjected to column chromatography on silica gel (15 g) using the solvent mixture $CHCl_3$/MeOH with increasing polarity and 12 fractions were collected. The lactone containing fractions (IR-control) were further purified.

Xerantholide (**1**) (380 mg) crystallized easily and was purified by recrystallization ($CHCl_3$) from fraction 2 (800 mg). The residue was separated by CC over silica gel (30 g) into 5 subfractions using $CHCl_3$/MeOH (30:1 v/v). Purification of the subfraction 2/1 by prep. TLC using cyclohexane/acetone (7:1 v/v) as eluent afforded taraxasterol acetate (2.5 mg), taraxasterol (2 mg) and β-sitosterol (1.5 mg). Subfraction 2/2 (40 mg) was separated by MPCC-LiChroprep RP 18 (40–63 μm) using solvent mixture MeOH/H_2O (7:3 v/v) to give **7** (4 mg) and **8 (**3 mg). Prep. TLC of the subfraction 2/3 (50 mg) ($CHCl_3$/Et_2O, 5:1 v/v) afforded **9** (5 mg).

Repeated column chromatography of fraction 4 (290 mg) over silica gel (29 g) yielded subfractions 4/1–4/3. Subfraction 4/1 (9 mg), purified by prep. TLC (cyclohexane/Et_2O, 1:6, v/v) furnished 3,7-dimethylocta-1,5-dien-3,7-diol (1.4 mg) and a mixture of two diastereomers of 3,7-dimethylocta-1,7-dien-3,6-diol (1.2 mg). Subfraction 4/2 (17 mg), after prep. TLC (cyclohexane/Et_2O, 1:20 v/v), afforded **2** (1.84 mg), **3** (1.5 mg) and **5** (1.3 mg). Lactones **4** (1.2 mg) and **6** (5 mg) were isolated from subfraction 4/3 by prep. TLC ($CHCl_3$/MeOH, 30:1 v/v, 2×).

1α-Hydroxyxerantholide (**2**): Colorless oil. – IR (film): ν_{max} = 3450, 1750, 1690, 1640 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 262 (90) $[M]^+$, 244 (28) $[M-H_2O]^+$, 229 (13), 216 (58), 208 (10), 202 (28), 187 (22), 137 (36). – ^{1}H NMR: see Table I.

6α-Hydroxyxerantholide (**3**): Colorless oil. – IR (film): ν_{max} = 3450, 1750, 1690, 1640 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 262 (33) $[M]^+$, 244 (2) $[M-H_2O]^+$, 233 (100), 215 (17) $[233-H_2O]^+$, 205 (3), 187 (24), 173 (7), 159 (7), 145 (9), 137 (11), 123 (29). – ^{1}H NMR: see Table I.

10α-Hydroxy-11β,13-dihydroxerantholide (**4**): Colorless oil. – IR (film): ν_{max} = 3450, 1760, 1680, 1640 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 264 (17) $[M]^+$, 249 (4) $[M-15]^+$, 246 (6) $[M-18]^+$, 236 (27) $[M-28]^+$, 221 (7) $[236-15]^+$, 218 (30) $[236-18]^+$, 203 (12) $[218-15]^+$, 189 (17) $[218-29]^+$, 161 (20), 135 (28), 109(40), 57 (100). – ^{1}H NMR: see Table I.

8α-Hydroxyxeranthemolide (**5**): Colorless oil. – IR (film): ν_{max} = 3450, 1750, 1680, 1640 cm^{-1}. – EIMS (15 eV): *m/z* (rel. int.) = 508 (<1) $[M]^+$, 262 (14) $[C_{15}H_{18}O_4]^+$, 246 (86) $[C_{15}H_{18}O_3]^+$, 244 (28) $[262-18]^+$, 226 (100) $[244-18]^+$, 218 (30) $[246-28]^+$, 211 (25) $[226-15]^+$, 175 (64), 161 (70), 149 (24), 136 (38), 110 (37). – ^{1}H NMR: see Table II. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 207.0 (C-3), 179.9 (C-12), 170.2 (C-12′), 169.9 (C-5), 139.4 (C-4 or C-11′), 139.1 (C-11′ or C-4), 137.9 (C-2′), 137.1 (C-3′), 121.0 (C-13′), 80.1 (C-8), 75.3 (C-6′), 73.9 (C-10′), 71.5 (C-8′), 65,9 (C-5′), 64.8 (C-1′ or C-4′), 61.1 (C-4′ or C-1′), 55.9 (C-11), 52.2 (C-7′), 45.1 (C-9′), 45.0 (C-1), 42.7 (C-7), 41.0 (C-2), 40.8 (C-9), 35.7 (C-13), 32.6 (C-10), 32.1 (C-6), 29.8 (C-14′), 13.3 (C-15′), 12.9 (C-14), 8.3 (C-15).

