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NEW CACALOL DERIVATIVES FROM *ROLDANA HETEROGAMA*

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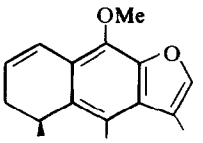
Key Word Index—*Roldana heterogama;* Senecioneae; Compositae; new cacalol derivatives; naphthafurans.

Species of the genus *Roldana*, earlier combined with *Senecio*, have not been investigated chemically, though there are 48 species mainly in Mexico and Guatemala. The roots of *R. heterogama* (Hemsl.) R. et B. contain several derivatives of cacalol. Besides **1–4** two new ones have been isolated. The structures of the two further cacalol derivatives **5** and **6** were readily elucidated by the ^{1}H-NMR spectra. The position of the acetate groups in **6** has been shown by decoupling experiments. Irradiation of 12-H sharpens the signals of the 13-H. All the other NMR-data are very similar to those of similar compounds isolated before [3] (see Table 1). The assignment of all signals has been established by double resonance experiments. Following the observed coupling constants and Dreiding models, **6** must have a conformation with a quasi axial 4-methyl, probably due to steric hindrance with the aldehyde group. The constituents isolated from the first *Roldana* species to have been investigated show clear relationships to *Cacalia* [2] and some *Senecio* species [3].

* Part 129 in the series 'Naturally Occurring Terpene Derivatives'; for part 128 see: Bohlmann, F. and Fiedler, L. (1978) *Phytochemistry* **17**, 566.

EXPERIMENTAL

IR. Beckman IR 9, CCl_4; ^{1}H-NMR. Bruker WH 270; MS. Varian MAT 711, 70 eV. The air dried plant material (collected by Dr. R. M. King, Smithsonian Institution, Washington, in



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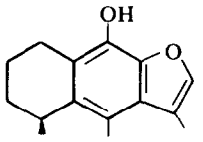

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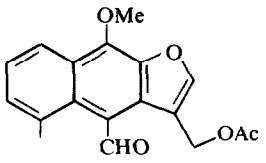

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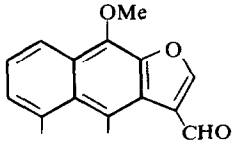
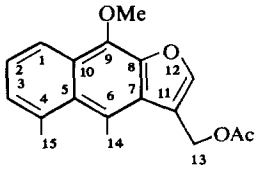


4(3)



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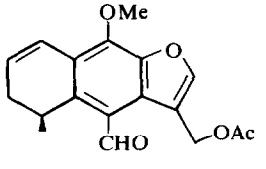

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Table 1. ^{1}H-NMR-data of **5** and **6** (270 MHz, δ-values, TMS as internal standard, $CDCl_3$

	5	**6**
1-H	*d(br)* 8.21	*dd* 6.92
2-H	*dd* 7.30	*dddd* 6.03
3α-H	*d(br)* 7.23	*dddd* 2.57
3β-H		*ddd* 2.27
4-H	—	*dq(br)* 3.99
12-H	*s(br)* 7.71	*s(br)* 7.73
13-H	*s(br)* 5.38	*d(br)* 5.43 *d(br)* 5.37
14-H	*s* 3.06	*s* 10.57
15-H	*s(br)* 2.97	*d* 1.21
OAc	*s* 2.13	*s* 2.09

J(Hz): **5**: 1,2 = 8; 2,3 = 7; **6**: 1,2 = 9.5 1,3α = 3; 2,3α = 3; 2,3β = 7; 3α,3β = 17; 3α,4 7,3β,4 = 1; 4,15 = 7; 13,13 = 13.

Guatemala, voucher RMK 7264) was extracted with Et_2O–petrol (1:2) and the extract separated first by column chromatography (Si gel, act. grade II) and further by TLC (Si gel, GF 254) using Et_2O–petrol mixtures as solvents. 80 g of roots afforded 7 mg **1**, 8 mg **6** (Et_2O–petrol, 1:3), 30 mg **2**, 3 mg **4**, 20 mg **5** (Et_2O–petrol, 1:3) and 120 mg **3**.

13-Acetoxy-1,2,3,4-tetradehydrocacalol methyl ether (**5**). Colourless crystals from Et_2O-petrol, mp 83°, IR OAc 1750, 1240; benzofuran 1640, 1603, 1515 cm^{-1}. MS. M^+ *m/e* 298.121 (68%) (calc. for $C_{18}H_{18}O_4$ 298.121): —$^{\cdot}CH_3$ 283 (1): —$H_2C{=}C{=}O$ 256 (25): —AcOH 238 (48); 238 —$^{\cdot}CH_3$ 223 (100) Me CO^+ 43 (63).

13-Acetoxy-14-oxocacalohastin (**6**). Colourless oil, IR OAc 1750, 1240; CHO 1690; aromat 1600, 1555: C=C 1630 cm^{-1} MS. M^+ *m/e* 314.115 (33%) (calc. for $C_{18}H_{18}O_5$): —C_3H_7 271 (4), —AcOH 254 (55); 254 —$^{\cdot}CH_3$ 239 (100), 239 —CO 211 (47); Me CO^+ 43 (28).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436}{+61.7 \quad +65.7 \quad +80\,3 \quad +215\,5^\circ} \quad (c = 0.76)$$

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NEUE NEROLIDOL-DERIVATE AUS *AGERATINA ASCHENBORNIA**

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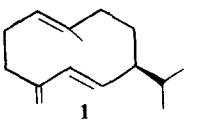
Die Wurzeln der in Mittelamerika heimischen *Ageratina aschenbornia* (Schauer) K. et R. (Tribus Eupatorieae) enthalten neben Germacren D (**1**) die Chromene **2**–**6**. Auch die oberirdischen Teile liefern **1**, **2** und **6** sowie drei Sesquiterpenalkohole, denen auf Grund spektroskopischer Daten die Konstitutionen **7**–**9** zukommen. **7** haben wir kürzlich aus *Eupatorium perfoliatum* isoliert [1]. Für die Konstitution **9** spricht neben den NMR-Daten das Fragmentierungsverhalten im Massenspektrometer. Auch die Daten des nach Acetylierung erhaltenen Acetats **10** bestätigen die Struktur. Wir möchten **9** Ageraborniol nennen. Über die Konfigurationen an C-7 und C-8 sind noch keine Aussagen möglich. Nerolidol-Derivate haben wir vor allem aus *Brickellia*-Arten isoliert [2]. Allerdings enthält auch *Ageratina boustomenta* (fälschlich als *A. scorodonioides* bezeichnet) ein typisches Nerolidol-Derivat [3]. Weitere Untersuchungen müssen zeigen, ob diesen Verbindungen chemotaxonomische Bedeutung zukommt.



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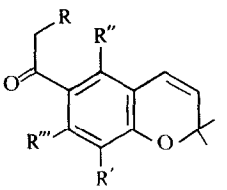

	2(4)	**3**(3)	**4**(4)	**5**(5)	**6**(4)
R	= H	OiBu*	OAc	H	H
R′	= H	H	H	OMe	OMe
R″	= H	H	H	OH	H
R‴	= OH	OH	OH	H	OH

* iBu = isobutyryl.

* 128. Mitt. in der Serie 'Natürlich vorkommende Terpen-Derivate'; 127. Mitt. Bohlmann, F und Suwita, A. (1978) *Phytochemistry* **17**, 567