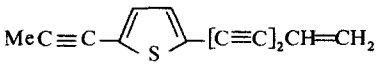
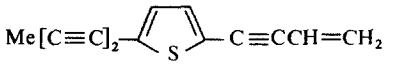
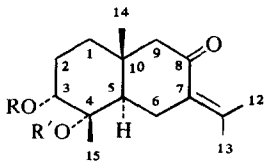


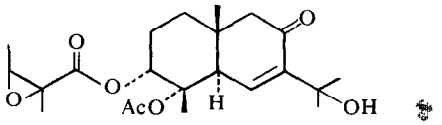
1[3]



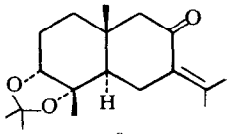
2[3]



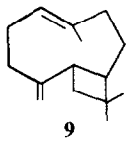
	3 [1]	4 [1]	5 [2]	6
R	Epoxyang	Ang	Epoxyang	H
R′	H	H	Ac	H



7



8



9

90 mg **4**, 140 mg **3**, 180 mg **5**, 14 mg **7** (CH_2Cl_2–MeOH, 9:1) und 18 mg **6** (CH_2Cl_2–MeOH, 9:1).

Cuauhtemon (**6**). Farblose Kristalle aus Ether, Schmp. 143°. IR ($CHCl_3$). OH 3620, 3300; C=C—C=O 1670 cm^{-1}. MS. M^+ *m/e* 252.1725 (100%) (ber. für $C_{15}H_{24}O_3$ 252.1725); $-{}^{\cdot}CH_3$ 237 (12); $-H_2O$ 234 (19); 234 $-{}^{\cdot}CH_3$ 219 (17); 219 $-H_2O$ 201 (40); 219 −CO 191 (23). Die Daten entsprechen denen des durch Verseifung von **5** erhaltenen Diols [2]. 10 mg **6** in 2 ml Aceton versetzte man mit 10 mg *p*-Toluolsulfonsäure. Nach 12 hr Stehen bei Raumtemp. wurde neutralisiert, in Ether aufgenommen und der Rückstand durch DC (Et_2O–Petrol. 1:1) gereinigt. Man erhielt 7 mg **8**, farbloses Öl. IR. C=C—C=O 1690, 1610 cm^{-1}.

4α-Acetoxy-3α-(2-methyl-2,3-epoxy-butyryloxy)-11-hydroxy-6,7-dehydroeudesman-8-on (**7**). Farbloses Öl. IR. OH 3500; CO_2R, OAc 1750; C=C—C=O 1665 cm^{-1}. MS. M^+ *m/e* 408 (0.3%); $-H_2C{=}C{=}O$ 366 (4); −AcOH 348 (2); 348 $-{}^{\cdot}CH_3$ 333 (100).

$$[\alpha]_{24}^{\lambda} \quad \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+104.6 \quad +109.0 \quad +123.0 \quad +213.8^{\circ}} \quad (c = 1.4)$$

Anerkennung—Herrn Dr. R. M. King, Smithsonian Institution, Washington, danken wir für das Pflanzenmaterial, der Deutschen Forschungsgemeinschaft für die Förderung dieser Arbeit.

LITERATUR

1. Bohlmann, F. und Zdero, C. (1976) *Chem. Ber.* **109**, 2653.
2. Nakanishi, K., Crouch, R., Miura, I., Dominguez, X., Zamudio, A. und Villarreal, R. (1974). *J. Am. Chem. Soc.* **96**, 609.
3. Bohlmann, F., Burkhardt, T und Zdero, C. (1973) *Naturally Occurring Acetylenes* Academic Press, London.

Phytochemistry, 1978, Vol. 17, pp. 1190–1191 © Pergamon Press Ltd Printed in England 0031-9422/78/0701-1190$02.00/0

A NEW GLAUCOLIDE DERIVATIVE FROM *ERLANGEA REMIFOLIA**

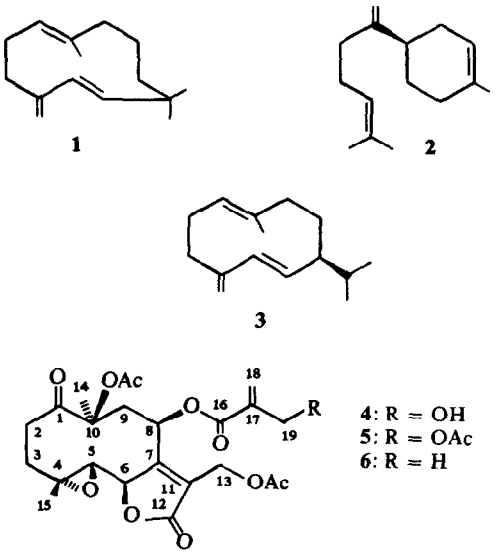
FERDINAND BOHLMANN and HORST CZERSON
Institute of Organic Chemistry, Technical University Berlin, Strasse d. 17. Juni 135, D-1000 Berlin 12, W. Germany

(*Received* 22 *November* 1977)

Key Word Index—*Erlangea remifolia*; Compositae; Vernonieae; glaucolide.

