afforded 44 mg lupeyl acetate and 11 mg caryophyllen-1,10-epoxide, while TLC of fraction 3 (CH_2Cl_2–C_6H_6–Et_2O, 1 1 1) gave a mixture of **2**–**4** and the known compounds described in the text Separation by HPLC (RP 8, MeOH–H_2O, 3 2, flow rate *ca* 3 ml/min and 300 bar) gave a mixture of **4** and onoseriolide (I, R_t 10 1 min), a mixture of the latter, **2** and **3** (II, R_t 11 4 min) and a mixture of **2**, **3**, alantolactone and onoseriolide (III, R_t 12 2 min) TLC of I (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) gave 4 mg of the latter and 2 5 mg **4** (R_f 0 3) TLC of II (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) gave 2 5 mg onoseriolide, 2 1 mg **3** and 1 mg **2**, while TLC of III (SiO_2, $AgNO_3$-coated, Et_2O–petrol, 2 3, 2 developments) afforded 2 mg onoseriolide, 3 mg alantolactone and 2 5 mg **3**

1,2,4,15-*Tetradehydro*-4,5-*dihydrosteiractinolide* (**4**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1770 (γ-lactone), MS *m/z* (rel int) 230 146 $[M]^+$ (5) (calc for $C_{15}H_{18}O_2$ 230 146), 215 $[M-Me]^+$ (2 5), 173 $[215-C_3H_6]^+$ (100), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS as internal standard) δ 5 39 *dt* (H-1), 5 52 *dt* (H-2), 2 89 *br d* and 2 74 *br dd* (H-3), 2 10 *br d* (H-5), 2 10 *br dd* (H-6), 1 93 *ddd* (H-6'), 3 33 *m* (H-7), 4 80 *ddd* (H-8), 2 15 *br d* (H-9), 1 33 *dd* (H-9'), 6 32 *d* and 5 54 *d* (H-13), 0 80 *s* (H-14), 4 93 and 4 71 *br s* (H-15), [*J* (Hz) 1, 2 = 10, 1, 3 = 2, 2, 3 = 3 5, 5, 6' = 6, 6' = 6', 7 = 12, 5, 6 = 6, 7, 8 = 7, 3, 17 = 3 5, 7, 13' = 3, 8, 9 ~ 7, 8, 9' = 11, 9, 9' = 13]

Callitrin [7] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5 75 *dd* (H-1), 4 93 *dd* (H-2*c*), 4 89 *dd* (H-2*t*), 4 89 *dq* (H-3), 4 64 *br s* (H-3'), 1 67 *br d* (H-5), 2 06 *m* (H-6), 2 30 *m* (H-7), 4 60 *ddd* (H-8), 1 90 *dd* (H-9), 1 40 *dd* (H-9'), 2 56 *dq* (H-11), 1 20 *d* (H-13), 1 00 *s* (H-14), 1 72 *br s* (H-15), [*J* (Hz) 1, 2*c* = 10, 1, 2*t* = 17, 2*c*, 2*t* = 1, 3, 5 = 3, 15 = 1 5, 5, 6 = 12, 7, 8 = 8, 7, 11 = 12, 8, 9 = 6, 8, 9' = 11, 9, 9' = 14, 11, 13 = 7]

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FURTHER CADINENE DERIVATIVES FROM *HETEROTHECA LATIFOLIA*

FERDINAND BOHLMANN, CHRISTIAN WOLFRUM, JASMIN JAKUPOVIC, ROBERT M KING* and HAROLD ROBINSON*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany, *Smithsonian Institution, Department of Botany, Washington, D C 20560, U S A

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Key Word Index—*Heterotheca latifolia*, Compositae, sesquiterpenes, cadinene derivatives

Abstract—A reinvestigation of the aerial parts of *Heterotheca latifolia* afforded four new cadinene derivatives

