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SESQUITERPENE DERIVATIVES FROM *OTHONNA* AND RELATED SPECIES

J. JAKUPOVIC, V. P. PATHAK, M. GRENZ, S. BANERJEE, C. WOLFRUM, R. N. BARUAH and F. BOHLMANN

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.

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Key Word Index—*Othonna species; Senecio macrospermus; Euryops pedunculatus*; Compositae; sesquiterpenes; caryophyllene derivative; bicyclogermacrene derivative; furoeremophilanes; bisabolones.

Abstract—The investigation of several South African representatives of the tribe Senecioneae afforded in addition to known compounds a caryophyllene and a bicyclogermacrene derivative, two furoeremophilanes, three bisabolone derivatives and a guaiane derivative.

INTRODUCTION

From the large South African genus *Othonna* with about 150 species so far 20 species have been studied chemically [1–8]. Most species afforded furanoeremophilanes which are also widespread in *Senecio* and *Euryops*. Only a few species gave other constituents like diterpenes [4], *p*-hydroxyacetophenones [1, 8] and different sesquiterpenes [1]. We now have studied seven further species and a South African *Senecio* and a *Euryops* species. The results are presented in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Othonna leptodactyla* Harv. afforded in addition to known furoeremophilanes (Table 2) a new diol (**1**: R = CH_2OH, R^1 = H, R^2 = OAng, R^3 = H, X = H_2), the structure of which followed from its ^{1}H NMR spectrum which was close to that of similar compounds from *Othonna* species [2]. The natures and the relative positions of the oxygen functions were also deduced from the ^{1}H NMR data. Spin decoupling allowed the assignment of all signals though a few were multiplets. The ^{13}C NMR spectrum also supported the structure.

The aerial parts of *O. obtusiloba* (DC) Sch. Bip. gave several known furoeremophilanes (Table 2) and one new ester (**1**: R = Me, R^1 = iVal, R^2 = H, X = H_2, R^3 = OH). The structure could be deduced easily from the ^{1}H NMR spectrum which was close to that of the corresponding senecioate [9]. The nature of the ester group followed from the typical signals. Furthermore the *p*-methoxyphenethyl alcohol esters **9** and **10** were present. Their structures also followed from the spectroscopic data.

The aerial parts of *O. cf. graveolens* O. Hoffm. gave no furoeremophilanes but two sesquiterpene senecioates (**11** and **12**). The structure of **11** was deduced from the molecular formula ($C_{20}H_{30}O_2$) and the ^{1}H NMR data. The typical signals of a senecioate indicated the nature of the oxygen function. The remaining signals were close to those of caryophyllene. The position of the ester was determined by NOE difference spectroscopy which gave clear effects between H-13 and H-9 as well as between H-14 and H-1. The corresponding 13-*O*-acetate has been isolated from a *Helichrysum* species [10].

The ^{1}H NMR spectrum of **12** clearly showed that we were dealing with a senecioyloxy derivative of bicyclogermacrene. Accordingly, most signals were close to those of the hydrocarbon, only one methyl singlet being replaced by a pair of doublets (H-12). Again the position of the ester group was determined by clear NOEs between H-13, H-6 and H-7. Spin decoupling allowed the assignment of all signals. The aerial parts of four further *Othonna* species gave known compounds (Table 2).

The reinvestigation of the aerial parts of *Euryops pedunculatus* N.E.Br. gave in addition to compounds

Table 1. ^{1}H NMR spectral data of **5**–**7** (400 MHz, $CDCl_3$, TMS as int. standard)

	5	**6**	**7**
H-1	5.75	5.85	5.75 *d*
H-4	3.42	3.43	3.41 *d*
H-5α	2.56	2.59	2.54 *ddd*
H-5β	2.19	2.19	2.18 *dd*
H-6	2.77	2.76	2.77 *ddd*
H-8	5.07	5.09	5.05 *m*
H-9	2.34	2.32	2.32 *m*
H-10	5.03	5.04	5.02 *brt*
H-12	1.65	1.64	1.65 *brs*
H-13	1.59	1.59	1.59 *brs*
H-14	5.10	5.07	5.08 *brs*
H-14′	5.23	5.22	5.22 *brs*
H-15	1.42	1.44	1.43 *s*
OAng	6.09	6.04	— *qq*
	1.97	1.95	— *dq*
	1.87	1.87	— *dq*
OSen	5.63	5.64	5.68, 5.64 *qq*
	2.12	2.14	2.18, 2.14 *d*
	1.84	1.84	1.84, 1.88 *d*

J (Hz): 1,6 = 12; 4,5 = 4.5; 5α,5β = 16; 5α,6 = 7.5; 5β,6 = 11; 9,10 = 7; OAng: 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5; OSen: 2′,4′ = 2′,5′ = 1.3.

