Phytochemistry, 1978, Vol 17, pp 471-474 Pergamon Press Printed in England

NEW GERMACRANOLIDES FROM *ISOCARPHA* SPECIES*

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(*Received* 23 *July* 1977)

Key Word Index—*Isocarpha oppositifolia*; *I. atriplicifolia*; Compositae; heliangolides; sesquiterpene lactones; dihydroeuparine derivative.

Abstract—The investigation of two *Isocarpha* species has yielded eight new germacranolides most of them belonging to the heliangolides. In addition to known *p*-hydroxyacetophenone-derivatives, a new dihydroeuparine derivative was isolated. The chemotaxonomical aspects are discussed.

INTRODUCTION

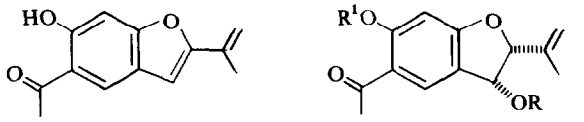
In a first note [1] the taxonomic position of the Tropical American genus *Isocarpha* was discussed in connection with the constituents isolated from *I. oppositifolia*. As only very little material was available we have investigated the same species again as well as a second one to establish the relationship of the constituents with those of other representatives of the tribe *Eupatorieae*.

RESULTS

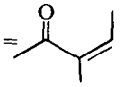
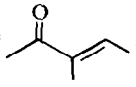
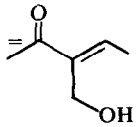
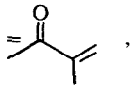
The roots of *I. oppositifolia* yielded euparine (**1**) together with three dihydro derivatives (**2–4**), the last one has not been isolated previously. Compounds **2** and **3** have also been obtained from the aerial parts. The aerial parts of the plant also yielded a series of sesquiterpene lactones of the general heliangolide type. These were related to compounds known in various Eupatorieae, including similar lactones in species of *Eupatorium* [2] and various lactones including provincialin (**6**) from species of *Liatris* [3]. One of the *I. oppositifolia* compounds was chromolaenide (**5**) which was previously isolated from *Chromolaena glaberrima* [4]. The other lactones of the series are new natural products.

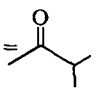
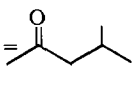
Of the new sesquiterpene lactones, the most abundant had the molecular formula $C_{22}H_{28}O_8$; the molecular ion could not be detected, but the fragment for M-H_2O showed the expected composition and the acetylation product gave a molecular ion at *m/e* 504 ($C_{26}H_{32}O_{10}$). At room temperature the PMR-signals of the lactone were not so well resolved as in the spectrum of **5**. However, the similarity of the spectra was obvious. At 72° in deuteriobenzene the signals were much sharper and the

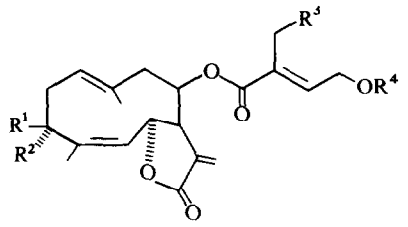
* Part 120 in the series 'Naturally Occurring Terpene Derivatives'; for part 119 see: Bohlmann, F. and Knoll, K. H. (1978) *Phytochemistry* **17**, 461.



	2	3	4
R	Ang*	Ang*	Tigl*
R^1	H	Me	H

* Ang =  , Tigl =  , TiglOH =  , Meacr =  ,

i-Bi =  , *i*-Val = 

2 

	5	6	7	8	9	10
R^1	OAc	OAc	OAc	OAc	H	OAc
R^2	H	H	H	H	OAc	H
R^3	H	OTiglOH	OH	OTigl	OAc	H
R^4	H	H	H	H	H	OAc

Table 1. PMR-data of compounds **7**–**12**, δ-values in ppm, 270 MHz, TMS as internal standard