Xeranthemolide (**6**): Yellow oil. – IR (film): ν_{max} = 3450, 1750, 1680, 1640 cm^{-1}. – EIMS (15 eV): *m/z* (rel. int.) = 492 (<1) $[M]^+$, 246 (100) $[C_{15}H_{18}O_3]^+$, 231 (19) $[246-15]^+$, 228 (90) $[246-18]^+$, 218 (27) $[246-28]^+$, 213 (37) $[228-15]^+$, 203 (46) $[218-15]^+$, 200 (39) $[218-18]^+$, 185 (21) $[203-18]^+$, 175 (45), 161 (44), 136 (23), 110 (29). – ^{1}H NMR: see Table II.

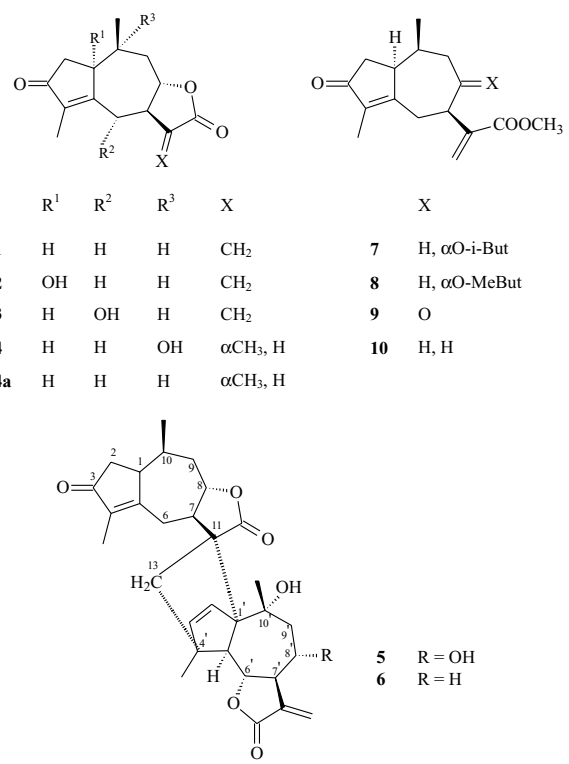
Methyl 8α-isobutyryloxy-3-oxo-4,11(13)-guaiadien-12-oate (**7**): Colorless oil. – IR (film): ν_{max} = 1720, 1690, 1640, 1440, 1380 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 278 (3) $[M-C_4H_7O]^+$, 260 (100)$[M-C_4H_8O_2]^+$, 245 (16) $[260-CH_3]^+$, 228 (77), 213 (18), 200 (77), 185 (18), 161 (57), 71 (41) $[C_4H_7O]^+$, 43 (84). – ^{1}H NMR: see Table I.

Methyl 8α-(2-methylbutanoyloxy)-3-oxo-4,11(13)-guaiadien-12-oate (**8**): Colorless oil. – IR (film): ν_{max} = 1720, 1690, 1640, 1440, 1380 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 278 (5) $[M-C_5H_9O]^+$, 260 (94) $[M-C_5H_{10}O_2]^+$, 245 (10) $[260-CH_3]^+$, 228 (74), 213 (10), 200 (67), 185 (11), 161 (52), 85 (26) $[C_5H_9O]^+$, 57 (100), 41 (24). – ^{1}H NMR: see Table I.

Methyl 3,8-dioxo-4,11(13)-guaiadien-12-oate (**9**): Colorless oil. – IR (film): ν_{max} = 1710, 1690, 1630 cm^{-1}. – EIMS (70 eV): *m/z* (rel. int.) = 276 (12) $[M]^+$, 261 (14) $[M-CH_3]^+$, 244 (100) $[M-CH_3OH]^+$, 216 (28), 201 (16), 191 (10), 173 (31). – ^{1}H NMR: see Table I. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 208.8 (C-3), 207.0 (C-8), 168.9 (C-12), 147.9 (C-5), 139.6 (C-4), 138.9 (C-11), 126.5 (C-13), 52.3 (OCH_3), 51.7 (C-9), 48.8 (C-7), 44.5 (C-1), 40.7 (C-2), 32.3 (C-10), 30.1 (C-6), 13.1 (C-14), 8.3 (C-15).

