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ISOFUKINONE, AN EREMOPHILANE FROM *LIGULARIA SPECIOSA**

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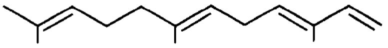
Key Word Index—*Ligularia speciosa*; Compositae; isofukinone; new eremophilane derivative.

The investigation of the roots of *Ligularia speciosa* Fisch. et Mey. afforded, in addition to several known compounds (**1**, **3**, **7**–**9**, **11** and squalene), a ketone, which has not been isolated before. The ^{1}H NMR data clearly indicated that we were dealing with the isomer **12** of fukinone [1] (Table 1). While the gross structure easily follows from the observed NMR data, the question of the relative stereochemistry at C-5 and C-7 is more difficult to decide. This problem is present also in the two isomers petasol (**13**) and neopetasol (**14**) [2]. Here the stereochemistry was deduced from the X-ray analysis. In both cases the proton at C-7 is axially orientated. Therefore the ^{1}H NMR spectral data of **13** and **14** are very similar, but in the spectra of all compounds of these types there are characteristic differences in the chemical shift of 12-H (7α-H: 12-H *br. s* 4.75, 7β-H: 12-H *br. s* 4.84). The corresponding chemical shift in the spectrum of **12** therefore indicated a 7β-substituent, though the ring situation is somewhat different. The aerial parts also contained squalene, **3**, **7**, **8**, and **11** as well as **2**, **4**–**6** and **10**.

The chemistry of *L. speciosa* is very close to that of *L. intermedia* [1], which also contains benzofurans, the norsesquiterpene **8** and the isomer of **12**, while most of the *Ligularia* species contain furanoeremophilanes [1].

EXPERIMENTAL

The plant material grown from seeds at the Botanical Garden Turku (voucher 79/1383) was cut and extracted with Et_2O–petrol (1:2). The extracts obtained were separated first by CC (Si gel, act. grade II) and TLC (Si gel GF 254). 150 g of roots afforded 50 mg **1**, 22 mg squalene, 17 mg **3** [4], 21 mg **7** [8], 10 mg **8** [9], 1 mg **9** [3], 8 mg **11** and 14 mg **12** (Et_2O–petrol, 1:10), while 150 g aerial parts yielded 10 mg squalene, 35 mg **2**, 3 mg **3**, 1 mg **4** [5], 1 mg **5** [6], 3 mg **6** [7], 2 mg **7**, 2 mg **8**, 1 mg **10** [10] and 1 mg **11**.



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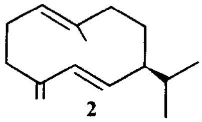

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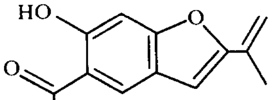

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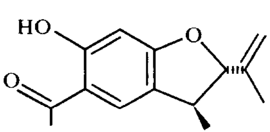
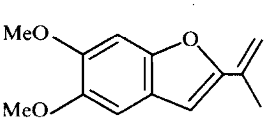


4 R = H
5 R = OH
6 R = OAng



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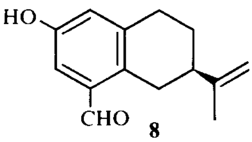

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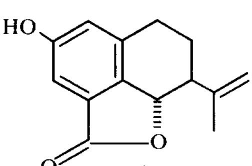

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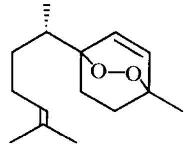

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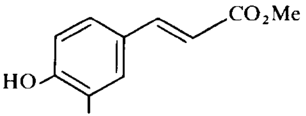

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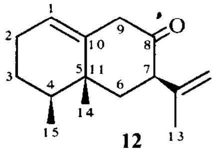
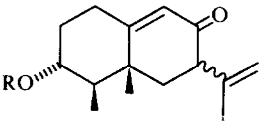


12



13 7α-H **14** 7β-H

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*Part 282 in the series "Naturally Occurring Terpene Derivatives". For Part 281 see Bohlmann, F., Zdero, C., Gupta, R. K., King, R. M. and Robinson, H. (1980) *Phytochemistry* (in press).

Table 1. ^{1}H NMR spectral data of compound **12** (270 MHz, TMS as internal standard)

	$CDCl_3$	C_6D_6		$CDCl_3$	C_6D_6
1-H	5.48 *m*	5.20 *m*	9β-H	2.80 *d*	2.73 *d*
2-H	2.07 *m*	1.85 *m*	12-H	4.94 *br. s*	5.00 *dq*
3,4-H	1.60 *m*	1.38 *m*	12′-H	4.73 *br. s*	4.79 *dq*
6β-H	1.65 *dd*	1.47 *dd*	13-H	1.71 *br. s*	1.82 *dd*
6α-H	1.93 *dd*	1.80 *dd*	14-H	1.04 *s*	0.80 *s*
7α-H	2.88 *dd*	2.86 *dd*	15-H	0.97 *d*	0.77 *d*
9α-H	3.17 *dddd*	2.97 *dddd*			

J (Hz): 1,9α = 2; 2,9α = 3; 4, 15 = 6.5; 6α,6β = 14; 6α,7α = 4.5; 6β,7α = 13.5: 7α,12 = 12,12′ ~ 1.5; 9α,9β = 17; 12, 13 = 1.5.

Isofukinone (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=O); 1645, 895 (C=CH$_2$); MS *m/e* (rel. int.): 218.167 (M^+, 69)($C_{15}H_{22}O$), 203 (M − Me, 25), 176 (M − C_3H_6, 31), 161 (176 − ·Me, 35), 122 ($C_9H_{14}^+$, 98), 107 (122 − ·Me, 100); $[\alpha]_D$ + 102° (*c*1.4, $CHCl_3$).

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