	7 ($CDCl_3$)	C_6D_6 72°	**8** (C_6D_6)	**9** (C_6D_6)	**10** ($CDCl_3$)	**11** ($CDCl_3$)	**12** ($CDCl_3$)
1-H	*m* 5.25	*d*(*br*) 4.90*	*m* 4.71	*dd*(*br*) 4.60	*m* 5.25	*dd*(*br*) 4.94	*m* 4.90
2-H†		*ddd* 1.91	*d*(*br*) 1.98	*ddd* 2.74		*ddd* 2.32	*d*(*br*) 2.34
2'-H		*ddd* 2.48	*ddd* 2.44	*m* 1.90		*ddd* 2.50	*m* 2.50
3-H	*m* 5 25	*dd* 5.14	*dd* 5.13	*dd* 5 69	*dd* 5.26	*dd*(*br*) 4.33	*dd*(*br*) 5.24
5-H		*dq* 4.91	*dq* 4.80	*d*(*br*) 4.86	*d*(*br*) 5 20	*d*(*br*) 4.82	*m* 4.90
6β-H	*d*(*br*) 5.95	*dd* 5.95	*dd* 5.95	*d*(*br*) 5.35	*d*(*br*) 5.88	*dd* 5.17	*dd* 5.09
7α-H	*s*(*br*) 3.01	*ddd* 2.45	*s*(*br*) 2.25	*s*(*br*) 2.33	*s*(*br*) 2.99	*ddd*(*br*) 2.90	*m* 2.90
8α-H	*m* 5.25	*dd*(*br*) 5.18	*s*(*br*) 5.21	*dd*(*br*) 5.16	*s*(*br*) 5.30	*d*(*br*) 5.83	*s*(*br*) 5.85
9-H	*d*(*br*) 2.45	*dd* 2.07	*d*(*br*) 2.04	*dd* 1.94	*d*(*br*) 2.45	*d*(*br*) 2 32	*d*(*br*) 2.34
9'-H	*d*(*br*) 2.75	*dd* 2.69	*d*(*br*) 2.68	*dd* 2.65	*d*(*br*) 2 74	*dd* 2.85	*dd* 2.85
13-H	*d* 6.34	*d* 6.27	*d* 6.32	*d* 6.29	*d* 6.37	*d* 6.25	*d* 6.27
13'-H	*d* 5.80	*d* 5.30	*d* 5.21	*d* 5.20	*d* 5 77	*d* 5.59	*d* 5.60
14-H	*s*(*br*) 1.78	*s*(*br*) 1.70	*s*(*br*) 1.75	*d* 1.64	*s*(*br*) 1.78	*s*(*br*) 1.48	*s*(*br*) 1.49
15-H	*s*(*br*) 1.82	*d* 1.54	*s*(*br*) 1.51	*s*(*br*) 1.92	*s*(*br*) 1.81	*s*(*br*) 1.76	*s*(*br*) 1.77
18-H	*t* 6.91	*t* 6.99	*t* 7.16	*t* 7.16	*t* 6.95	*t* 7.08	*t* 7.00
19-H	*d*(*br*) 4.38	*d*(*br*) 4.08	*dd* 4.14	*d*(*br*) 4.08	*d* 4.87	*ddd* 4.56	
			dd 4.04			*ddd* 4.46	*m* 4.90
20-H	*s*(*br*) 4.31	*s*(*br*) 4 28	*d* 5.00	*d* 4.78	*d* 4.81	*d* 5.01	
			d 4.92	*d* 4.70	*d* 4.75	*d* 4.89	
OCOR	*s* 2.12	*s* 2 04	*s* 2.07	*s* 1.88	*s* 2.11	*qq* 6.77	*qq* 6.78
			qq 6.90	*s* 1.67	*s* 2.05	*d* 1.78	*s*(*br*) 1.77
			dq 1.41		*s* 2.04	*s*(*br*) 1.80	
			s(*br*) 1.75				