Results and Discussion

The air-dried plant material was extracted with MeOH and worked up (see Experimental) to give the corresponding crude lactone fraction. Repeated CC and prep. TLC afforded β-sitosterol, taraxasterol, taraxasterol acetate, 3,7-dimethylocta-1,5-dien-3,7-diol (Takaoka and Hiroi, 1976), two diastereomers of 3,7-dimethylocta-1,7-dien-3,6-diol (Tsankova *et al.*, 2003), and xerantholide (**1**) (Samek *et al.*, 1977). Furthermore, five sesquiterpene lactones (**2**–**6**) [two of which are dimeric



	R^1	R^2	R^3	X
1	H	H	H	CH_2
2	OH	H	H	CH_2
3	H	OH	H	CH_2
4	H	H	OH	αCH$_3$, H
4a	H	H	H	αCH$_3$, H

	X
7	H, αO-i-But
8	H, αO-MeBut
9	O
10	H, H

5 R = OH
6 R = H

Fig. 1. Xerantholide (**1**); 1α-hydroxyxerantholide (**2***); 6α-hydroxyxerantholide (**3***); 10α-hydroxy-11β,13-dihydroxerantholide (**4***); 11β,13-dihydroxerantholide (**4a**); 8α-hydroxyxeranthemolide (**5***); xeranthemolide (**6***); methyl 8α-isobutyryloxy-3-oxo-4,11(13)-guaiadien-12-oate (**7***); methyl 8α-(2-methylbutanoyloxy)-3-oxo-4,11(13)-guaiadien-12-oate (**8***); methyl 3,8-dioxo-4,11(13)-guaiadien-12-oate (**9***); methyl pechueolate (**10**).
* New compound

Table I. ^{1}H NMR data of **2**, **3**, **4**, **7**, **8**, and **9** (250 MHz, $CDCl_3$).

H	**2**	**3**	**4**	**7**	**8**	**9**
1α	–	3.37 brd (6.8)	3.21 brd (6.4)	3.20 m	3.20 m	3.50 m
2α	2.51 brd (18.1)	2.65 dd (18.6, 6.8)	2.47 ddd (19.3, 6.4, 1.0)	2.59 dd (18.8, 6.6)	2.60 dd (18.8, 6.6)	2.69 ddd (18.8, 6.7, 1.0)
2β	2.75 brd (18.1, 0.9)	2.18 d (18.6)	2.62 ddd (19.3, 2.1, 1.0)	2.07 dd (18.8, 2.0)	2.07 dd (18.8, 2.0)	2.17 ddd (18.8, 1.6, 1.0)
6α	3.10 ddq (19.1, 3.0, 1.4)	–	3.04 brd (19.6, 1.4)	2.80 d*** (7.0)	2.80 d*** (7.0)	2.58 dd (19.0, 12.0)
6β	2.52* (19.1, 11.5, 1.4)	4.78 dd (9.8, 4.7**)	2.40 ddq (19.6, 11.0, 1.4)	2.80 d*** (7.0)	2.80 d*** (7.0)	2.85 ddq (19.0, 3.0, 1.2)
7α	3.75 m	3.17 dddd (9.8, 9.8, 3.3, 3.1)	2.20 *	3.25 dt (10.3, 7.0, 7.0)	3.25 dt (10.3, 7.0, 7.0)	4.12 dd (12.0, 3.0)
8β	4.05 ddd (12.6, 9.5, 3.0)	4.00 ddd (12.1, 9.8, 2.5)	3.98 ddd (12.4, 9.7, 3.6)	5.13 ddd (10.3, 7.4, 2.3)	5.13 ddd (10.3, 7.4, 2.3)	–
9α	2.46 td (12.6, 4.2)	2.00 ddd (13.2, 12.1, 4.9)	1.98 t (12.4)	2.18 ddd (13.6, 3.7, 2.3)	2.18 ddd (13.6, 3.7, 2.3)	3.13 dd (11.6, 5.4)
9β	2.14 ddd (13.0, 3.0, 3.0)	2.32 ddd (13.2, 2.5, 2.5)	2.57 dd (12.4, 3.6)	1.80 ddd (13.6, 7.4, 2.6)	1.79 ddd (13.6, 7.4, 2.6)	2.57 dd (11.6, 4.5)
10α	2.40–2.50*	2.35 m	–	2.20 m	2.21 m	2.37 m
11	–	–	2.40 dq (11.8, 7.0)	–	–	–
13	5.53 d (3.2)	6.27 dd (3.1, 0.8)	1.30 d (7.0)	6.25 brs	6.25 brs	6.51 brs
13′	6.25 d (3.5)	6.35 dd (3.3, 0.8)	–	5.63 brs	5.62 brs	5.82 brs
14	0.83 d (7.6)	0.69 d (7.2)	1.02 s	0.79 d (6.9)	0.79 d (6.9)	0.62 d (7.0)
H_{15}	1.76 t (1.4)	1.89 d (0.9)	1.71 dd (3.3, 1.4)	1.66 brs	1.66 brs	1.72 brs
OCH_3	–	–	–	3.77 s	3.77 s	3.77 s

