*Phytochemistry*, 1980, Vol. 19, pp. 1850–1851. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0801-1851 $02.00/0

# THYMOL DERIVATIVES FROM *DORONICUM HUNGARICUM**

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(*Received* 23 *November* 1979)

**Key Word Index**—*Doronicum hungaricum*; Compositae; new thymol derivatives.

The genus *Doronicum* (tribe Senecioneae) has been investigated before. In addition to benzofurans [1–3] and thymol derivatives [1, 2], a few other types of natural products were isolated, the widespread pentaynene **1** [1–3], an unusual sesquiterpene [3] and from one species a pyrrolizidine alkaloid [4]. The roots of *D. hungaricum* Reichb. (= *D. longifolium* Griseb. et Schenk.) also contain **1**, the benzofurans **3** and **4**, as well as the thymol derivatives **5–8**, all being angelicates not isolated before.

The structures clearly follow from the mass spectra and especially from the $^1$H NMR data (see Table 1). The relative position of the different ester groups in **5–8**, however, can only be assigned by comparison of the observed chemical shifts with those of corresponding esters [1–3]. The aerial parts also contain **6–8** and dehydro-ent-kaurenic acid (**2**). These results again confirm that thymol and benzofurans, especially of type **4**, are characteristic of this genus.

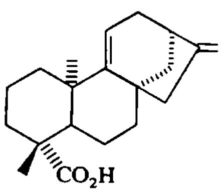
Table 1. $^1$H NMR data of **5–8** (270 MHz, $CDCl_3$, TMS as internal standard)

| | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| 2-H | 6.94 *s*(*br*) | 7.13 *s*(*br*) | 7.13 *s*(*br*) | 7.13 *s*(*br*) |
| 5-H | 7.38 *d* | 7.51 *d* | 7.51 *d* | 7.51 *d* |
| 6-H | 7.07 *d*(*br*) | 7.25 *d*(*br*) | 7.24 *d*(*br*) | 7.24 *d*(*br*) |
| 7-H | 2.37 *s*(*br*) | 5.12 *s*(*br*) | 5.12 *s*(*br*) | 5.12 *s*(*br*) |
| 9-H | 4.54 *d* | 4.54 *d* | 4.54 *d* | 4.54 *d* |
| 9′-H | 4.20 *d* | 4.20 *d* | 4.20 *d* | 4.20*d* |
| 10-H | 3.03 *d* | 3.05 *d* | 3.06 *d* | 3.06 *d* |
| 10′-H | 2.83 *d* | 2.84 *d* | 2.84 *d* | 2.84 *d* |
| OAc | 2.03 *s* | 2.01 *s* | 2.01 *s* | 2.01 *s* |
| OAng | 6.30 *qq* | 6.33 *qq* | 6.33 *qq* | 6.33 *qq* |
| | 2.09 *dq* | 2.09 *dq* | 2.09 *dq* | 2.09 *dq* |
| OCOR | 2.07 *s*(*br*) | 2.07 *s*(*br*) | 2.07 *s*(*br*) | 2.07 *s*(*br*) |
| | — | 2.61 *qq* | 2.43 *tq* | 2.26 *d*(*br*) |
| | — | 1.20 *d* | 1.70 *ddq* | 2.08 *m* |
| | | | 1.52 *ddq* | 0.97 *d* |
| | | | 0.91 *t* | |
| | | | 1.18 *d* | |

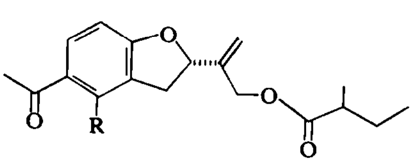
*J* (Hz): 5,6 = 8; 9,9′ = 12.5; 10,10′ = 5; OAng: 3′,4′ = 7; 3′,5′ = 1; OiBu: 7; OMeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; $3'_1,3'_2$ = 14; OiVal: 7.

$Me[C\equiv C]_5CH = CH_2$

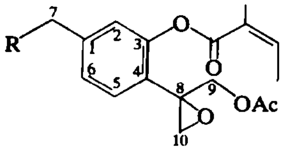
**1**



**2**



**3** R = H
**4** R = OH



**5** R = H
**6** R = OiBu
**7** R = OMebu
**8** R = OiVal

## EXPERIMENTAL

IR: $CCl_4$; $^1$H NMR: 270 MHz; MS: 70 eV. The fresh plant material (voucher 79/1334, from seeds, Bot. Garden, Moscow) was cut and extracted with $Et_2O$–petrol (1:2). Roots (75 g) afforded 1 mg **1**, 4 mg **3**, 20 mg **4**, 30 mg **5** ($Et_2O$–petrol, 1:3), 4 mg **6** ($Et_2O$–petrol, 1:3) and 7 mg **7** and **8** [$Et_2O$–petrol, 1:3, not separated (*ca* 3:1)], while 150 g of aerial parts yielded 10 mg **2**, 14 mg **6–8** (*ca* 3:3:1).

9-*Acetoxy*-8,10-*dihydro*-8,10-*epoxythymol-angelate* (**5**); Colourless oil, IR ($cm^{-1}$): 1740, 1225 ($C{=}CCO_2Ph$, OAc); MS: $M^+$ *m/e* 304.131 (5%) ($C_{17}H_{20}O_5$); $-O{=}C{=}C(Me)CH{=}CH_2$; $-$ HOAc 244 (12); 232 (53); $-RCO_2H$ 204 (55); 204 $-$ ketene 162 (40); $C_4H_7CO^+$ 83 (100).