* *J*(Hz) compounds **7**, **8** and **10**. 1,2 = 6; 1,2' = 9; 2,2' = 15; 2,3 = 3.5; 2',3 = 2.5; 5,6 = 11; 5,15 = 1.3; 6,7 = 2.3; 7,13 = 2.5; 7,13' = 2; 8,9 = 3; 8,9' = 3.5; 9,9' = 14; 18,19 = 6 compound **8**: 19,19' = 15; 19,OH = 6; 20,20' = 12; (Tigl:vicinal compound 7, allylic 1) compound **9**: 1,2 = 8; 1,2' = 7; 2,2' = 13; 2.3 = 12; 2',3 = 5; 5,15 = 1; 9,9' = 14; 20,20' = 12 compounds **11** and **12** 1,2 = 12; 1,2' = 4; 2,2' = 12; 2,3 = 8; 2',3 = 4; 5,6 = 10; 6,7 = 9; 8,9 = 4; 9,9' = 15; 18,19 = 6.5; 19,19' = 16; 19, OH = 5.

† In all cases 2 and 9 are probably α and 2 and 9β-H-signals.

interpretation using double irradiation experiments was possible for all signals (Table 1). The data were in good agreement with the structure **7**, a hydroxy derivative of **5**. A second lactone showed a very similar PMR-spectrum. The only difference was the presence of additional ester signals indicating that the *cis*-sarracinic acid part was esterified further with tiglic acid. The structure, therefore, should be **8**. A third heliangolide differed from **7** and **8** in the stereochemistry at C-3. While in the 3β-acetoxy-compounds **7** and **8** the coupling constants $J_{2,3}$ were 3 and 3 Hz, in the third lactone they were 12 and 5 Hz, a clear indication of the α-orientation of the acetate group. Also the ester residue at C-8 was modified. The PMR-data showed that it was an acetate of *cis*-sarracinic acid ester. Therefore the structure of this lactone could be **9**. Probably **7** and **8** both have the same conformation with a 'quasi'-axial orientated oxygen function at C-3 and C-9, while in **9** the C-3 function is equatorial. The resulting angles would be in good agreement with the observed coupling constants. The last lactone was a *trans,trans*-germacranolide as shown by the couplings of 6-H (J = 10 and 9 Hz). All the other data were very similar to those of **8** showing that it was the 3-desacetyl-4, 5-*trans*-isomer **11**. Also the diacetate **12** established this assumption.

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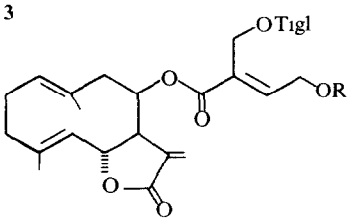


11: R = H
12: R = Ac

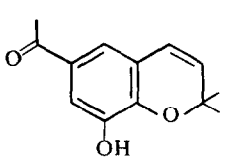
Table 2. PMR data of compounds **16**–**19** (δ-values, TMS as internal standard, $CDCl_3$)

	16	**17**	**18**	**19**
2-H	*s* 5.59	*s* 5.59	*s* 5 59	*s* 5.59
5-H	*dq* 5.94*	*dq* 5 94	*dq* 5.94	*dq* 5.93
6-H	*dq* 5.28	*dq* 5.34	*dq* 5.28	*dq* 5.34
7-H	*m* 3.70	*m* 3.67	*m* 3.70	*m* 3.65
8-H	*ddd* 5.18	*ddd* 5.21	*ddd* 5.18	*ddd* 5.23
9α-H	*dd* 2.55	*dd* 2.48	*dd* 2.52	*dd* 2.48
9β-H	*dd* 2.31	*dd* 2 24	*dd* 2 30	*dd* 2.22
13-H	*d* 6 35	*d* 6.35	*d* 6.33	*d* 6.36
13-H	*d* 5.67	*d* 5.67	*d* 5.65	*d* 5.68
14-H	*s* 1.48	*s* 1.48	*s* 1 48	*s* 1.48
15-H	*dd* 2.07	*dd* 2.07	*dd* 2.07	*dd* 2.07
OCOR	*s*(*br*) 6.02	*qq* 2.46	*qq* 6.76	*dd* 2.09
	dq 5.60	*d* 1.08	*dq* 1.78	*m* 1.98
	s(*br*) 1.86	*d* 1.07	*s*(*br*) 1.74	*d* 0.90
		d 0 87		

* *J*(Hz): 5,6 = 2.5; 5,15 = 1.5; 6,7 = 2; 6,15 = 1 5; 7,8 = 3; 7,13 = 3; 7,13' = 2.5; 8,9α = 5; 8,9β = 3; 9α,9β = 15; compound **18**. 18,19 = 7, 18,20 = 19,20 = 1; compound **19**. 18,19 = 7.

