Stems and leaves (780 g) were extracted in 3 l. of $CHCl_3$ and worked up according to a standard procedure [3] to yield 14.5 g of crude syrup. The syrup was chromatographed over 250 g of Si gel taking 20 ml fractions. $CHCl_3$ was used an an eluant followed by $CHCl_3$–Me_2CO mixtures (95:5, 90:10, 80:20, etc). Fractions 25–33 contained melampodinin, and fractions 35–46 yielded 130 mg crystalline longipin, mp 203–206° (EtOAc); CD (c 4.31 × 10^{-5}, MeOH) $[\theta]_{216} = -7.89 \times 10^4$, $[\theta]_{251} = 5.57 \times 10^3$; IR ν_{max}: 3500 (OH), 1760 (γ-lactone), 1730 (ester), 1225 (acetate); the low resolution MS (70 eV) showed significant peaks at m/e (rel. int.): 464 (0.01, M^+), 422 (0.02, $M-C_2H_2O$), 404 (0.04, $M-C_2H_4O_2$), 350 (0.03, $M-C_5H_6O_3$), 349 (0.17, $M-C_5H_7O_3$), 290 (0.06, $M-C_2H_4O_2-C_5H_6O_3$), 289 (0.35, $M-C_5H_7O_3-C_2H_4O_2$), 288 (0.28, $M-C_5H_8O_3-C_2H_4O_2$), 270 (0.31, $M-C_5H_8O_3-C_2H_4O_2-H_2O$), 256 (0.70, $M-C_5H_8O_3-C_2H_4O_2-CH_4O$), 71 (0.26, C_4H_7O), 43 (100, C_2H_3O); (Calc. for $C_{16}H_{18}O_5$: 290.1154. Found: (MS) 290.1161).

Acetylation of 100 mg of **2a** in 1 ml of Py and 1 ml Ac_2O for 24 hr followed by the usual work-up gave **1b** (gum); IR ν_{max} (CCl_4): 1765 (γ-lactone), 1750, 1730, 1720 (esters), 1670, 1650 (double bonds); the low resolution MS (70 eV) showed significant peaks at m/e (rel. int.): 506 (0.01, M^+), 464 (0.01, $M-C_2H_2O$), 446 (0.02, $M-C_2H_4O_2$), 404 (0.02), $M-C_2H_4O_2-C_2H_2O$), 392 (0.02, $M-C_5H_6O_3$), 391 (0.01, $M-C_5H_7O_3$), 350 (0.03, $M-C_5H_6O_3-C_2H_2O$), 332 (0.02, $M-C_5H_6O_3-C_2H_4O_2$), 300 (0.03, $M-C_5H_6O_3-C_2H_2O-C_2H_4O_2$), 272 (1.00, $M-C_5H_6O_3-C_2H_4O_2-C_2H_4O_2$), 240 (0.27, $M-C_5H_6O_3-C_2H_4O_2-C_2H_4O_2-CH_4O$), 71 (0.17, C_4H_7O), 43 (0.96, C_2H_3O).

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GERMACRENE-D FROM *FALCARIA VULGARIS**

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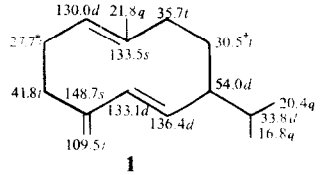
Key Word Index—*Falcaria vulgaris*; Apiaceae/Umbelliferae; essential oil; sesquiterpene; germacrene-D; spectroscopy.

From the essential oil of the fresh herb of *Falcaria vulgaris* Bernh., germacrene-D (**1**) was isolated by column chromatography on Si gel. The structure was determined by comparing GLC behaviour and IR, MS, ^1H NMR spectra with published data [1, 2] and ^{13}C NMR spectroscopy. Assignments of chemical shifts are indicated on structure **1**. The splittings refer to the off-resonance spectrum.



1

As far as we know, germacrene-D, a key intermediate in sesquiterpene biogenesis, has been found for the first time in a volatile oil of the Apiaceae. A similar high amount (71%) of this sesquiterpene hydrocarbon has been isolated from aerial parts of *Acanthopanax sciaphylloides* (Araliaceae) [3], showing once more the close chemical relationship of these two families.

EXPERIMENTAL

Above ground parts of flowering plants were collected near Wuerzburg in August 1977. The volatile oil (0.3–0.4% yield) was obtained from the fresh herb by steam distillation with a receiver, as used by the European Pharmacopoeia for determination of volatile oil in drugs. The pale yellow oil (d_{20}^{20} = 0.8925; n_D^{20} = 1.5040) was subjected to CC using Si gel for dry CC (Woelm) and *n*-pentane as eluent [4]. Repeated chromatography of the hydrocarbon fraction (nearly 90% of the total oil) at −20° with Si gel–pentane [5] yielded 62% germacrene-D, which was identified by GLC and spectrometric methods. $C_{15}H_{24}$ (M^+ at m/e 204). GLC: $I^{150°}_{carbowax\ 20M}$ = 1715. MS m/e (rel. int.): 161 (100), 105 (40), 204 (34), 41 (33), 91 (32).

* Part 5 in the series "On the Essential Oils from the Apiaceae." For Part 4 see Kubeczka, K.-H. (1976) *Z. Naturforsch.* **31**, 283.