9-*Acetoxy*-7-*isobutyryloxy*-8,10-*dihydro*-8,10-*epoxythymol-angelate* (**6**). Colourless oil, IR ($cm^{-1}$): 1750, 1235 ($C{=}CCO_2Ph$, OAc, $CO_2R$); MS: $M^+$ *m/e* 390.168 (6%) ($C_{21}H_{26}O$); $-C_4H_7CO_2H$ 290 (20); 290 $-$ HOAc 230 (49); $C_4H_7CO^+$ 83 (100); $C_3H_7CO^+$ 71 (14).

9-*Acetoxy*-7-[2′-*methylbutyryloxy*]- *respectively isovaleryloxy*-8,10-*dihydro*-8,10-*epoxythymol-angelate* (**7** *and* **8**).

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* Part 278 in the series "Naturally Occurring Terpene Derivatives". For Part 277 see Bohlmann, F., Fritz, U., King, R. M., and Robinson, H. (1980) *Phytochemistry* **19**, (in press).

Colourless oil, IR ($cm^{-1}$): 1740, 1230 ($C{=}CCO_2Ph$, OAc, $CO_2R$); MS: $M^+$ $m/e$ 404.184 (3%) ($C_{22}H_{28}O_7$); $-C_4H_7CO_2H$ 304 (30); $C_4H_9CO^+$ 85 (12); $C_4H_7CO^+$ 83 (100).

*Acknowledgements*—We thank the Deutsche Forschungsgemeinschaft for financial support, A. K. D. and M. A. for a DAAD-stipendium.

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*Phytochemistry*, 1980, Vol. 19, pp. 1851-1853. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0801-1851 $02.00/0

# NEW SESQUITERPENES FROM *SENECIO* SPECIES*

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(*Received* 8 *October* 1979)

**Key Word Index**—*Senecio pseudoorientalis; S. vitalis;* Compositae; furanoeremophilane; germacrene derivative.

As a continuation of our investigations of *Senecio* species [1] we have studied the constituents of *S. pseudoorientalis* Schischk. The roots contain β-farnesene (**1**), furanoeremophil-1(10)-ene (**11**) [2], 6β-isobutyryloxy-furanoeremophil-1(10)-ene-9-one (**12**) [2], furanoeremophil-1(2)-en-3-one (**13**) [3, 4], 6α-angeloyloxy-furanoeremophil-9-en-1-one (**14**) [5], 6β-hydroxy-furanoeremophil-9-en-1-one (**15**) [2], 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2]. The 6α-isomer of 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2] was also obtained and was assigned structure **17** by comparing the $^1H$ NMR chemical shifts of the C-6 proton in 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2] and **17** (Table 1). The aerial parts also contained β-farnesene (**1**), furanoeremophil-1(2)-en-3-one (**13**) [3, 4] and 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [5] as well as the diterpene hydrocarbon 9-geranyl-α-terpinene (**5**) [6]. The polar fraction afforded two compounds, which most probably are artifacts formed by oxidation in methanolic solution. The crystalline compound was obviously identical to 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien-12-oic acid lactone (**18**) [7], already isolated from another *Senecio* species. The $^1H$ NMR data are fully in agreement with those reported for 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien-12-oic acid lactone (**18**) [7]. The second compound was identified as the corresponding acid **19**. No molecular ion could be detected in the MS, however, a fragment at $m/e$ 263 ($C_{15}H_{19}O_4$) indicated a probable loss of $\cdot OMe$. Consequently lactonization of **19** yielded 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien(12-oic acid lactone (**18**) [7]. The roots of *S. vitalis* N.E.Br. afforded the hydrocarbons germacrene D (**2**), germacrene C (**3**) and bicyclogermacrene (**4**), the triterpenes oleanoic aldehyde (**6**) [8], oleanoic acid (**7**) [8], lupenone (**8**) [9] and the germacrene derivative 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2], while the aerial parts yielded germacrene D (**2**), bicyclogermacrene (**4**), lupenone (**8**) [9], lupeol (**9**) [8], lutin-5(6)-en-3β-ol (**10**) [10] and the germacrene derivatives 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2], 3β-angeloyloxy-4,5-epoxy-6β-hydroxygermacr-1(10)-ene (**22**) [11], 4,5-epoxy-6β-hydroxy-3β-senecioyloxygermacr-1(10)-ene (**23**) [11] and 4,5-epoxy-6β-hydroxy-3β-tigloyloxygermacr-1(10)-ene (**24**) [2] together with the corresponding ester **21** as deduced from the differences in the $^1H$ NMR spectra (Table 1). While all signals were more or less identical to those of 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2] the typical signals at δ 5.72, 2.16 and 1.73 clearly indicated the nature of the ester group. Acetylation of 4,5-epoxy-6β-hydroxy-3β-senecioyloxygermacr-1(10)-ene (**23**) [11] afforded an acetate, which was identical to the isolated acetate, **21**.

While *S. vitalis* belongs to the succulent species, where the absence of furanoeremophilanes is typical, *S. pseudoorientalis* seems to be closely related to *S. nemorensis*.

## EXPERIMENTAL

IR: $CCl_4$ or $CHCl_3$; $^1H$ NMR: 270 MHz, $CDCl_3$, TMS as int. standard; MS: 70 eV; optical rotation: $CHCl_3$. The fresh plant material was chopped and extracted with $Et_2O$–petrol (1:2). Extracts of aerial parts were first treated with MeOH to remove saturated hydrocarbons. The resulting extracts were separated first by CC (Si gel, grade II) and then by

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* Part 271 in the series "Naturally Occurring Terpene Derivatives". For Part 270 see Bohlmann, F., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19** (in press).