Though the relative positions of the ester groups at C-3 and C-8 in **7**, **8** and **9** were not really established their co-occurence with **11** indicates that the situation is most probably the same in both types. As in the case of **5** partial saponification was unsuccessful, however small changes in the chemical shift of the 8α-H on acetylation of **5** without any change of the position of the 3α-H-signal further support our assumption [4].

The roots of *I. atriplicifolia* also contained **1** together with further *p*-hydroxyacetophenone derivatives (**13**–**15**). The structure of **15** clearly followed from the PMR-data. The more polar fractions again contained sesquiterpene



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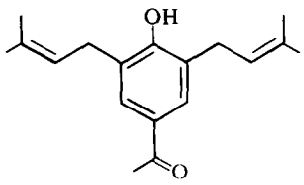

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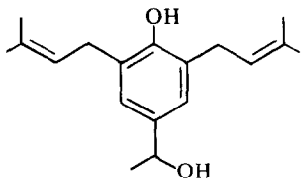

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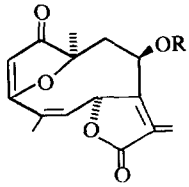

	16	17	18	19	20
R	Meacr	*i*-Bu	Tigl	*i*-Val	H

lactones all very closely related to budlein-A [5, 6]. However the 15-hydroxy group was missing in all four lactones, which differed only in the ester residues. The spectroscopic data showed that the 8β-hydroxy group was esterified with methylacrylic-, isobutyric-, angelic- and isovaleric acid leading to the structures **16–19**. For the unisolated 8β-hydroxy parent compound (**20**) we propose the name atripliciolide. The 8α-epimeric compounds (ciliarin and orizabin), closely related to **16–19**, which first were formulated as Δ^4-*trans*-isomers, have to be changed to heliangolides as shown with the structure elucidation of woodhousin [7].

DISCUSSION

In the past *Isocarpha* has been placed in various tribes of the family *Compositae* including the Eupatorieae, but tradition of the last 100 years has assigned the genus to the Heliantheae. The recent use of numerous anatomical [8] and cytological [9] characters including chromosome number, spore size, anther structure and details of the achene has dictated a proper relationship of *Isocarpha* in the Eupatorieae with no particularly close relation to Heliantheae other than that seen in all members of the Eupatorieae. Features shared by *Isocarpha* and the Heliantheae have been shown to reflect convergent evolution or more general traits reflecting the position of both the tribes Eupatorieae and Heliantheae in the subfamily Asteroideae. In view of its relationship the chemistry of *Isocarpha* holds particular interest.

Both the basic types of germacranolides isolated from *Isocarpha* are known from both tribes. The heliangolides (**5**, **7–9**) obtained from *I. oppositifolia* include one shared with the Eupatorian genus *Chromolaena* [4] and others from *I. oppositifolia* resemble those found in other Eupatorieae such as *Liatris* [3] and *Eupatorium* [2]. In the Heliantheae, heliangin, a similar lactone in the genus *Helianthus* [10], is an epoxide and has no further oxygen function in the ester side chain. The atripliciolide derivatives extracted from *I. atriplicifolia* (**16–19**) are of a type also found in *Liatris* in the Eupatorieae [11] but also in an *Eremanthus* species (Vernonieae) [12] and from *Helianthus* and *Viguiera* species (Heliantheae) [7].

The *p*-hydroxy acetophenone derivatives from *Isocarpha* also represent types widely distributed in the Compositae. The benzofurans isolated from both species of *Isocarpha*, however, are a type particularly common in the Eupatorieae [4] and comparatively rare in the Heliantheae. Reports from the Heliantheae are from the genera *Helianthella* [13], *Encelia* [14] and *Flourensia* [15] which are all placed with *Helianthus* in the subtribe Helianthineae. No benzofurans are reported from the subtribe Galinsoginae of the Heliantheae, the subtribe in which *Isocarpha* has been placed in one recent treatment [16]. *Isocarpha* would also be out of place in the Helianthineae by the lack of both style structure [17] and acetylenes typical of that subtribe [18]. In both these respects *Isocarpha* is like other genera of the Eupatorieae.

