shielding-Effekt der 1α-OH-Gruppe. Bei **2** und **5** handelt es sich um Derivate des Rupicolins A (**6**) [2].

EXPERIMENTELLES

IR: Beckman IR 9, CCl_4; ^{1}H-NMR: Bruker WH 270, δ-Werte, TMS als innerer Standard; MS: Varian MAT 711, 70 eV, Direkteinlaß; optische Rotation: Perkin–Elmer-Polarimeter, $CHCl_3$. 30 g lufttrockene oberirdische Teile (Dr. S. B. Jones, Univ. of Georgia, Dept. of Botany, Herbar Nr. 76-159) wurden grob zerkleinert mit Et_2O–Petrol (1:2) extrahiert, der Extrakt durch SC (Si gel, Akt.-St. II) und anschließend weiter durch DC (Si gel, GF 254) getrennt. Als Laufmittel dienten Petrol–Et_2O-Gemische bzw. EtOAc. Man erhielt 15 mg **1**, 35 mg **2** (Et_2O–Petrol, 5:1) und 4 mg **5** (Et_2O).

3α,4α-Diacetoxy-3,4-dihydro-rupicolin A-8-(2-α-acetoxyethyl acrylat (**2**). Zähes, farbloses Öl, IR: γ-Lacton 1775; OAc 1750, 1230; C=C CO_2R 1720, 1660 cm^{-1}. MS: M^+ *m/e*, —AcOH 444 (2); 444 —RCO_2H 286 (6); 286 —AcOH 226.099 (75) (ber. für $C_{15}H_{14}O_2$ 226.099).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-175 \quad -183 \quad -210 \quad -382^{\circ}} \quad (c = 2.3)$$

10 mg **2** in 1 ml MeOH rührte man 10 min. bei RT mit 25 mg K_2CO_3 in 0.15 ml H_2O. Nach Zugabe von Wasser nahm man CH_2Cl_2 auf und reinigte durch DC (EtOAc). Man erhielt 6 mg **3**, das in 1 ml Aceton mit 5 mg *p*-Toluolsulfonsäure 21 hr bei RT stehengelassen wurde. Nach Zugabe von Wasser nahm man in CH_2Cl_2 auf und reinigte durch DC (EtOAc). Man erhielt 5 mg **4**, farbloses Öl, MS: *m/e*; —$^{\cdot}CH_3$ 435.202 (3%) (ber. für $C_{23}H_{31}O_8$ 435.202)

15-Acetoxy-1β-hydroxy-rupicolin A-(2-α-acetoxyethylacrylat) (**5**). Zähes, farbloses Öl, IR: OH 3620, 3490; γ-Lacton 1775; OAc 1745, 1235; C=C CO_2R 1725, 1650 cm^{-1}. MS: M^+ *m/e* 460 (0.1%) —AcOH 400.152 (7) (ber. für $C_{22}H_{24}O_7$ 400.152); —RCO_2H 242 (37); AcOCH (Me) C (=CH_2) CO^+ 141 (100); 141 —AcOH 81 (71).

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NEW GERMACRANOLIDES FROM *DICOMA ANOMALA**

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Key Word Index—*Dicoma anomala*; *D. argyrophylla*; Mutisieae; Compositae; new germacranolides.

Abstract—The aerial parts of *D. anomala* contain, besides known compounds, two new 7,8-germacranolides. The structures have been elucidated by spectroscopic methods. *D. argyrophylla* lacks lactones.

The South African genus *Dicoma* has been very little investigated chemically. *D. zeyheri* afforded the acetylenic compounds **1** and **2**, also present in species from the tribe Centaureae, and the allenic acid **3** together with the ester **4** [1]. From *D. anomala* Sond. caffeic acid only has been reported [2]. The roots of *D. anomala* Sond. ssp. *cirsioides* (Harv.) Willd. have now afforded the triynediene **5** [3], while the aerial parts contain **6** [3] and lupeol (**7**) together with some sesquiterpene lactones. The most polar is the known lactone albicolide (**8**) [4], while the main constituent with molecular formula $C_{19}H_{24}O_7$ must be a diacetate with an additional free hydroxyl group. The ^{1}H-NMR-data (Table 1) clearly show that the acetate groups are located at C-14 and C-15 and that the remaining O-functions are at C-6 and C-8. To decide

