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15α-METHYLACRYLOYLOXY-*ENT*-KAURENIC ACID FROM *ICHTHYOTHERE* SPECIES*

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Key Word Index—*Ichthyothere connata*; *I. latifolia*; *I. rufa*; *I. terminalis*; *Delilia biflora*; Compositae; diterpene acid; new *ent*-kaurenic acid derivative.

The genus *Ichthyothere* (Compositae), is placed in the tribe Heliantheae, and is usually regarded as a member of the subtribe Melampodiinae. The genus is named after the ability of the plant to kill fish when pieces of the plant are placed in water. Analyses have shown that the unstable toxin involved is the tetrahydropyran, ichthyotherol, an acetylenic compound first reported from *I. terminalis* [2]. The literature also includes a report of *ent*-kaurenic acid from another species of the genus [3]. We now have investigated four species from Brazil. They all contain the widespread pentaynen **1**, *ent*-kaurenic acid and several derivatives (**3**–**8**) [4, 5] (Table 1), only one, the methyl acrylate **8** being new, but present also in a *Mikania* species (Bohlmann, F., unpublished data). The structure clearly follows the ^{1}H NMR data, which are very similar to those of the esters of **4**–**7**. Two species afforded ozic acid (**12**) [6], which was accompanied by *ent*-biformene (**11**) [7] in one case. Furthermore, spathulenol [8] and several widespread sesquiterpenes were present. Ichthyotherol [2] was not isolated, though it was possibly present in the living plants.

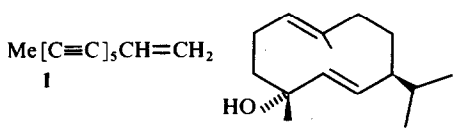
One recent system of classification places *Ichthyothere* in the subtribe Milleriinae where the genera *Clibadium* and *Delilia* are also included [1]. The more recent classification of Robinson (unpublished results) places *Delilia* in the subtribe Ecliptinae and places *Clibadium* in a separate subtribe Clibadiinae which seems related to the Ecliptinae, and both genera are found to differ significantly from *Ichthyothere* in a number of basic structures. *Clibadium* is another genus long noted for its fish-killing activity and recently ichthyotherol has been demonstrated from several species [9]. Despite the one similarity, the overall picture of the chemistry of *Ichthyothere* is very uniform and different from *Clibadium*, where so far no diterpenes have been isolated [6]. *Delilia biflora* (L.) O. Kuntze, one of the two species of this genus, only afforded the pentaynene **1** and also no diterpenes.

EXPERIMENTAL

The extracts of the plant material (Et_2O–petrol, 1:2) were separated by column chromatography and TLC (SiO_2, GF 254). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material. The results are summarized in Table 1.

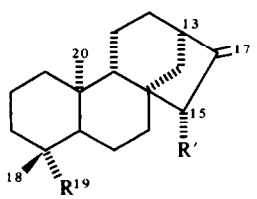
Delilia biflora (*voucher RMK* 7451). The roots (60 g) afforded 0.1 mg **1** and the aerial parts (180 g) 50 mg linoleic acid.

15α-[2-*Methylacryloyloxy*]-ent-*kaurenic acid* (**8**). MS *m/e* (rel. int.): 400.261 (M^+, 7) ($C_{25}H_{36}O_4$); purified as its methyl

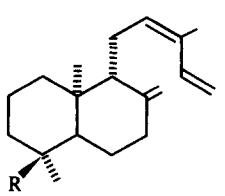


1

2



	3	4	5	6	7	8	9	10
R	CO_2H	CO_2H	CO_2H	CO_2H	CO_2H	CO_2H	CO_2Me	CH_2OH
R′	H	OAng	OSen	OTigl	OiVal	OMeacr	OMeacr	H



11 R = Me
12 R = CO_2H

* Part 308 in the series "Naturally Occurring Terpene Derivatives". For Part 307 see Bohlmann, F., Zdero, C., Grenz, M., Dhar, A. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 281.

Table 1. Constituents of the *Ichthyothere* species*

	I. connata Blake (RMK 8273)		*I. latifolia* (Benth.) Gardn. (RMK 8218)		*I. rufa* Gardn. (RMK 8241)		*I. terminalis* (Spreng.) Malme (RMK 8270)	
	Roots (140 g)	Leaves (1 kg)	Roots (30 g)	Leaves (450 g)	Roots (20 g)	Leaves (250 g)	Roots (120 g)	Leaves (650 g)
1	0.1	—	0.05	—	0.05	—	0.1	—
2	—	—	—	30	—	10	—	—
3	400	150	100	60	50	100	200	500
4	—	—	—	—	—	—	—	50
5	60	—	1	60	5	5	—	100
6	120	—	—	120	5	10	—	50
7	—	—	—	—	—	—	—	50
8	120	—	2	120	2	5	—	50
10	—	—	—	—	5	—	30	—
11	5	—	—	—	—	—	—	—
12	300	300	50	500	—	—	—	—
Germacrene D	15	20	15	60	20	30	40	90
Bicyclogermacrene	20	30	5	40	1	30	10	40
Spathulenol	—	40	—	30	—	—	—	70
α-Pinene	30	—	4	—	—	—	—	—
γ-Humulene	—	—	—	—	—	—	2	3
Germacrene C	—	—	—	10	—	—	—	—
Thujanol	—	—	—	—	—	—	—	30
Terpinen-4-ol	—	—	—	—	—	—	—	60
Cycloartenol	—	—	—	10	—	—	—	—

*Quantities in mg, voucher No. in parentheses.

ester **9** from the other compounds, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R); ^1H NMR ($CDCl_3$, 270 MHz): δ 1.16 (*s*, 18-H), 0.85 (*s*, 20H), 2.79 (*m*, 13-H), 5.31 (*br. s*, 15-H), 5.16 (*br. s*, 17-H), 5.09 (*br. s*, 17'-H), 3.64 (*s*, OMe), 6.09 (*dq*, J = 1.5, 1 Hz, 3_1'-H), 5.54 (*dq*, J = 1.5, 1.5 Hz, 3_2'-H), 1.95 (*dd*, J = 1, 1.5 Hz, 4'-H).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-60.3 \quad -64.2 \quad -73.9 \quad -125.0} \quad (c = 1.7, CHCl_3).$$

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