EXPERIMENTAL

The air dried plant material (collected in Guatemala, voucher RMK 7365 and RMK 7376) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by repeated TLC (Si gel, GF 254). Known compounds were identified by comparison of the PMR- and IR-spectra with those of authentic samples.

Isocarpha oppositifolia (*L.*) *R. Br.* 45 g roots afford 50 mg **1** [14], 30 mg **2** [19], 20 mg **3** [19] and 6 mg **4** (Et_2O–petrol, 1.3). 80 g of aerial parts yielded 15 mg **2**, 20 mg **3**, 5 mg **5**, 9 mg **8** (MeOH–Et_2O, 1:20), 40 mg **9** (MeOH–Et_2O, 1.20), 35 mg **11** (MeOH–Et_2O, 1:20) and 110 mg **7** (MeOH–Et_2O, 1.20).

3α-Tiglinoyloxy-2,3-dihydroeuparin (**4**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. *o*-hydroxyacetophenone 3300–2600, 1640, 1600; C=C CO_2R 1710. MS *m/e* (rel. int.): 316.131 (5, M^+) (calc. for $C_{18}H_{20}O_5$ 316.131); 216 (90, $M-C_4H_7$ CO_2H); 201 (77, $216-{}^{\bullet}CH_3$); 83 (100) $C_4H_7CO^+$; 55 (97, 83–CO). PMR: 13.04 (OH); 7.81 (4-H, *s*); 6.46 (7-H, *s*); 5.15 (2-H, *d*, J = 6); 6.28 (3-H, *d*, J = 6); 1.80 (C(Me)=CH_2, *s(br)*, 5.23 *s(br)*; 5.10 *s(br)*; 2.56 (COMe, *s*); 6.83 (tigl *qq*); 1.78 (*dq*, J = 7, 1); 1.79 *s(br)*.

20-Hydroxychromolaenide (**7**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. OH 3625; γ-lactone 1760; OAc 1740, 1260; C=C CO_2R 1720, 1660. MS *m/e* (rel. int.): 420 (0.1, M^+); 402.168 (7, $M-H_2O$) (calc. for $C_{22}H_{26}O_7$ 402.168); 387 (4, $402-{}^{\bullet}CH_3$) 43 (100, $MeCO^+$).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589}{-118} \quad \frac{578}{-125} \quad \frac{546}{-143} \quad \frac{436\text{ nm}}{-184} \quad (c = 1.1)$$

20 mg of **7** was heated in 2 ml Ac_2O for 1 hr. After evapn and TLC 12 mg of **10** was isolated, colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: γ-lactone 1760; OAc 1750, 1260; C=C CO_2R 1720, 1660. MS *m/e* (rel. int.): 504.220 (0.1, M^+) (calc. for $C_{26}H_{32}O_{10}$ 504.220); 43 (100, $MeCO^+$).

20-Tinglinoyloxy-chromolaenide (**8**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH 3630; γ-lactone 1765; OAc 1750, 1250; C=C CO_2R 1700, 1645. MS *m/e* (rel. int.). 502.220 (3, M^+) (calc. for $C_{27}H_{34}O_9$ 502.220); 402 (1, $M-C_4H_7CO_2H$); 289 (14, $M-RCO_2{}^{\bullet}$); 229 (15, 289–AcOH); 97 (81, H_2C=CH—C(=CH_2)CO^+); 83 (85, $C_4H_7CO^+$); 55 (100, 83–CO); 43 (98, $MeCO^+$).

$$[\alpha]\ \frac{\lambda}{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-95 \quad -99 \quad -114 \quad -205^\circ}\ (c = 0.7)$$

3-epi-20-Acetoxychromolaenide (**9**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. OH 3600; γ-lactone 1760; OAc 1740, 250; C=C CO_2R 1730, 1665. MS *m/e* (rel. int.): 462.188 (0.1, M^+) (calc. for $C_{24}H_{30}O_9$ 462.189); (0.5, M − AcOH 402); 228 (7, 402 − RCO_2H); 97 (56, $H_2C{=}C{-}C(=CH_2)CO^+$); 43 (100, $MeCO^+$).