$MeCH{=}CH[C{\equiv}C]_3CH{=}CHCH(Cl)CH_2OR$
trans *trans* **1**·R = Ac **2**·R = H

$Me(CH_2)_{10}CH{=}C{=}CH(CH_2)_3CO_2R$ **3**·R = H **4**·R = Me

$Me[C{\equiv}C]_3[CH{=}CH]_2(CH_2)_3OH$
trans,trans

5

$MeCH{=}CH[C{\equiv}C]_4CH{=}CH_2$

6

	9	**10**	**11**	**12**
R	CH_2OAc	CH_2OAc	CHO	CHO
R′	H	Ac	H	Ac

* Part 134 in the series 'Naturally Occurring Terpene Derivatives'; for part 133 see: Bohlmann, F., Brindöpke, G and Rastogi, R. C. (1978) *Phytochemistry* **17**, 475

Table 1. ^{1}H-NMR-data of **9**, **10** and **12**

H	**9** C_6D_6 77°	**10** C_6D_6 77°	**12** $CDCl_3$
1	*dd(br)* 5.30	*dd(br)* 5.28	*dd* 6.60
2	*m* 1.96	*m* 1.9	*m* 2.65, *m* 2.44
3	*ddd* 2.04	*m* 2.00	*m* 2.40
3′	*m* 1.82	*m* 1.8	
5	*d(br)* 5.13	*d(br)* 5.02	*d(br)* 5.09
6β	*dd* 4.33	*dd* 5.45	*dd* 5.24
7α	*dddd* 2.51	*dddd* 2.69	*m* 2.78
8β	*ddd* 3.45	*ddd* 3.70	*m* 4.09
9α	*dd* 2.36	*dd* 2.35	*m* 2.40
9β	*dd* 2.20	*dd* 2.25	
13	*dd* 6.31	*d(br)* 6.20	*d* 6.34
13′	*dd* 6.10	*d(br)* 5.51	*d* 5 82
14	*d(br)* 4.60	*d(br)* 4.68	*s* 9.53
14′	*d(br)* 4.44	*d(br)* 4.44	
15	*d* 4.55	*d* 4.58	*d* 4.78
15′	*d* 4.08	*d* 4.52	*d* 4.68
OAc	*s* 1.84	*s* 1.84	*s* 2.10
	s 1.73	*s* 1.74	*s* 1.09
		s 1.70	

J(Hz): 1,2 = 7; 1,2′ = 8; 2,3 = 3.5; 3,3′ = 12; 5,6 = 13; 6,7 = 9; 7,8 = 8, 7,13 = 3; 8,9α = 3; 8,9β = 5; 9α,9β = 15; 13,13′ = 1; 14,14′ = 13; 15,15′ = 12.

whether a 6,7- or a 7,8-lactone is present, we acetylated the alcohol. In the NMR spectrum of the triacetate, there was a considerable downfield shift for the proton under what was previously the hydroxyl group. At room temperature the spectra are not completely clear; however in deuteriobenzene at 77° all signals can be interpreted (see Table 1). As this proton is also coupled with the olefinic proton at C-5 the structure must be **9**, with **10** being the triacetate. The 14-desacetoxy compound we have named dicomanolide. In a second lactone, which could only be purified after acetylation, the situation at C-14 must be changed to an aldehyde. The position of this group follows from the observed shift of the signal of 1-H. Therefore the structure is **11**.

The roots of *D. argyrophylla* Oliv. contain **1**–**4** and **15**, while the aerial parts only afford linoleic and linolenic acid together with their methyl esters. Further species must be investigated to see whether the lactones of *D. anomala* constitute an exception or not.