* Overlapping signals.
** $J_{6,OH}$.
*** AB part of ABX system.
7: *i*-But: 2.39 qq (7.0), 1.05 d (7.0), 1.04 d (7.0).
8: 2-MeBut: 2.37 m, 1.60 m, 1.50 m, 1.08 d (7.0), 0.86 t (7.0).

guaianolides (**5** and **6**)] and three sesquiterpene acids (**7, 8** and **9**) were found to be new natural compounds (Fig. 1).

The MS of compounds **2** and **3** furnished a molecular ion at *m/z* 262 ([M]$^+$) assignable to a molecular formula $C_{15}H_{18}O_4$ and a fragment at *m/z* 244 ([M-18]$^+$) indicative for the presence of an OH group. The close similarity of their ^{1}H NMR spectra (Table I) to that of xerantholide (**1**) suggested that **2** and **3** were hydroxy derivatives of **1**. Thus, the absence of the signal for H-1 as well as the vicinal coupling of the C-2 methylene protons in the ^{1}H NMR spectrum of **2** showed that the hydroxyl group was attached at C-1. Its α orientation was derived from the downfield shift of the signals of H-7, H-2β and H-9α. However, in the ^{1}H NMR spectrum of **3** the doublet of doublets at δ 4.78 (which collapsed to a doublet after D_2O exchange) for a carbinolic proton indicated the presence of a secondary OH group. COSY experiment revealed its location at C-6, while its α orientation was deduced from the magnitude of the coupling constant $J_{6,7}$ = 9.8 Hz, the paramagnetic shift of the signal for H-13 at δ 6.27, and the downfield shift of H-1α at δ 3.37 compared with those of **1**. Accordingly, compounds **2** and **3** were identified as 1α-hydroxyxerantholide and 6α-hydroxyxerantholide, respectively.

Compound **4** had the molecular formula $C_{15}H_{20}O_4$ (*m/z* 264 [M]$^+$). The ^{1}H NMR data (Table I) of **4** agreed well with a structure similar to that of 11β,13-dihydroxerantholide (**4a**) (Bohlmann and Borthakur, 1982). However, an additional OH group in **4** was required of the MS fragment at *m/z* 246 ([M–H_2O]$^+$). Its position at C-10 followed from the methyl singlet at δ 1.02. The relative stereochemistry at the chiral centers C-7, C-8, and C-11 was assigned on the basis of the coupling constants, while that at C-10 was deduced from the observed NOE interaction between H-8 and C-10 methyl group. Hence, the new lactone **4** was identified as 10α-hydroxy-11β,13-dihydroxerantholide.

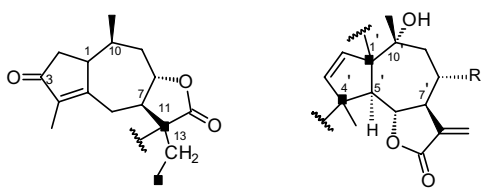
Compound **5**, named 8α-hydroxyxeranthemolide was isolated in very small amount. The ^{13}C NMR spectrum (Experimental) exhibited signals

Table II. ^{1}H NMR data of **5** and **6** in $CDCl_3$ (250 MHz).