† Indicates a possible signal reversal.

^{13}C NMR spectra were measured at 22.63 MHz in the Fourier transform mode. Chemical shifts were all measured in C_6D_6 soln and are expressed in δ values relative to internal TMS. IR and ^1H NMR spectra were identical with published data [1, 2].

Acknowledgement—I thank Mr. Formacek, Bruker Physik AG, Rheinstetten, Germany, for performing the ^{13}C NMR spectroscopy.

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EINE NEUE DITERPENSÄURE AUS *CENTIPEDA ORBICULARIS**

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Key Word Index—*Centipeda orbicularis*; Compositae; new diterpene acid; new flavones.

Die Stellung der Gattung *Centipeda* ist botanisch problematisch. Sie wird üblicherweise in die Tribus Anthemideae in der Nähe von *Cotula* eingeordnet. Pollenmorphologische Untersuchungen deuten jedoch eher eine Stellung in der Nähe der Tribus Astereae an [1]. Die bisherigen Ergebnisse über Inhaltsstoffe aus dieser Gattung erlauben keine Entscheidung. Aus einer Art sind lediglich weitverbreitete Triterpene isoliert worden [2], und aus einer anderen Chrysanthemylacetat [3], sowie ein nicht identifiziertes Derivat des weitverbreiteten Pentainens [4]. Wir haben jetzt *Centipeda orbicularis* Lour., die in Assam heimisch ist, näher untersucht.

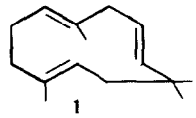
Die oberirdischen Teile enthalten die bekannten Verbindungen **1**–**6**, sowie als Hauptinhaltsstoff eine Diterpensäure, der aufgrund der spektroskop schen Daten die Konstitution **7** zukommen muß (s. Tabelle 1). Die ^1H-NMR-Daten zeigen klar, daß ein β-substituiertes Furan vorliegt. Alle übrigen Signale zeigen, daß eine normale Farnesolkette vorliegen muß, bei der eine Methylgruppe zur Carboxylgruppe oxydiert ist. Die Stellung ergibt sich aus Doppelresonanz-Experimenten. Durch Einstrahlung auf 13-H läßt sich das dem 12-H zuzuordnende dt ermitteln. Dieses koppelt jedoch nicht mit dem zur Estergruppe β-ständigen olefinischen Proton. Somit muß die Carboxylgruppe an C-6 stehen, da eine derartige Gruppe an C-2 zweifellos zu einer Tieffeldverschiebung der nachbarständigen Methylgruppe führen müsste. **7** möchten wir Centipedasäure nennen. Die polaren Anteile enthalten schließlich noch zwei schwer trennbare Flavone, denn die Strukturen **9** und **10** zukommen dürften. Dafür sprechen die ^1H-NMR-Daten zusammen mit denen der Acetate **11** und **12** (s. Tabelle 2). Auch die Wurzeln enthalten **1**–**7**.

Überblickt man die hier isolierten Inhaltsstoffe, so

Tabelle 1. ^1H- und ^{13}C-NMR-Daten von **7** und **8** ($CDCl_3$, TMS als innerer Standard)

	7	**8**	^{13}C			
1-H	*s(br)* 1.60	*s(br)* 1.59	C-1	*q* 25.7	C-11	*d* 124.6
3-H	*tqq* 5.10	*tqq* 5.09	C-2	*s* 131.8	C-12	*t* 25.1
4-H	*dt(br)* 2.14	*dt(br)* 2.04	C-3	*d* 123.7	C-13	*t* 28.6
5-H	*m* 2.28	*t(br)* 2.25	C-4	*t* 28.1	C-14	*s* 125.0
7-H	*t(br)* 6.00	*t(br)* 5.84	C-5	*t* 34.8	C-15	*d* 111.1
8-H	*dt(br)* 2.64	*dt(br)* 2.53	C-6	*s* 132.0	C-16	*d* 142.6
9-H	*t(br)* 2.14	*t(br)* 2.04	C-7	*d* 141.8	C-17	*d* 138.9
11-H	*tq* 5.20	*tq* 5.19	C-8	*t* 28.0	C-18	*q* 15.9
12-H	*m* 2.28	*dt(br)* 2.25	C-9	*t* 39.3	C-19	*s* 168.4
13-H	*t(br)* 2.46	*t(br)* 2.46	C-10	*s* 135.1	C-20	*q* 17.7
15-H	*s(br)* 6.27	*s(br)* 6.27	OMe	*q* 51.0		
16-H	*dd* 7.33	*dd* 7.35				
17-H	*dt* 7.20	*dt* 7.20				
18-H	*s(br)* 1.60	*s(br)* 1.59				
20-H	*s(br)* 1.69	*s(br)* 1.69				
OMe		*s* 3.74				

J(Hz): 1,3 = 3,20 = 1; 3,4 = 4,5 = 7,8 = 7; 8,9 = 7.5; 11,12 = 6.5; 12,13 = 7; 13,17 = 1; 15,16 = 16,17 = 1.5.



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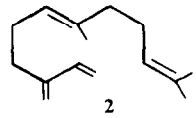

2

$H_2C{=}CHCH(OH)[C{\equiv}C]_2\,CHCH{=}_{cis}CH(CH_2)_5CH{=}CH_2$
|
OR

3 R = Ac
4 R = H

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