EXPERIMENTAL

IR: Beckmann IR9, CCl_4; ^{1}H-NMR: Bruker WH 270, δ-values, TMS as int. stand., signal interpretation established by double resonance experiments. MS: Varian MAT 711, 70 eV; optical rotation: Perkin–Elmer-polarimeter, $CHCl_3$. The air dried plant material, collected in February 1977 in Natal, was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by column chromatography (Si gel, act. grade II) and further by TLC (Si gel GF 254) using Et_2O–petrol and Et_2O–MeOH as solvents. Known compounds were identified by comparison of the IR and NMR spectra.

Dicoma anomala *Sond. ssp.* cirsioides (*Harv.*) *Willd.* (Voucher 77/53). 160 g roots afforded 1 mg **5** amd 72 g aerial parts 0.1 mg **6**, 40 g **7**, 170 mg **9** (ether) 10 mg **8** and 20 mg **11** (isolated as diacetate)

Dicoma argyrophylla *Oliv.* (Voucher 77/172). 230 g roots afforded 1 mg **13**, 1 mg **1**, 10 mg **4**, 110 mg **3** and 1 mg **2**, while 360 g aerial parts yielded 40 mg linoleic and linolenic acid methyl ester and 200 mg of the corresponding acids (*a* 1:1).

14-Acetoxydicomanolide (**9**). Colourless oil, IR: OH 3620; lactone 1775; OAc 1745, 1220 cm^{-1}. MS: M$^+$ *m/e* 364.152 (0.5%) (calc. for $C_{19}H_{24}O_7$ 364.152); —•OAc 305 (25); —AcOH 304 (3); 304 —$H_2C{=}C{=}O$ 262 (6); 262 —H_2O 244 (26); $MeCO^+$ 43 (100).

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-35.3 \quad -37 \quad -43.7 \quad -89.9°} (c = 2.6)$$

To 30 mg **9** in 2 ml Ac_2O and 0.1 ml Py 10 mg 4-pyrrolidinopyridine [5] was added. After 12 hr the product was purified after usual work up by TLC (Et_2O–petrol, 1:1, ×3). 20 mg **10** were obtained, colourless oil, IR: methylene lactone 1775; OAc 1740, 1230 cm^{-1}. MS: M$^+$ *m/e*; —•OAc 347.149 (5%) (calc. for $C_{19}H_{23}O_6$ 347.149); —AcOH 346 (1); 346 —•OAc 287 (2); Ac^+ 43 (100).

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+15 \quad +15.6 \quad +17.5 \quad +27.4°} (c = 1.06)$$

14-Oxodicomanolide (**11**). Not isolated in pure state, after acetylation as above and TLC (Et_2O, ×4) 20 mg **12** were obtained, colourless oil, IR: C=CCHO 2720, 1695, 1645; lactone 1775; OAc 1750, 1235 cm^{-1}. MS: M$^+$ *m/e* 362 (1%); 2 × AcOH 242.093 (100) (calc. for $C_{15}H_{14}O_3$ 242.094).

$$[\alpha]^{\lambda}_{24°} = \frac{589 \quad 578 \quad 564 \quad 436\,\text{nm}}{+68 \quad +71 \quad +81 \quad +137°} (c = 1.9)$$

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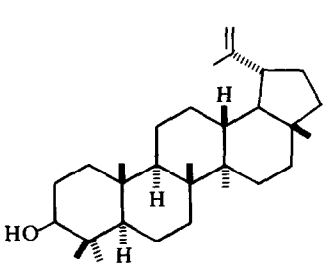

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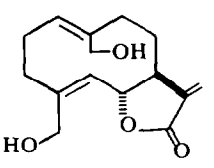

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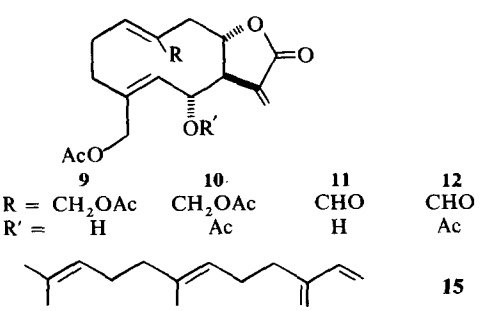

	9	**10**	**11**	**12**
R =	CH_2OAc	CH_2OAc	CHO	CHO
R′ =	H	Ac	H	Ac

15