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NEW FURANOEREMOPHILANE DERIVATIVES FROM *LIGULARIA THYRSOIDEA**

FERDINAND BOHLMANN and CHRISTA ZDERO

Institute for Organic Chemistry, Technical University of Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, W. Germany

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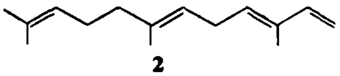
Key Word Index—*Ligularia thyrsoidea*; Compositae; new furanoeremophilanes.

The investigation of the roots of *L. thyrsoidea* afforded, in addition to the known hydrocarbons **1–3** and angelic acid as the main constituent, an acid (**5**), which on esterification yielded the already known methyl ester **6** [1]. The ^1H NMR spectra data of a less polar compound clearly showed that it was a furanoeremophilane with structure **9**. All NMR spectral data were very close to the known 3-angeloyloxy derivative [2] (Table 1). The 10β-H configuration clearly followed from the observed coupling of 9-H ($J = 11.7$ and 7.5 Hz). The configuration at C-6 is uncertain but it is most probably the same as that of the lactone **7** [3].

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

1



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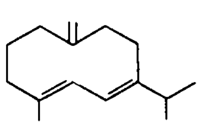

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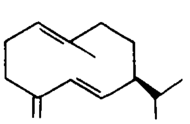

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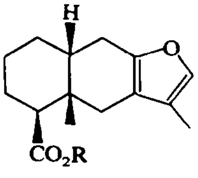
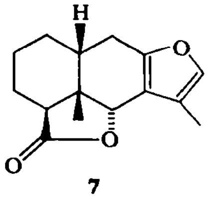


5 R = H
6 R = Me



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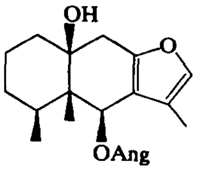

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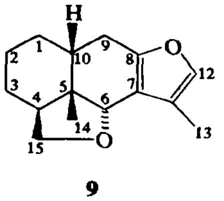

9

Table 1. ^1H NMR spectral data of compound **9**

1-H	1.58 *m*	10-H	2.20 *dddd*
1′-H	1.43 *m*	12-H	7.03 *s*(*br*)
4-H	1.98 *m*	13-H	2.04 *d*
6-H	4.64 *s*(*br*)	14-H	1.16 *s*
9-H	2.66 *dd*(*br*)	15-H	3.92 *dd*
9′-H	2.49 *dd*(*br*)	15′-H	3.55 *dd*

J(Hz): 1,10 ~ 7; 4,15 = 7.5; 4,15′ = 11; 9,10 = 10; 9′,10 = 7; 9,9′ = 17; 12,13 = 1.3; 15,15′ = 7.5.

The aerial parts contain compounds **3**, **4**, **7** and **8**. The isolated compounds are very similar to those isolated from other *Ligularia* species [1, 3, 4, 5].

EXPERIMENTAL

IR: CCl_4; ^1H NMR: 270 MHz, $CDCl_3$, TMS as int. standard; MS: 70 eV; the plant material (voucher No. 79/1379) was chopped and extracted with Et_2O–petrol (1:2). The obtained extracts were first separated by CC (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254). Known compounds were identified by comparison of their IR and ^1H NMR spectra with those of authentic compounds. Roots (300 g) afforded 5 mg **1**, 10 mg **2** [6], 20 mg **3** [7], 10 mg angelic acid, 40 mg **5** (Et_2O–petrol; 1:1) and 8 mg **9** (Et_2O–petrol, 1:10), while 1.5 kg aerial parts yielded 5 mg **3**, 3 mg **4** [8], 15 mg **7** and 5 mg **8**.

6,15-Epoxy-10β-H-furanoeremophilane (**9**). Colourless crystals, mp 110° (petrol), $bp_{0.1}$ 120°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1570, 865 (furane). MS *m/e* (rel. int.): 232.146 (M^+, 100%) ($C_{15}H_{20}O_2$); 217 $M^+ - {}^{\cdot}Me$, (13); 202 $M^+ - CH_2O$, (12); 187 $202 - {}^{\cdot}Me$, (20).