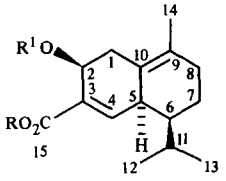
So far the chemical investigations of *Heterotheca* species have shown that cadinene derivatives are characteristic for this genus [1, 2] A reinvestigation of the aerial parts of *H latifolia* Buckley afforded in addition to compounds isolated previously [1] the cadinene derivatives **1**–**4** which were isolated as their methyl esters (**1a**–**4a**) The structures of **1a** and **2a** could be deduced from the ^{1}H NMR spectral data (Table 1) which were close to those of the corresponding esters of **1a** [1] Also the ^{13}C NMR spectrum (see Experimental) supported the structure of **1a** which finally was established by saponification of the corresponding acetate [1] After addition of diazomethane, a methyl ester was obtained which was identical with **1a** The structures of **3a** and **4a** also could be deduced from the ^{1}H NMR spectra (Table 1) The presence of hydroperoxides followed from the low-field broadened singlets at δ 7 45 and 7 28, respectively, while several signals were close to those of methyl-13-hydroxy-δ-cadinen-15-oate [1] However, in the spectrum of **3a** the Δ^9 bond was replaced by a 9,14-double bond, which followed from the typical signals of exocyclic olefinic protons Their chemical shifts already indicated that the hydroperoxy group

Table 1 ^{1}H NMR spectral data of **1a–4a** (400 MHz, $CDCl_3$, TMS as int standard)

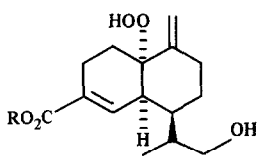
	1a	C_6D_6	**2a**	**3a**	**4a**
H-1	2 99 *dd*	2 99 *dd*	3 09 *dd*	2 14 *m*	5 86 *br dd*
H-1′	1 95 *m*	1 83 *m*	1 80 *br d*	1 70 *br d*	
H-2	4 65 *br s*	4 79 *br s*	4 24 *br s*	2 37 *m*	3 10 *dddd*
H-2′					3 01 *dddd*
H-4	7 12 *d*	7 21 *d*	7 15 *d*	7 08 *ddd*	7 25 *ddd*
H-5	2 66 *br d*	2 50 *br d*	2 63 *br d*	2 98 *br dd*	3 30 *dddd*
H-6	1 25 *m*	1 16 *dddd*	1 28 *m*	1 28 *m*	1 3 *m*
H-7		1 50 *br d*		1 73 *m*	1 67 *m*
H-7′		1 09 *dddd*		1 29 *m*	1 48 *m*
H-8	2 03 *m*	1 89 *br dd*	2 05 *br dd*	2 47 *ddd*	2 22 *m*
H-8′		1 82 *br d*	1 92 *br d*	2 14 *m*	2 12 *ddd*
H-11	2 12 *dqq*	1 98 *dqq*	2 13 *dqq*	2 14 *dqq*	2 22 *dqq*
H-12	0 99 *d*	0 84 *d*	0 97 *d*	1 01 *d*	1 06 *d*
H-13	0 82 *d*	0 69 *d*	0 81 *d*	3 78 *dd*	3 82 *dd*
H-13′				3 53 *dd*	3 54 *dd*
H-14	1 75 *br s*	1 75 *br s*	1 71 *br s*	5 15 *dd*	1 51 *s*
				4 97 *dd*	
OMe	3 78 *s*	3 59 *s*	3 76 *s*	3 74 *s*	3 84 *s*
			3 42 *s*	—	—
OOH	—	—	—	7 45 *br s*	7 28 *br s*

J (Hz) compounds **1a** and **2a** 1, 1′ = 15, 1, 2 = 2 5, 1′, 2 ~ 2, 4, 5 = 2, 5, 6 = 8, 7, 7′ = 12, 7, 8 = 12, 7′, 8 = 4 5, 8, 8′ = 15, 11, 12 = 11, 12 = 11, 13 = 7, compound **3a** 1, 1′ = 14, 2, 4 = 2′, 4 = 1 5, 4, 5 = 4, 5, 6 = 10, 7, 8 = 7′, 8 = 4, 8, 8′ = 14 5, 8, 14 = 14, 14′ ~ 1 5, 11, 13 = 5, 11, 13′ = 7, 13, 13′ = 10 5, compound **4a** 1, 2 = 1, 2′ = 3 5, 2, 2′ = 22, 3, 4 = 1 5, 2, 5 = 7, 2′, 4 = 1, 2′, 5 = 7, 4, 5 = 4, 5, 6 ≈ 10, 7, 8 = 7′, 8 = 3, 8, 8′ = 14, 11, 13 = 6, 11, 13′ = 8, 13, 13′ = 10