4,5-trans-3-Desacetyl-20-tiglinoyloxy-chromolaenide (**11**). Colourless crystals, mp 149°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH 3620; γ-lactone 1760; C=C CO_2R 1715, 1645. MS *m/e* (rel. int.). 460.209 (0.5, M^+) (calc. for $C_{25}H_{32}O_8$ 460.210); 360 (1, $M - C_4H_7CO_2H$); (25, M − RCO_2H 246); 228 (35, 246 − H_2O); 97 (81, $H_2C{=}CH{-}C(=CH_2)CO^+$); 83 (100, $C_4H_7CO^+$); 55 (62, 83 − CO). 10 mg **11** was heated with 1 ml Ac_2O for 1 hr. After evapn and TLC 7 mg of **12** was obtained, colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: γ-lactone 1770; OAc 1750, 1230; C=C CO_2R 1720. MS *m/e* (rel. int.): 542 (0.1, M^+) ($C_{29}H_{36}O_{10}$); 83 (100, $C_4H_7CO^+$).

Isocarpha artiplicifolia (*L.*) *R. Br.* 90 g of roots afforded 4 mg **1**, 8 mg **13** [2], 22 mg **14** [13], 6 mg **15**, 6 mg **17**, 9 mg **16**, 9 mg **19** (Et_2O–petrol, 1:1) and 5 mg **18** (Et_2O–petrol, 1:1).

Atripliciolide-tiglate (**18**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. γ-lactone 1770; C=C CO_2R, C=C C=O 1720, 1660, 1585. MS *m/e* (rel. int.). 358.143 (11, M^+) (calc. for $C_{20}H_{22}O_6$ 358.143); (8, M − $C_4H_7CO_2H$ 158); 83 (100, $C_4H_7CO^+$).

Atripliciolide isovalerate (**19**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1} γ-lactone 1770; C=C—C=O 1720, 1660. MS *m/e* (rel. int.): 360.156 (21, M^+) (calc. for $C_{20}H_{24}O_6$ 360.157); 276 (32, M − CH=C=O); $C_4H_9CO^+$ 85 (100).

$$[\alpha]\ \frac{\lambda}{24^\circ} = \frac{589 \quad 578 \quad 546\,nm}{-41 \quad -43 \quad -48^\circ}\ (^8 = 0.8).$$

Atripliciolide-isobutyrate (**17**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. γ-lactone 1770, O COR 1740. MS *m/e* (rel. int.). 346.142 (17, M^+) (calc. for $C_{19}H_{22}O_6$ 346.142); 71 (100, $C_3H_7CO^+$).

Atripliciolide-(2-methylacrylate) (**16**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1} γ-lactone 1770; C=C CO_2R 1720, 1650. MS *m/e* (rel. int.). 344.127 (11, M^+) (calc. for $C_{19}H_{20}O_6$ 344.127); 257 (8, M − $C_3H_5CO_2^\cdot$); 69 (100, $C_3H_5CO^+$).

2,6-Di-(3,3-dimethylallyl)-4-(1-hydroxyethyl)-phenol (**15**). Colourless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}. OH 3620 PMR: 6.99 (2H, *s*, 3 and 5-H) 5.19 (2H, *tq*, J = 7, 1, olef. H), 3.20 (4H, *d(br)*, J = 7, benzylic H); 4.85 (1H, *q*) and 1.75 (3H, *d*, J = 6.5, (CH(OH)Me); 1.86 (6H, *s(br)*, olef. CH_3). MS *m/e* (rel. int.) 274.193 (50, M^+) (calc. for $C_{18}H_{26}O_2$ 274.193); 259 (37, M − $^\cdot CH$); 256 (100, M − H_2O).

Acknowledgements—We are indepted to the Deutsche Forschungsgemeinschaft for the support of this work.

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