Table 2. Investigated species and constituents

Name (voucher)	Wt. of aerial parts (g)	Constituents
Othonna cf. arbuscula (Thunb.) Sch. Bip. (81/155)	76	22 mg **1** (R = Me, R^1 = Meacr, R^2 = OMeacr, R^3 = X = H) [5], 10 mg eremophilenolide [16], 5 mg 8β-hydroxyeremophilenolide [17]
O. furcata (Lindl.) Bruce (81/157)	30	5 mg **1** (R = Me, R^1 = Sen, R^2 = OSen, R^3 = H, X = O) [5], 7 mg **1** (R = Me, R^1 = Meacr, R^2 = OSen, R^3 = H, X = O) [5], 9 mg **1** (R = Me, R^1 = iBu, R^2 = OMeacr, R^3 = H, X = O) [4], 2 mg **1** (R = Me, R^1 = Meacr, R^2 = OTigl, R^3 = H, X = O) [5]
O. cf. graveolens O. Hoffm. (81/156)	30	11 mg **11**, 7 mg **12**
O. lasiocarpa (DC) Sch. Bip. (81/161)	22	11 mg **1** (R = Me, R^1 = Sen, R^2 = OSen, R^3 = H, X = O), 15 mg **1** (R = Me, R^1 = Meacr, R^2 = OSen, R^3 = H, X = O), 17 mg **1** (R = Me, R^1 = iBu, R^2 = OMeacr, R^3 = H, X = O), 5 mg **1** (R = Me, R^1 = Meacr, R^2 = OTigl, R^3 = H, X = O), 11 mg **2**
O. leptodactyla Harv. (81/170)	160	18 mg **1** (R = CH_2OH, R^1 = H, R^2 = OAng, R^3 = X = H), 10 mg **1** (R = CO_2H, R^1 = iBu, R^2 = OAng, R^3 = X = H) [4], 10 mg **1** (R = CO_2H, R^1 = iVal, R^2 = OAng, R^3 = X = H) [4]
O. obtusiloba (DC) Sch. Bip. (81/162)	75	800 mg **1** (R = Me, R^1 = Meacr, Sen, R^2 = R^3 = H, X = O), 8 mg **1** (R = Me, R^1 = Sen, R^2 = X = H, R^3 = OH) [10], 2 mg **9**, 2 mg **10**, 4 mg *cis*- and 2 mg *trans*-caryophyllene
O. sedifolia DC (81/166)	110	80 mg *ent*-kaurenic acid, 10 mg 16,17-epoxy-*ent*-kaurenic acid, 4 mg manoyl oxide, 3.5 mg 17-hydroxyisokaurenic acid
Euryops pedunculatus N.E.Br. (81/251) collected in Transvaal	100	3 mg **1** (R = Me, R^1 = Ac, R^2 = R^3 = H, X = O), 3 mg of the corresponding 1,10-dehydro and 3 mg of the 1,10-epoxy derivative [13], 3 mg **8**
Senecio macrospermus DC (Hilliard 3/3/82) collected in Natal	250	42 mg **3** (R = OAc) [18], 12 mg **3** (R = OH) [19], 40 mg **3** (R = H) [19], 15 mg **4** (R = H) [20], 30 mg **4** (R = OMe), 12 mg **5**, 7 mg **6**, 16 mg **7**, 7 mg **5** (R = Sen, R^1 = H), 3 mg **5** (R = Ang, R^1 = OAng)

isolated previously [11] (Table 2) the guaiane derivative **8**. The structure followed from the ^{1}H NMR spectrum. Starting with the olefinic methyl spin decoupling, the whole sequence could be determined. From the observed couplings of H-1, the relative configuration at C-1 and C-10 could be deduced by inspection of models. As usual all sesquiterpenes from Compositae have the 7α-H configuration, also H-1 and H-10 are most likely α-oriented.

The aerial parts of *Senecio macrospermus* DC afforded several furanoeremophilanes of the cacalol type and several bisabolone derivatives (Table 2). In addition to known ones [12, 13], three new bis-esters (**5–7**) were isolated. The ^{1}H NMR spectra (Table 1) were of course close to that of the bisangelate [12]. Only the chemical shifts of H-1 and H-8 showed small differences. As in similar cases the replacement of an angelate by a seneciote residue caused a small upfield shift of the corresponding proton under the ester group. The configuration at C-8 could not be determined.