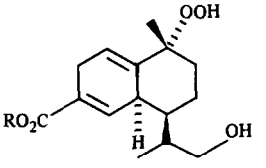
most likely was at C-10 Though only one of the H-8 signals was not overlapped, the clear couplings of this one showed that H-8′ was coupled with H-14 Irradiation of the signal at δ2 22 collapsed the methyl doublet to a singlet and the H-13 double doublets to doublets The oxygen function at C-10 is most likely α as the H-6 signal is shifted downfield when compared with that in the cadinen-3-enes The presence of a 1(10), 3-diene in the hydroperoxide **4a** clearly followed from the downfield shift of the signals of H-2 and H-5 A large coupling (~ 7 Hz) between H-2 and H-5 further supported the presence of such a diene As in this case the signal of the olefinic methyl at C-9 was replaced by a singlet at δ1 51, the hydroperoxy group was at C-9 Inspection of a model indicated that an α-orientation was more likely as the attack of oxygen from the α side of methyl-13-hydroxy-δ-cadinen-15-oate seems to be favoured for steric reasons Compounds **3** and **4** are probably formed by reaction of 13-hydroxy-δ-cadinen-15-oic acid [1] with oxygen This investigation again showed the taxonomic importance of cadinene derivatives for distinguishing the genus *Heterotheca* from other related genera



	1	**1a**	**2**	**2a**
R	H	Me	H	Me
R^1	H	H	Me	Me



3 R=H
3a R=Me



4 R=H
4a R=Me

EXPERIMENTAL

The air-dried aerial parts (210 g) (voucher RMK 9311, collected in DE, U S A) were worked up in the usual fashion [3] and one-eighth of the CC fraction with Et_2O (280 mg) was esterified with CH_2N_2 TLC (Et_2O–petrol, 1 1) gave 85 mg of the esters of **1a** (2-*O*-isobutyrate, 2-*O*-isovalerate, 2-methylbutyrate), 52 mg of the acetate of **1a**, a mixture of **1a** and **3a** as well as a mixture of **3a** and **4a** Both mixtures were separated by TLC (Et_2O–petrol, 4 1). The less polar fraction afforded 10 mg **1a** (R_f 0 62) and 5 mg **3a** (R_f 0 53), and the more polar fraction gave 12 mg **4a** (R_f 0 45) One-sixth of the CC fraction with Et_2O–MeOH, 9 1 (250 mg) was esterified with CH_2N_2 TLC (Et_2O–petrol, 7 3) gave a mixture of **1a** and **2a** as well as 60 mg **1a** and 50 mg methyl-13-

hydroxy-δ-cadinen-15-oate TLC of the mixture of **1a** and **2a** (Et_2O–petrol, 3 2) gave 70 mg **2a** (R_f 0 70). Known compounds were identified by comparison of the 400 MHz ^1H NMR spectra with those of authentic material and by co-TLC

Methyl 2β-hydroxy-δ-cadinen-15-oate (**1a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3560 (OH, hydrogen bonded), 1710, 1655 (C=CCO_2R), MS *m/z* (rel int) 264 173 $[M]^+$ (24) (calc for $C_{16}H_{24}O_3$ 264 173), 246 $[M-H_2O]^+$ (20), 203 $[246-CHMe_2]^+$ (80), 187 $[246-CO_2Me]^+$ (100), 176 $[246-H_2C{=}CHCHMe_2$, RDA$]^+$ (30), ^{13}C NMR (C_6D_6, C-1–C-15) 33 2*t*, 65 4*d*, 124 0*s*, 144 4*d*, 41 0*d*, 44 0*d*, 21 7*t*, 34 6*t*, 129 6*s*, 133 0*s*, 27 0*d*, 19 1*q*, 21 5*q*, 15 7*q*, 167 5*s*, 51 3*q* (OMe)

Preparation of **1a** *from the acetate* To 23 mg 2β-acetoxy-δ-cadinen-15-oic acid in 2 ml MeOH, 0 5 ml 2 N KOH was added After 2 hr the crude acid was esterified with CH_2N_2 TLC (Et_2O–petrol, 4 1) gave 16 mg **1a** (R_f 0 60) identical with the methyl ester obtained from the natural product (^1H NMR and co-TLC)

