lings observed. Spin decoupling allowed the assignment of all signals. **4** we have named methyl hypocretenoate and **2** hypocretenolide. Though **2** and **4** have somewhat unusual structures, their close relationship to lactucin-like lactones is obvious.

EXPERIMENTAL

The fresh plant material (grown from the seeds from the Botanical Garden, Dijon, voucher 81/1510, deposited in the Institute of Organic Chemistry, Berlin) was extracted with Et_2O–petrol, 1:2, and the resulting extracts were separated by CC (Si gel) and repeated TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. The roots (50 g) gave 10 mg taraxasterol, 2 mg lupeol and 20 mg of its acetate together with its Δ 12-isomer, while the aerial parts (250 g) afforded 10 mg taraxasterol, 200 mg lupeol, 100 mg lupeyl acetate and its Δ 12-isomer, 10 mg phytol, 21 mg **1**, 1 mg **2** (Et_2O-petrol, 3:1) and 2 mg **4** (Et_2O–petrol, 3:1).

Hypocretenolide (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1740 (δ-lactone), 1710 (C=CC=O); MS *m/z* (rel. int.): (CI, isobutane): 245 $[M+1]^+$ (100) ($C_{15}H_{16}O_3 + 1$), 217 $[245 - CO]^+$ (5), 201 $[245 - CO_2]^+$ (5).

To 1 mg **2** in 0.5 ml Et_2O excess of CH_2N_2 in Et_2O was added. After 5 min evaporation afforded 1 mg **3**, colourless solid, MS *m/z* (rel. int.): 258.126 $[M - N_2]^+$ (100) ($C_{16}H_{18}O_3$), 230 $[258 - CO]^+$ (3), 215 $[230 - Me]^+$ (2);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 426\,\text{nm}}{-30 \quad -30 \quad -40 \quad -100} \quad (c = 0.08, \text{CHCl}_3).$$

Methyl hypocretenoate (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3400 (OH), 1725 (CO_2R), 1710, 1630 (C=CC=O); MS *m/z* (rel. int.): 276.136 $[M]^+$ (10), ($C_{16}H_{20}O_4$), 258 $[M - H_2O]^+$ (100), 226 $[258 - MeOH]^+$ (25), 211 $[226 - Me]^+$ (14);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+35 \quad +41 \quad +42 \quad +53} \quad (c = 0.1, \text{CHCl}_3).$$

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GUAIANOLIDES FROM *AINSLIAEA FRAGRANS*[*]

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Key Word Index—*Ainsliaea fragrans*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—Five sesquiterpene lactones were isolated from *Ainsliaea fragrans*, two of them being new.

The medicinal plant *Ainsliaea fragrans* Champ. (tribe Mutisieae) has long been used in north China for arresting haemorrhages, curing wounds and dispersing blood clots [1]. The chemistry so far has not been investigated. We have now isolated five guaianolides all being 6, 12-*trans*-lactones, two of them being new. The aerial parts of *A. fragrans* afforded stigmasterol, caryophyllene, zaluzanin C (**1**) [2], 8-α-hydroxy-11α, 13-dihydrozaluzanin C (**2**), 11α, 13-dihydrozaluzanin C (**5**) and a mixture of 4β, 14-dihydrozaluzanin C (**7**) and 4β, 14, 11α, 13-tetrahydrozaluzanin C (**8**). The structure of **2** was deduced by detailed examination of its expanded 400 MHz ^1H NMR spectrum (Table 1) and from spin decoupling experiments. Acetylation of **2** yielded the acetates **3** and **4**. Careful spin decoupling of the diacetate **4** allowed the assignment of all signals. Irradiation of the H-3α signal at δ 5.54 col-

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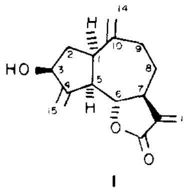
[*] Part 426 in the series "Naturally Occurring Terpene Derivatives". For Part 425, see Bohlmann, F., Jakupovic, J. and Ahmed, M. (1982) *Phytochemistry* **21**, 2027.

