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),

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

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*

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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

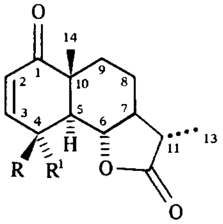
The aerial parts of *Artemisia judaica* L have been investigated previously [1–3], and we have studied now material collected in Egypt In addition to tauremisin (= vulgarin, **1**) [4, 5] isolated previously from this species [1, 2], we obtained the isomer **3** and the hydroperoxide **2** and in addition 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 (δ22 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

Table 1 ^{1}H and ^{13}C NMR spectral data of compounds 1–3 (400 MHz, $CDCl_3$, TMS as int standard)

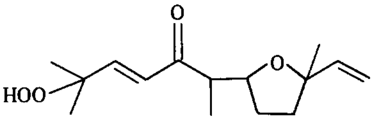
	1*	2	3		1	3
H-2	5 90*d*	6 00*d*	5 87*d*	C-1	201 6*s*	203 1
H-3	6 61*d*	6 74*d*	6 50*d*	C-2	125 7*d*	125 3
H-5	2 43*d*	2 82*d*	2 02*d*	C-3	151 7*d*	150 2
H-6	4 16*dd*	4 12*dd*	4 33*dd*	C-4	70 1*s*	68 2
H-7	1 67*dddd*	1 66*dddd*	1 66*dddd*	C-5	54 7*d*	51 0
H-8α	1 98*dddd*	1 98*dddd*	2 0*m*	C-6	79 6*d*	79 2
H-8β	1 56*dddd*	1 55*m*	1 51*m*	C-7	52 5*d*	52 3
H-9α	1 47*ddd*	1 47*m*		C-8	22 7*t*	22 8
H-9β	2 03*ddd*	2 04*ddd*	2 0*m*	C-9	34 3*t*	32 5
H-11	2 35*q*	2 33*dq*	2 33*dq*	C-10	46 2*s*	45 9
H-13	1 23*d*	1 21*d*	1 58*d*	C-11	40 6*d*	40 1
H-14	1 19*s*	1 22*s*	1 31*s*	C-12	178 1*s*	179 0
H-15	1 54*s*	1 47*d*	1 58*s*	C-13	12 4*q*	12 5
				C-14	19 7*q*	20 6
				C-15	23 8*q*	31 7

*Chemical shift slightly varying by concentration

J (Hz) 2, 3 = 10, 5, 6 = 11, 6, 7 = 10, 7, 8α = 3 5, 7, 8β = 12, 7, 11 = 12, 8α, 8β = 13, 8α, 9α = 3 5, 8α, 9β = 3 5, 8β, 9α = 12 5, 8β, 9β = 3, 9α, 9β = 14, 11, 13 = 7



	1	2	3
R	Me	Me	OH
R^1	OH	OOH	Me



4

shifted downfield, most likely due to its quasi-equatorial orientation

EXPERIMENTAL

The air-dried aerial parts (220 g, collected from Wadi Hof, Egypt, March 1984) was worked-up in the usual fashion [9] CC fractions were as follows 1 (petrol), 2 (Et_2O–petrol, 1 20), 3 (Et_2O–petrol, 1 10), 4 (Et_2O–petrol, 1 4) and 5 (Et_2O and Et_2O–MeOH, 10 1) TLC of fraction 1 (petrol) gave 50 mg α-pinene and of fraction 2 (Et_2O–petrol, 1 15), 3 mg chrysanthenone, 2 mg camphor, 2 mg ethyl cinnamate and 10 mg piperitone TLC of fraction 3 (Et_2O–petrol, 1 4) gave 5 mg piperitone and 5 mg verbenol and TLC of fraction 4 (Et_2O–petrol, 9 11) 5 mg **4** TLC of fraction 5 (Et_2O–petrol, 9 1) gave 5 mg **3** (R_f 0 52), 3 mg **1** (R_f 0 40) and 5 mg **2** (R_f 0 35) Known compounds were identified by comparing the spectral data, especially the 400 MHz ^{1}H NMR spectra, with those of authentic material Due to the small amounts **2** and **3** could not be induced to crystallize though they were homogeneous by ^{1}H NMR spectroscopy

4α-Hydroperoxy-desoxyvulgarin (**2**) (*gum*) ^{1}H NMR see Table 1 To 5 mg **2** in 0 5 ml $CDCl_3$, 20 mg triphenyl phosphine was added After 10 min at room temp the ^{1}H NMR spectrum had completely changed to that of **1** TLC (Et_2O) gave **1**, identical with authentic vulgarin

4-Epi-vulgarin (**3**) (*gum*) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600, 3440 (OH), 1790 (γ-lactone), 1690 (C=CC=O), MS *m/z* (rel int) 264 136 $[M]^+$ (6) (calc for $C_{15}H_{20}O_4$ 264 136), 249 $[M-Me]^+$ (12), 98 (57), 55 (100)

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