Phytochemistry, Vol. 20, No. 10, pp. 2431–2432, 1981.
Printed in Great Britain.

0031-9422/81/102431-02 \$02.00/0

A HELIANGOLIDE FROM *SCHKUHRIA PINNATA**

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(*Received* 13 *February* 1981)

Key Word Index—*Schkuhria pinnata*; Compositae; sesquiterpene lactones; heliangolides.

Abstract—Re-investigation of the aerial parts of *Schkuhria pinnata* afforded in addition to the heliangolides isolated previously a new one, the structure of which followed from the spectroscopic data.

From the aerial parts of *Schkuhria pinnata* (Lam.) O. Ktze (Compositae, tribe Heliantheae) so far, in addition to widely distributed compounds, the two heliangolides **1** and **3** were reported [1], **1** being present also in *S. virgata* [2]. Furthermore, the unusual aromatic compound schkuhrianol has been isolated [3]. A re-investigation afforded in addition to **1**, **3** and **7** [4, 5] a further heliangolide, which, however, could only be isolated as its diacetate **6**. The molecular formula $C_{29}H_{36}O_{11}$ and the ^{1}H NMR data (Table 1) indicated that a dehydro compound of the diacetate of **3** was present. While most signals were nearly identical with those of **2** and **4**, the ester residue at C-3 was obviously different. A quartet of quartets at 3.26 ppm (in C_6D_6), had to be assigned to the proton of an isopropyl group, which was coupled with methyl groups (1.17 *d* and 1.06 *d*). The chemical shift and the mass spectrum, where loss of $C_5H_8O_3$ could be recognized, indicated the presence of a 2-oxo-isovalerate, while the second ester residue obviously was the same as in **2** and **4**. Though the distribution of the two ester groups could not be established, biogenetic considerations suggest that the same group is attached to C-8 in all three heliangolides.

EXPERIMENTAL

The fresh aerial parts (Botanic Gardens Berlin-Dahlem, voucher 80/1393 A) was extracted with Et_2O–petrol, 1:2 and the resulting extract was separated first by CC (Si gel). The polar fractions (Et_2O–MeOH, 20:1) were further separated by TLC (Si gel, $CHCl_3$–C_6H_6–Et_2O, 1:1:1) affording 30 mg **1**, 10 mg **3**, 2 mg **7** and a mixture of **1**, **3** and **5**, which after acetylation could be separated by HPLC (reversed phase, MeOH–H_2O, 3:2). Finally, in addition to **2** and **4**, 2.5 mg **6** were obtained, colourless gum, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1770 .(γ-lactone), 1745, 1225 (OAc), 1730 ($C{=}CCO_2R$, $-COCO_2R$); MS *m/z* (rel. int.): 560.226 $[M]^+$ (0.5) ($C_{29}H_{36}O_{11}$), 444 $[M - RCO_2H]^+$ (0.5), 344 $[M - R'CO_2H]^+$ (1), 329 $[344 - {}^{\cdot}Me]^+$ (3), 229 $[344 - RCO_2^{\cdot}]^+$ (44), 228 $[344 - RCO_2H]^+$ (44), 157

Table 1. ^{1}H NMR spectral data of compounds **2** and **6** (400 MHz, C_6D_6)

	2 (77°)	**6** (50°)		**2**	**6**
H-1	4.91 *m*	4.83 *m*	H-3′	7.05 *t*	7.05 *t*
H-2	2.50 *ddd*	2.44 *br dd*	H-M′$_1$	4.72 *d*	4.95 *dd*
H-2′	1.94 *ddd*	1.91 *m*	H-4′$_2$		4.85 *dd*
H-3	5.18 *dd*	5.04 *br dd*	H-5′$_1$	4.83 *s*	5.11 *d*
H-5	4.91 *ddq*	4.81 *br d*	H-5′$_2$		5.06 *d*
H-6	5.89 *dd*	5.86 *br d*	H-3″	—	3.26 *qq*
H-7	2.45 *br s*	2.28 *br s*	H-4″	—	1.17 *d*
H-8	5.24 *ddd*	5.21 *dd*	H-5″	—	1.06 *d*
H-9	2.10 *dd*	2.0 *br d*	OAc	1.82 *s*	1.83 *s*
H-9′	2.69 *dd*	2.76 *br dd*		1.72 *s*	1.74 *s*
H-13	6.27 *d*	6.25 *d*		2.07 *s*	
H-13′	5.28 *d*	5.18 *d*			
H-14	1.58 *d*	1.50 *d*			
H-15					

J (Hz): compound **6**: 1,2 = 9.5; 2,2′ = 14; 5,6 = 10; 7,13 = 2.5; 7,13′ = 2; 8,9 = 8,9′ = 3; 9,9′ = 14; 3′,4′ = 6; 4′$_1$,4′$_2$ = 15; 5′$_1$,5′$_2$ = 12.5; 3″,4″ = 3″,4″ = 7.

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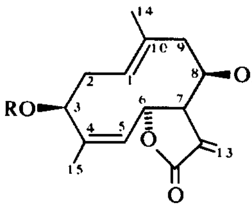
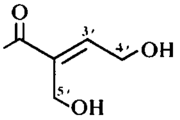
*Part 373 in the series "Naturally Occurring Terpene Derivatives". For Part 372 see Bohlmann, F. and Gupta, R. K. (1981) *Phytochemistry* **20**, (in press).



	1	2	3	4	5	6	7
R	Ac	Ac	B	B	C	C	Ac
R'	A	A-Ac	A	A-Ac	A	A-Ac	D

A =



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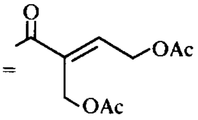

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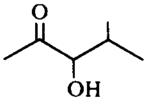

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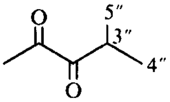

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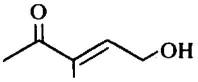

$[HOCH_2CH{=}C(OAc)CO]^+$ (100), 115 $[157 - \text{ketene}]^+$ (95), 71 $[C_3H_7CO]^+$ (71).

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{-62 \quad -63 \quad -73 \quad -134 \quad -218}$$

($c = 0.21$, $CHCl_3$).

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for financial support.

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