Table 1. ^{1}H NMR spectral data of **2**–**6** (400 MHz, $CDCl_3$, TMS as int. standard)

	2	**3**	**4**	**5**	**6**
H-1	2.90 *m*	2.92 *m*	2.94 *m*	2.87 *ddd*	2.92 *ddd*
H-2	1.69 *ddd*	1.65 *ddd*	1.77 *ddd*	1.73 *ddd*	1.78 *ddd*
H-2′	2.30 *ddd*	2.43 *ddd*	2.44 *ddd*	2.33 *ddd*	2.46 *ddd*
H-3	4.51 *ddd*	5.50 *ddd*	5.54 *ddd*	4.54 *ddd*	5.54 *ddd*
H-5	2.88 *dd*	2.90 *dd*	2.99 *dd*	2.82 *ddd*	2.84 *ddd*
H-6	4.12 *dd*	4.16 *dd*	4.11 *dd*	4.14 *dd*	4.10 *dd*
H-7	2.37 *ddd*	2.37 *ddd*	2.62 *ddd*	1.90 *dddd*	1.91 *dddd*
H-8	3.79 *m*	3.77 *m*	4.83 *ddd*	1.41 *dddd*	1.41 *dddd*
H-8′	—	—	—	2.37 *dddd*	2.39 *dddd*
H-9	2.20 *dd*	2.19 *dd*	2.14 *dd*	1.98 *ddd*	2.00 *ddd*
H-9′	2.71 *dd*	2.69 *dd*	2.80 *dd*	2.54 *ddd*	2.50 *ddd*
H-11	2.87 *dq*	2.86 *dq*	2.76 *dq*	2.78 *dq*	2.70 *dq*
H-13	1.29 *d*	1.28 *d*	1.15 *d*	1.17 *d*	1.16 *d*
H-14	5.00 *s br*	4.99 *s br*	5.07 *s br*	4.92 *s br*	4.89 *s br*
H-14′	5.08 *s br*	5.01 *s br*	5.09 *s br*	4.95 *s br*	4.93 *s br*
H-15	5.32 *dd*	5.29 *dd*	5.32 *dd*	5.03 *dd*	5.23 *dd*
H-15′	5.42 *dd*	5.44 *dd*	5.46 *dd*	5.30 *dd*	5.43 *dd*
Ac	—	2.08 *s*	2.09 *s*	—	2.11 *s*
OH	1.60 *s br*	1.91 *s br*	—	1.62 *s br*	—

J (Hz): 7, 11 = 7; compounds **2**, **3** and **4**: 1, 2 = 1, 5 = 9; 2, 3 = 7; 2, 2′ = 14; 3, 15 = 2; 5, 6 = 6, 7 = 10; 7, 11 = 7; 7, 8 = 11; 8, 9 = 8.5; 8, 9′ = 5; 9, 9′ = 12.5; 11, 13 = 7.5; compounds **5** and **6**: 1, 2 = 7; 1, 5 = 8; 2, 3 = 7; 2, 2′ = 14; 3, 15 = 2; 5, 6 = 6, 7 = 10; 7, 8 = 4.5; 7, 8′ = 10; 8, 9 = 4; 8, 9′ = 4; 8′, 9 = 4; 8′, 9′ = 10; 9, 9′ = 13; 8, 8′ = 13; 7, 11 = 7; 11, 13 = 7.

lapsed the H-2 signal (δ 1.77 *ddd* and 2.44 *ddd*) to a doublet of doublets and irradiation of the H-8 signal (4.83 *ddd*) collapsed the H-9 signals (2.14 *dd* and 2.80 *dd*) to doublets and the threefold doublet at δ 2.62 (H-7) into a doublet of doublets. Similarly, irradiation of the H-6β, H-7α, H-13 signals allowed the assignments of the signals of H-5, H-8, H-11. The ^{1}H NMR spectral data of **5** were close to those of 11β, 13-dihydrozaluzanin C (**10**) [3], which recently was isolated from *Brachylaena transvaalensis*. They differ in the chemical shift of H-11 and in the coupling $J_{7,11}$. Accordingly, **5** was the 11-epimer of **10**. 4β, 14, 11α, 13-tetrahydrozaluzanin C (**8**) has been prepared by the $NaBH_4$ reduction of 4β, 14, 11α, 13-tetrahydro-3-dehydrozaluzanin C [4], but has not been isolated from plants.