H	**5**	**6**	NOEs of **5** and **6**
1	3.19 m	3.18 m	2α, 7
2α	2.62 dd (19.0, 6.6)	2.62 dd (19.0, 6.5)	1
2β	2.09 brd (19.0)	2.08 brd (19.0)	14
6α	2.72 brd (18.2)	2.73 d (18.5)	13α, 15
6β	2.10–2.30*	2.12–2.30*	–
7	2.30–2.40*	2.30–2.45*	–
8	4.03 ddd (12.5, 9.5, 3.6)	4.03 ddd (12.3, 9.5, 3.6)	14
9α	1.84 ddd (12.5, 12.5, 4.0)	1.75–1.95*	–
9β	2.40 ddd (13.0, 3.6, 3.6)	2.39 ddd (13.1, 3.6, 3.6)	–
10	2.15–2.30*	2.15–2.30*	–
13α	2.20 d (12.0)	2.27 d (12.0)	6α, 5′
13β	1.75 d (12.0)	1.75 d (12.0)	–
14	0.70 d (7.2)	0.69 d (7.2)	8, 2β
15	1.65 d (1.5)	1.65 d (1.4)	6α
2′	6.02 d (5.6)	6.07 d (5.6)	14′
3′	5.86 d (5.6)	5.83 d (5.6)	15′
5′	3.42 d (10.0)	3.34 d (10.0)	13α
6′	4.00 t (10.0)	4.08 t (10.0)	–
7′	3.37 dddd (10.0, 10.0, 3.3, 2.8)	3.35 m	–
8′	3.92 brt (10.0)	1.83–1.95*	–
9′	2.00–2.10*	1.48–1.60*	–
13a′	5.96 d (2.8)	5.38 d (3.3)	–
13b′	6.19 d (3.3)	6.11 d (3.6)	–
14′	1.45 s*	1.38 s	2′
15′	1.46 s*	1.45 s	3′, 13α, 13β

* Overlapping signals.

for 30 carbon atoms, but the ^{1}H NMR spectrum (Table II) looked like that of a mixture of two sesquiterpene lactones in ratio of ca 1:1. One part of the NMR signals suggested the presence of the lactone xerantholide (**1**). However, the C-13 exomethylene protons were replaced by an isolated methylene group the protons of which appeared as doublets at δ 2.20 and δ 1.75, obviously connected with two quaternary carbon atoms one of which must be C-11. Hence, one part of the molecule of **5** was the presented partial structure **A** (Fig. 2). The remaining signals correlated well with the structure of 8α,10α-dihydroxy-2,11(13)-guaiadien-12,6-olide. The doublets for the olefinic protons H-2′ and H-3′ at δ 6.02 and δ 5.86 ($J_{2',3'}$ = 5.6 Hz) showed that carbon atoms C-1′ and C-4′ adjacent to the double bond were quaternary (partial structure **5B** in Fig. 2). Mass spectrum of compound **5** exhibited a very weak molecular ion at *m/z* 508 ($C_{30}H_{36}O_7$) and significant peaks at *m/z* 246 and 262 corresponding to the structural units **A** and **5B,** respectively. The prominent peaks at *m/z* 244 [262-H_2O]$^+$ and 226 ([262-2H_2O]$^+$) confirmed affiliation of two hydroxyl groups to a molecular fragment **5B**. Accordingly, compound **5** was



A **5B** R = OH **6B** R = H

Fig. 2. Partial structures of **5** and **6**.

a dimeric guaianolide formed from Diels-Alder reaction in which C-C bond formation has taken place between C-11/C-1′ and C-13/C-4′ of the partial structures **A** and **5B**. The kind of junction of two monomers and the stereochemistry at C-1′, C-4′, and C-11 was deduced as follows. Observation of an NOE from H-5′α to H-13α showed that the C-13 has to be on the α-face of the monomer **5B**, while the situation of C-13 on the β-face of the monomer **A** was required of NOEs from H-15 to H-6α, H-6α to H-13α and H-14′ to H-9α.

The ^{1}H NMR (Table II) and MS data of compound **6** showed very close relationship between

its structure and that of **5**. The molecular formula $C_{30}H_{36}O_6$ was deduced by EIMS (*m/z* 492 $[M]^+$). The base peak at *m/z* 246 was in accordance with both structural fragments **A** and **6B** (Fig. 2). The loss of one molecule of water (*m/z* 228 $[246\text{-}18]^+$) was the most prominent feature in the spectrum of **6**. Its ^{1}H NMR spectrum was almost identical with that of **5** (Table II) but the signal for C-8 carbinolic proton was missing. The chemical shifts and the coupling patterns of all the proton signals in the spectrum of **6** coincided well with those of the compound **5** thus showing that they shared a common stereochemistry. COSY experiments and the observed NOEs indicated that **6** incorporated the same kind of linkage of the two monomers as that of **5**. Compound **6** was named xeranthemolide.