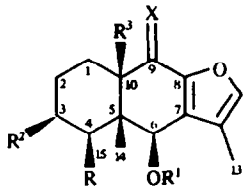
The new results on the chemistry of *Othonna* species established again that most species contain furoeremophilanes. But again one species had diterpenes while another one afforded only monosubstituted sesquiterpenes. There is still no clear chemical differentiation of the genera *Othonna*, *Euryops* and *Senecio*. In all three cases furoeremophilanes are most widespread, and there is a tendency in *Othonna* species to accumulate compounds with oxygen functions at C-15. However, there are several groups where these compounds are lacking [14]. Clearly our knowledge is still too limited for any final conclusions to be drawn, especially as the taxonomy of the whole tribe Senecioneae is still not solved.

EXPERIMENTAL

The *Othonna* species were grown in a greenhouse of the Botanic Research Institute in Pretoria. The air-dried aerial parts were extracted and from the extracts obtained the separation of the constituents was achieved as reported previously [15]. The results are summarized in Table 2. The conditions of the isolation of new compounds are given in parentheses. Known compounds were identified by comparing their 400 MHz ^{1}H NMR spectra with those of authentic material.

3β-Angeloyloxy-6β,15-dihydroxy-10βH-furoeremophilane. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (OH), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 330.183 $[M-H_2O]^+$ (40) (calc. for $C_{20}H_{26}O_4$: 330.183), 230 $[330-RCO_2H]^+$ (24), 83 $[C_4H_7CO]^+$ (100), 55 $[85-CO]^+$ (82); ^{1}H NMR ($CDCl_3$); δ2.16 (*m*, H-1), 1.41 (*br d*, H-1'), 1.90 (*m*, H-2), 5.30 (*ddd*, H-3), 2.26 (*ddd*, H-4), 4.57 (*br s*, H-6), 2.56 (*m*, H-9), 7.00 (*br s*, H-12), 1.99 (*d*, H-13), 1.35 (*s*, H-14), 3.92 and 3.67 (*dd*, H-15); OAng: 6.05 *qq*, 1.98 *dq*, 1.78 *dq*; *J* (Hz): 1,1' = 15; 3,4 = 5; 4,15 = 7.5; 4,15' = 11; 12,13 = 1; 15,15' = 12; OAng: 3',4' = 7; 3',5' = 4',5' = 1.5; ^{13}C NMR ($CDCl_3$, C-1–C-15): 25.6 *t*, 22.9 *t**, 81.1 *d*, 41.7 *d*, 41.8 *s*, 67.3 *d*, 120.1 *s*, 148.3 *s*, 22.7 *t**, 37.9 *d*, 119.0 *s*, 137.9 *d*, 8.3 *q*, 22.6 *q*, 67.0 *t*; OAng: 167.3 *s*, 127.6 *s*, 138.4 *d*, 20.7 *q*, 15.6 *q* (*values may be interchangeable); $[\alpha]_D^{24°}$ 5 ($CHCl_3$; *c* 0.9) (PTLC: Et_2O–petrol, 3:7, R_f 0.6).

6β-Isovaleryloxy-10β-hydroxyfuroeremophilane. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OH), 1720, 1650 (C=CCO$_2$R); MS *m/z*



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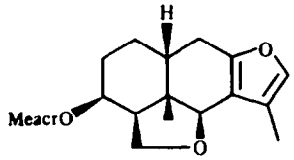

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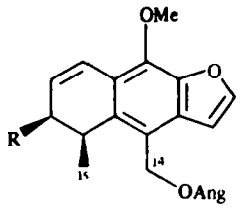

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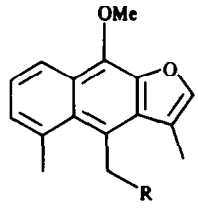

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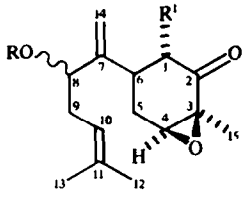
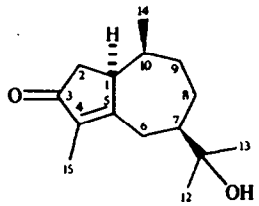