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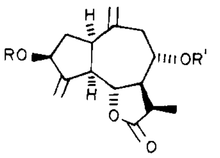
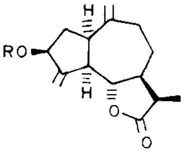
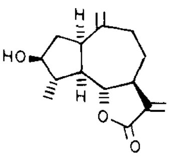


2 R = R′ = H
3 R = Ac, R′ = H
4 R = R′ = Ac



5 R = H
6 R = Ac



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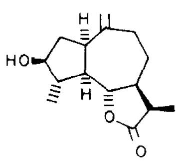

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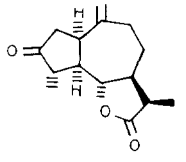

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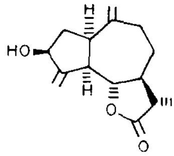

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EXPERIMENTAL

The air-dried aerial parts of *A. fragrans* (voucher deposited in the Shanghai Institute of Materia Medica) was extracted with Et_2O and the extract was first separated by CC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. 2.5 g extract (equal to 300 g plant material) afforded 3 mg stigmasterol, 8 mg caryophyllene, 15 mg **2**, 5 mg **5** and 15 mg of a mixture of **1**, **7** and **8**. The mixture was separated by TLC of their acetates and afforded 3 mg zaluzanin-C-acetate and 6 mg of a mixture of the acetates of **7** and **8**.

8α-Hydroxy-11α, 13-dihydrozaluzanin C (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3340 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 264 $[M]^+$ (18), 246 $[M-H_2O]^+$ (10), 228 $[M-2H_2O]^+$ (5), 173 (40), 155 (18), 145 (31), 131 (31), 109 (100), 105 (70).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-24 \quad -44 \quad -31.2 \quad +50} \quad (c = 0.25,\ CHCl_3).$$

6 mg **2** was heated with 0.5 ml Ac_2O at 80° for 1 hr. TLC gave 3.5 mg **4** and 1.5 mg **3** (^1H NMR spectra, see Table 1).

11α, 13-*dihydrozaluzanin C* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3470 (OH), 1785 (γ-lactone); MS m/z (rel. int.): 248 $[M]^+$ (9), 230 $[M-H_2O]^+$ (4), 177 (28), 157 (12), 152 (37), 134 (41), 121 (12), 105 (27), 81 (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-12 \quad -10 \quad +4 \quad +86.4} \quad (c = 0.25,\ CHCl_3)$$

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GERMACRANOLIDES FROM *DICOMA TOMENTOSA**

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Key Word Index—*Dicoma tomentosa*; Compositae; Mutisieae; sesquiterpene lactones; germacranolides; melampolides.

Abstract—An investigation of the aerial parts of *Dicoma tomentosa* afforded four new germacranolides and four melampolides together with urospermal A and its 11β,13-dihydroderivative. The structures were elucidated by spectroscopic methods. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Dicoma* (Compositae, tribe Mutisieae) is placed in the subtribe Gochanatiinae [1] Chemical investigations have shown that 14, 15-oxygenated germacranolides are present [2] in one species, while two others only afforded acetylenic compounds and an allenic acid [2, 3]. We have now investigated a further species, *D. tomentosa*, which again gave germacranolides.

RESULTS AND DISCUSSION

While the roots of *Dicoma tomentosa* only afforded the triterpenes taraxasterol, stigmasterol, sitosterol and lupeyl acetate, the aerial parts gave taraxasterol, urospermal A (**1**) [3] where the configuration of the 1,10 double bond has to be changed [Halsall T. G., unpublished], 11β,13-dihydrourospermal A (**10**) [4] and eight further sesquiterpene lactones, the melampolides **2–5** and the germacranolides **6–9**. The structure of **2** followed from the ^1H NMR spectral data (Table 1) which were close to those of **1**. As expected the H-15 signals were shifted downfield. The spectra of **8** and **9** (Table 1) showed that we were dealing with the mono- and diacetate of albicolide. All signals in the spectrum of **9** were assigned by spin decoupling. If the spectrum of **3** (Table 1) is compared with that of **8** the difference in the configuration of the 1, 10-double bond becomes obvious. The downfield shift of the H-1 signal in the spectrum of **3**, if compared with the H-1 shift of **8**, supported a *cis*-1, 10-double bond. The same is true in the spectrum of a diacetate isolated previously from a *Dicoma* species [2]. The configuration of the 1, 10-double bond has to be changed to 1,10-*cis*. The spectra of **4** and **5** (Table 1) showed that these lac-

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*Part 428 in the series "Naturally Occurring Terpene Derivatives". For Part 427 see Bohlmann, F., Singh, P., Joshi, K. C. and Singhi, C. L. (1982) *Phytochemistry* **21**, 1441.