Methyl 2β-methoxy-δ-cadinen-15-oate (**2a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1710, 1650 (C=CCO_2R), MS *m/z* (rel int) 278 188 $[M]^+$ (11) (calc for $C_{17}H_{26}O_3$ 278 188), 260 $[M-H_2O]^+$ (7), 246 $[M-MeOH]^+$ (51), 235 $[M-CHMe_2]^+$ (9), 203 $[235-MeOH]^+$ (100), 187 $[246-CO_2Me]^+$ (91), 176 $[246-H_2C{=}CHCHMe_2$, RDA$]^+$ (45), 145 $[187-C_3H_6]^+$ (76)

Methyl 13-hydroxy-10α-peroxy-cadina-3,9(14)-dien-15-oate (**3a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1710 (C=CCO_2R), MS (CI, isobutane) *m/z* (rel int) 297 $[M+1]^+$ (62) (calc for $C_{16}H_{24}O_5+1$), 279 $[297-H_2O]^+$ (100), 263 $[297-H_2O_2]^+$ (57), 247 $[279-MeOH]^+$ (38), EI 262 $[M-H_2O_2]^+$ (21), 231 $[262-OMe]^+$ (32), 203 $[231-CO]^+$ (42), 61 (100),

$$[\alpha]_{24°}^{\lambda} = \frac{578 \quad 546 \quad 436\,nm}{-10 \quad -19 \quad -63} \; CHCl_3,\ c = 0\,3$$

Methyl 13-hydroxy-9α-peroxy-cadina-1(10),3-dien-15-oate (**4a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1720 (C=CCO_2R), MS (CI, isobutane) *m/z* (rel int) 297 $[M+1]^+$ (10), (calc for $C_{16}H_{24}O_5+1$), 279 $[297-H_2O]^+$ (21), 263 $[297-H_2O_2]^+$ (14), 247 $[279-MeOH]^+$ (8), 209 $[297-C_5H_{12}O]^+$ (100), EI 262 $[M-H_2O_2]^+$ (2 5), 230 $[262-MeOH]^+$ (40), 61 (100)

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EUDESMANOLIDES FROM *ARTEMISIA JUDAICA*

MOHAMED A METWALLY, JASMIN JAKUPOVIC, MANSOUR I YOUNS* and FERDINAND BOHLMANN

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, W Germany, *Department of Chemistry, Faculty of Science, University of Assuit, Egypt

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Key Word Index—*Artemisia judaica*, Compositae, sesquiterpenes, eudesmanolides

Abstract—The aerial parts of *Artemisia judaica* afforded in addition to known compounds a hydroperoxide corresponding to vulgarin as well as an isomer of the latter The configurations of these lactones have been established by NOE difference spectroscopy

The aerial parts of *Artemisia judaica* L have been investigated previously [1–3], and we have studied now material collected in Egypt In addition to tauremisin (= vulgarin, **1**) [4, 5] isolated previously from this species [1, 2], we obtained the isomer **3** and the hydroperoxide **2** and in addition ethyl cinnamate, α-pinene, chrysanthenone, camphor, piperitone, verbenol and the hydroperoxide **4** isolated so far only from *Artemisia inculta* [6] The structure of **2** could be deduced from the spectral data of the product obtained by triphenyl phosphine-reduction which were identical with those of **1** The spectral data of **3** (Table 1) were close to those of **1** However, the chemical shifts of H-14 and H-15 differed characteristically. NOE difference spectroscopy with both **1** and **3** clearly indicated the configuration at C-4 While **1** gave clear NOEs between H-14 and H-15 and H-6, the isomer **3** showed NOEs between H-14 and H-6 as well as between H-15 and H-5 and H-3 The configuration of **3** has been assigned previously for a lactone named barrelin [7] Comparison of the ^{13}C NMR data, however, show that this lactone most likely is identical with vulgarin though the mp and the optical rotation differ The published ^{13}C NMR data of **1** [8] differ only in the chemical shift of C-14 which was erroneously assigned (δ 22 7 is the value of C-8 and not of C-14 which is 19 7) The ^{13}C NMR data of **1** and **3** show some clear differences In particular, the C-15 signal is