	5	6	7
R	Ang	Sen	Sen
R^1	OSen	OAng	OSen



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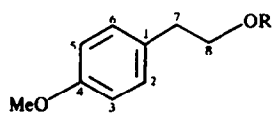
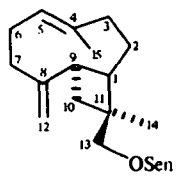


9 R = Sen
10 R = iVal



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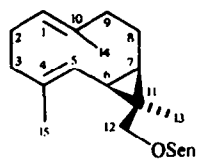

12

(rel. int.): 334.214 $[M]^+$ (1.4) (calc. for $C_{20}H_{30}O_4$: 334.214), 232 $[M-RCO_2H]^+$ (28), 85 $[C_4H_9CO]^+$ (45), 57 $[85-CO]^+$ (100); ^{1}H NMR ($CDCl_3$): 6.19 (*s*, H-6), 3.20 and 2.66 (*br d*, H-9), 7.10 (*br s*, H-12), 1.91 (*d*, H-13), 1.02 (*s*, H-14), 0.84 (*d*, H-15); OiVal: 2.19 (*d*, H-2'), 2.08 (*m* H-3'), 0.91 (*d*, 6H); *J* (Hz): 4,15 = 7; 9,9' = 18; 12,13 = 1; 2',3' = 3',4' = 3',5' = 7; (PTLC: Et_2O–petrol, 1:9, two developments, R_f 0.45).

1α-*Senecioyloxy*-8-*angeloyloxy*-3β,4β-*epoxybisabola*-7(14),10-*dien*-2-*one* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=O, C=CCO$_2$R), 1660 (C=C); MS *m/z* (rel. int.): 430.236 $[M]^+$ (0.4) (calc. for $C_{25}H_{34}O_6$: 430.236), 361 $[M-C_5H_9]^+$ (5), 330 $[M-RCO_2H]^+$ (5), 230 $[330-RCO_2H]^+$ (12), 83 $[C_4H_7CO]^+$ (100); $[\alpha]_D^{24°}$ -40 ($CHCl_3$; *c* 0.81) (HPLC: RP 8, MeOH–H_2O, 4:1, R_t 4.5 min).

1α-*Angeloyloxy*-8-*senecioyloxy*-3β,4β-*epoxybisabola*-7(14),10-*dien*-2-*one* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=CCO$_2$R, C=O), 1660 (C=C); MS *m/z* (rel. int.): 430.236 $[M]^+$ (0.5) (calc. for $C_{25}H_{34}O_6$: 430.236), 361 $[M-C_5H_9]^+$ (6), 330 $[M-RCO_2H]^+$ (1), 230 $[330-RCO_2H]^+$ (3), 83 $[C_4H_7CO]^+$ (100); $[\alpha]_D^{24°}$ -58 ($CHCl_3$; *c* 0.37) (HPLC: RP 8, MeOH–H_2O, 4:1, R_t 5.0 min).

1α,8-*Bissenecioyloxy*-3β,4β-*epoxybisabola*-7(14),10-*dien*-2-*one* (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=O, C=CCO$_2$R), 1660 (C=C); MS *m/z* (rel. int.): 430.236 $[M]^+$ (0.5) (calc. for $C_{25}H_{34}O_6$: 430.236), 361 $[M-C_5H_9]^+$ (6), 330 $[M-RCO_2H]^+$ (4), 230 $[330-RCO_2H]^+$ (6); $[\alpha]_D^{24°}$ -75 ($CHCl_3$; *c* 0.62) (PTLC: CH_2Cl_2–C_6H_6–Et_2O, 4:4:1, R_f 0.65).

3-*Oxo*-*guai*-4-*en*-11-*ol* (**8**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1685, 1628 (C=CC=O); MS *m/z* (rel. int.): 218.167 $[M-H_2O]^+$ (45) (calc. for $C_{15}H_{22}O$: 218.167), 203 $[218-Me]^+$ (6), 178 $[M-O=CMe_2]^+$ (11), 59 $[Me_2COH]^+$ (100); CIMS *m/z* (rel. int.): 237 $[M+1]^+$ (100), 219 $[237-H_2O]^+$ (44); ^{1}H NMR ($CDCl_3$): δ 3.04 (*br d*, H-1), 2.47 (*dd*, H-2), 1.96 (*d*, H-2'), 2.99 (*br d*, H-6), 2.10 (*br dd*, H-6'), 1.62 (*m*, H-7), 2.00 (*m*, H-10), 1.19

(*s*, H-12), 1.15 (*s*, H-13), 0.53 (*d*, H-14), 1.60 (*br s*, H-15) [*J* (Hz): 1,2 = 7; 1,10 ~ 2; 2,2′ = 19; 6,6′ = 20; 6.7 = 13; 6.15 ~ 1.5; 10,14 = 7]; $[\alpha]_D^{24°}$ + 18 ($CHCl_3$, *c* 0.2) (PTLC: Et_2O–MeOH, 20:1, R_f 0.35).