The ^{1}H NMR spectral data (Table I) of **7–9** showed signals confirming a guaiane framework. However, a methoxy singlet at δ 3.77 as well as slightly broadened singlets for exomethylene protons H-13 and H-13′ indicated the presence of a methyl ester of an acid rather lactone. On the other hand, ^{1}H NMR data of **7** and **8** were almost identical to those of the known methyl pechueolate (**10**) (Bohlmann and Borthakur, 1982), the only difference being the appearance of a lower-field three-fold doublet at δ 5.13 due to a proton geminal to an ester group. The latter collapsed to a doublet of doublets after irradiation of the H-7 signal (δ 3.25) thus indicating the location of the ester group at C-8. The *trans*-disposition of H-7 and H-8 followed from the observed large vicinal coupling $J_{7,8}$ = 10.3 Hz. Accordingly, the acids **7** and **8** were suggested to be 8α-acyloxy derivatives of methyl pechueolate (**10**). The nature of the ester groups were deduced to be isobutyryloxy and 2-methylbutanoyloxy, respectively, from typical ^{1}H NMR signals as well as from the mass spectral fragmentation. The similarity of chemical shifts and coupling constants of all signals in **7** and **8** were in agreement with the relative stereochemistry of the parent compound **10**.

The mass spectrum of **9** showed a molecular ion at *m/z* 276 which agreed with a molecular formula $C_{16}H_{20}O_4$. ^{1}H NMR spectral features of **9** were close to those of acids **7** and **8**. However, the H-8 signal was missing and the splitting of H-7, H-9α and H-9β signals was changed to doublet of doublets (Table I). Furthermore, the downfield shift of these signals ($\Delta\delta$ = 0.87, 0.77 and 0.95 ppm, respectively) was remarkable in comparison with those of **7** and **8**. All these data indicated the presence of a carbonyl group at C-8, which was supported by a carbon signal at δ 207.0 in ^{13}C NMR spectrum (Experimental). ^{1}H-^{1}H COSY and HMQC spectral data allowed the assignment of all signals, thus leading to the proposed structure of **9**. The NOE's correlation in the NOESY spectrum of **9** confirmed the relative stereochemistry.

The described above 3-oxo-guaia-4-en derivatives (analogues of xerantholide and pechueloic acid) have not been found in any other *Anthemis* species so far and could be used as chemotaxonomical markers of *Anthemis austriaca*. It should be noted that compounds **5** and **6** are the first dimeric lactones isolated from the species of the genus *Anthemis.*

Acknowledgements

The authors are grateful for the financial support of project B-1001 provided by the Bulgarian National Research Foundation.

Bohlmann F., Zdero C., and Schwarz H. (1974), New nerolidol derivatives. Chem. Ber. **107**, 1074–1080.

Bohlmann F. and Borthakur N. (1982), Sesquiterpenes and norsesquiterpenes from *Pechuel-Loeschea Leibnitziae*. Phytochemistry **21**, 1160–1162.

Fernandes R. (1976), Genus *Anthemis* L. In: Flora Europaea, Vol. 4 (Tutin T. G., Heywood V. H., Burges N. A., Moore D. M., Valentine D. H., Walters S. M., and Webb D. A., eds.). Cambridge University Press, Cambridge, pp.145–159.

Herz W., Srinivasan A., and Kalyanaraman P. S. (1975), Mikanokryptin, a new guaianolide from *Mikania.* Phytochemistry **14**, 233–237.

Holub M., Budešinský M., Samek Z., Drożdż B., Grabarczyk H., Ulubelen A, Öksüz S., and Rychlewska U. (1982), Absolute configuration of xerantholide, a sesquiterpenic lactone from *Anthemis austriaca* Jacq. Coll. Czech. Chem. Commun. **47**, 670–675.

Ognyanov I. and Todorova M. (1983), Sesquiterpene lactones and flavonoids in flowers of *Tanacetum vulgare.* Planta Med. **48**, 181–183.

Samek Z., Holub M., Drożdż B., Grabarczyk H., and Hladon B. (1977), Xerantholide – A new cytotoxically active sesquiterpenic lactone from *Xeranthemum cylindraceum.* Coll. Czech. Chem. Commun. **42,** 2441–2447.

Takaoka D. and Hiroi M. (1976), Two acyclic monoterpene diols from *Cinnamomum camphora*. Phytochemistry **15**, 330–330.

Tsankova E., Mustakerova E., and Todorova M. (2003), Acyclic terpenoids from *Achillea depressa* Janka. Compt. Rend. Acad. Bulg. Sci. **56**, 51–54.