6β-Angeloyloxy-10β-furanoeremophilane-15-acid (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1720 (CO_2H) 1720, 1650 ($C{=}CCO_2R$). ^1H NMR (C_6D_6, 75°): δ 2.60(*t*(*br*), $J = 5$ Hz, 4-H), 6.56 (*s*(*br*) 6-H), 2.73 (*dd*(*br*), $J = 17$, 7Hz 9-H), 2.27 (*dd*(*br*), $J = 17$, 5 Hz, 9′-H), 2.50 (*m*, 10-H), 6.98 (*s*(*br*), 12-H), 1.97 (*s*(*br*), 13-H), 0.89 (*s*, 14-H), 5.80 *qq*, 1.97 *dq* and 1.88 *dq* (OAng). To 20 mg **5** in 1 ml Et_2O excess CH_2N_2 in Et_2O was added. After evapn and TLC (Et_2O–petrol, 1:3), 20 mg **6** were obtained, identical to the previously isolated ester [1].

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*Part 274 in the series "Naturally Occurring Terpene Derivatives". For Part 273 see Bohlmann, F. and Bohlmann, R. (1980) *Phytochemistry* **19**, (in press).

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THE STRUCTURE AND STEREOCHEMISTRY OF SPERGULAGENOL, A TRITERPENE FROM *MOLLUGO SPERGULA*

A. K. Barua, S. K. Banerjee*, C. Das Gupta, K. Basu,
L. Bose and P. Chakrabarti

Department of Chemistry, Bose Institute, Calcutta 9, India

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Key Word Index—*Mollugo spergula*; Ficoidaceae; triterpene; (21α-H)-hopane; spergulagenol.

INTRODUCTION

The isolation of two new triterpenes, spergulagenic acid [1–3] and spergulagenin-A [4–11], has been reported earlier from this laboratory. Another new triterpenoid sapogenin called spergulagenin-C (**1**), $C_{30}H_{50}O_5$, mp 274–278° (decomp.), has also been isolated and it has been shown to be x-hydroxy spergulagenin-A [12]. Kitagawa *et al.* [13] reported a new sapogenin, spergulatriol, from the same source. The present paper reports the structure of a new triterpene, called spergulagenol (**2a**), from the ethanolic extract of the same plant.

RESULTS AND DISCUSSION

Spergulagenol (**2a**), $C_{30}H_{52}O_4$, mp 295–298°, $[\alpha]_D+46°$ (Py) gave a violet colour with the Liebermann–Burchard reagent but no colour with tetranitromethane. Its IR spectrum showed bands at 3320 and 3440 cm^{-1} for hydroxyl groups. Its MS showed the molecular ion peak at *m/e* 476 and a peak at *m/e* 59 due to the ion $(Me)_2C{=}\overset{+}{O}H$ formed by the cleavage of the hydroxy isopropyl sidechain (cf. mollugogenol-A [14, 15]). It also showed peaks at *m/e* 458 and 400 for the ion species **a** and **b** respectively.

Compound **2a** on treatment with acetic anhydride and pyridine at 0° yielded a triacetate (**2b**), $C_{36}H_{58}O_7$, mp 230–232°. Its MS did not show the molecular ion peak but showed a peak at *m/e* 584 for the $(M-H_2O)^+$ ion. Its ^1H NMR spectrum ($CDCl_3$, 90 MHz) showed singlets at δ0.87 (9H), 0.90 (3H), 1.03 (3H), 1.15 (3H) and 1.19 (6H) for the eight quarternary methyl groups $(-\overset{|}{\underset{|}{C}}-C\underline{H}_3)$. The singlets at δ2.02 (3H), 2.03 (3H) and 2.07 (3H) were attributed to the three acetoxy groups $(-O-CO-C\underline{H}_3)$. The broad signals centred at 4.49 (1H, *m*), 5.25 (1H, *m*) and 4.88 (1H, *m*) were assigned to 3-αH, 12-αH and 16-αH, respectively. The signal for the 22-OH group appeared at 3.5 and disappeared on D_2O exchange.

Oxidation of **2a** with CrO_3 in acetic acid at room temp. yielded a monohydroxy triketone (**3**), $C_{30}H_{46}O_4$, mp 254–256°. Its IR spectrum (in Nujol mull) showed bands at 3350 (OH) and 1695–1700 cm^{-1} (six-membered ring ketone). It gave a positive Zimmerman colour reaction (3-keto group) and did not respond to the ferric chloride colour test. Its MS did not show the molecular ion peak at *m/e* 470 but showed a strong peak at 452 $(M-H_2O)^+$. The MS fragmentation pattern was very characteristic of 12-keto compounds (cf. spergulagenin-A [4–11]). There was a peak at *m/e* 247, for the ion species **c** and at *m/e* 219 arising out of

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*St. Xavier's College, Calcutta.