2-[4-*Methoxyphenyl*]-*ethylsenecioate* (**9**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=CCO_2R); MS *m/z* (rel. int.): 234.126 $[M]^+$ (0.4) (calc. for $C_{14}H_{18}O_3$: 234.126), 134 $[M - RCO_2H]^+$ (100), 83 $[C_4H_7CO]^+$ (26); ^{1}H NMR ($CDCl_3$): δ 7.15 (*d*, H-2, H-6), 6.84 (*d*, H-3, H-5), 2.90 (*t*, H-7), 4.26 (*t*, H-8); OSen: 5.67 *qq*, 2.15 and 1.88 *d* [*J* (Hz): 2,3 = 8; 7,8 = 7; OSen: 2′,4′ = 2′,5 = 1] (PTLC: Et_2O–petrol, 1:9, R_f 0.70).

2-[4-*Methoxyphenyl*]-*ethylisovalerate* (**10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 236.141 $[M]^+$ (25) (calc. for $C_{14}H_{20}O_3$: 236.141), 134 $[M - RCO_2H]^+$ (100), ^{1}H NMR ($CDCl_3$): δ 7,13 (*d*, H-2, H-6), 6.84 (*d*, H-3, H-5), 2.87 (*t*, H-7), 4.24 (*t*, H-8); OiVal: 2.17 *d*, 2.07 *tqq*, 0.90 *d* [*J* (Hz): 2,3 = 8; 7,8 = 7; OiVal: 2′,3′ = 3′,4′ = 3′,5′ = 7] (PTLC: Et_2O–petrol, 1:9, R_f 0.68).

13-*Senecioyloxy-caryophyllene* (**11**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715 (C=CCO_2R); MS *m/z* (rel. int.): 302.225 $[M]^+$ (0.7) (calc. for $C_{20}H_{30}O_2$: 302.225), 202 $[M - RCO_2H]^+$ (5.5), 83 $[C_4H_7CO]^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.61 (*t*, H-1), 5.27 (*br dd*, H-5), 2.35 (*br q*, H-9), 4.99 and 4.86 (*br s*, H-12), 4.15 and 4.05 (*d*, H-13), 1.12 (*s*, H-14), 1.61 (*br s*, H-15); OSen: 5.69 *qq*, 2.17 and 1.90 *d* [*J* (Hz): 1,2 = 1,9 = 9; 5,6 = 12; 5,6′ = 4; 9,10 = 10; 13,13′ = 11] (PTLC: CH_2Cl_2–C_6H_6, 1:1, two developments, R_f 0.55).

12-*Senecioyloxy-bicyclogermacrene* (**12**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 302.225 $[M]^+$ (0.6) (calc. for $C_{20}H_{30}O_2$: 302.225), 202 $[M - RCO_2H]^+$ (7.5), 187 $[202 - Me]^+$ (9), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (35); ^{1}H NMR ($CDCl_3$): 4.84 (*br dd*, H-1), 2.03 (*m*, H-2α), 2.10 (*br d*, H-2β), 1.85 (*m*, H-3α), 2.21 (*ddd*, H-3β), 4.40 (*br d*, H-5), 1.49 (*dd*, H-6), 0.82 (*ddd*, H-7), 2.03 (*m*, H-8α), 1.31 (*dddd*, H-8β), 1.73 (*ddd*, H-9α), 2.43 (*ddd*, H-9β), 4.22 and 4.14 (*d*, H-12), 1.19 (*s*, H-13), 1.48 (*d*, H-14), 1.67 (*d*, H-15); OSen: 5.72 *qq*, 2.17 and 1.90 *d* [*J* (Hz): 1,2α = 6; 1,2β = 2α,2β = 3α,3β = 12; 2α,3β = 2β,3β = 3; 5,6 = 7,8β = 11; 6,7 = 8; 7,8α = 5; 8α,8β = 9α,9β = 13; 8α,9α = 8α,9β = 8β,9β = 4; 8β,9α = 12,12′ = 12; OSen: 2,4 = 2,5 = 1.3] (PTLC: CH_2Cl_2–C_6H_6, 1:1, two developments, R_f 0.61).

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