So far only two *Erlangea* species (Tribe Vernonieae, Subtr. Vernoniinae) have been investigated chemically, one containing unusual coumarin and chromone derivatives[1], the other guaianolides [2]. We now have investigated *E. remifolia* Willd. et Pope collected in Botswana. The roots contained the hydrocarbons **1** and **2**, while the aerial parts afforded besides germacrene D (**3**) in relatively high concentration a single lactone, closely related to glaucolide A (**6**) [3]. Though the MS did not show a molecular ion, all the data indicated that we were dealing with a glaucolide with an additional hydroxy group in the ester attached to C-8. The comparison of the 270 MHz NMR spectrum at 80° with that of glaucolide A clearly showed that the new lactone had structure **4**, which was supported by acetylation of the free hydroxyl (see Table 1). All assignments were established by extensive double resonance experiments. The isolation of **4** and the occurrence of guaianolides in *Erlangea inyangana* [2] may indicate a close relationship to the genus *Vernonia*. However, more species have to be investigated.

* Part 140 in the series "Naturally Occurring Terpene Derivatives", for part 139 see: Bohlmann, F. and Zdero, C., *Phytochemistry* (in press).



1 2 3

4: R = OH
5: R = OAc
6: R = H

EXPERIMENTAL

IR: measured in CCl_4; ^1H NMR: at 270 MHz in C_6D_6; MS: recorded at 70 eV; optical rotation: measured in $CHCl_3$. The plant material was obtained from Prof. Dr. S. Jones, Univ. of Georgia (voucher Biegel 5090). The airdried material was extracted at room temp with Et_2O–petrol (1:2) and the resulting extracts first separated by CC (Si gel, act. grade II) and further by TLC (Si gel, GF 254) using Et_2O–petrol mixtures as eluents. 50 g of roots afforded 1 mg **1** and 8 mg **2**, while 30 g of aerial parts yielded 1 mg **3** and 60 mg **4** (EtOAc).

19-Hydroxy glaucolide A (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600; lactone 1770; OAc 1740, 1230; C = C CO_2R 1725, 1635. MS *m/e* (rel. int.): No M^+; 378 (—2 × H_2C = C = O, 0.5); 276.100 (378 − $HOCH_2H$ (=CH_2) CO_2H, 9) (calc. for $C_{15}H_{16}O_5$ 276.100); 258 (276 − H_2O, 8) 234 (276 − H_2C = C = O, 22); 216 (276 − AcOH, 19); 85 ($HOCH_2CCO^+$, 81) (43(H_3CCO^+, 100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-22.9 \quad -23.4 \quad -26.2 \quad -38.0°} (c = 3.08).$$

15 mg **4** in 0.5 ml Ac_2O and 20 mg NaOAc at room temp. for 20 hr afforded 13 mg **5** (TLC, EtOAc), colourless oil, IR

Table 1. ^1H-NMR spectral data of compounds **4**–**6** (270 MHz, C_6D_6, 80°, δ-values, TMS as internal standard)

	4	**5**	**6**
2α-H	1.96 *d(br)*	1.98 *d(br)*	1.97 *d(br)*
2β-H	2.39 *ddd*	2.40 *ddd*	2.41 *ddd*
3α-H	2.17 *ddd(br)*	2.17 *ddd(br)*	2.18 *ddd(br)*
3β-H	1.31 *d(br)*	1.34 *d(br)*	1.32 *d(br)*
5-H	2.24 *d*	2.25 *d*	2.26 *d*
6-H	4.71 *d(br)*	4.71 *d(br)*	4.73 *d(br)*
8α-H	4.97 *dd*	4.95 *dd*	4.92 *d(br)*
9α-H	1.96 *d(br)*	1.98 *d(br)*	1.97 *d(br)*
9β-H	2.51 *dd*	2.54 *dd*	2.52 *dd*
13-H	4.96 *dd*	4.93 *d(br)*	4.93 *d(br)*
13'-H	4.80 *dd*	4.81 *d(br)*	4.77 *d(br)*
14-H	1.47 *d*	1.49 *s*	1.47 *s*
15-H	1.49 *s*	1.49 *s*	1.50 *s*
OAc	1.47 *s*	1.76 *s*	1.73 *s*
	1.65 *s*	1.68 *s*	1.65 *s*
		1.65 *s*	
OCOR	6.08 *dt*	6.18 *s(br)*	5.99 *s(br)*
	5.58 *dt*	5.53 *s(br)*	5.22 *s(br)*
	4.02 *s(br)*	4.71 *d(br)*	1.72 *s(br)*
		4.66 *d(br)*	

J(Hz): 2α, 2β = 15; 2α, 3α ~ 3; 2α, 3β ~ 3; 2β, 3α = 12; 2β, 3β ~ 3: 3α, 3β = 15; 3α, 14 = 1; 5,6 = 9.5; 6,13 = 1; 8α, 9α = 2; 8α, 9β = 7.5; 9α, 9β = 16; 13,13' = 12.5,

$\nu_{max}^{CCl_4}$ cm^{-1}: lactone 1773; OAc 1745, 1255; C = CCO_2R 1725, 1635.

Acknowledgements—We thank Prof. Dr. S. Jones, for the plant material, the 'Deutsche Forschungsgemeinschaft' for financial support and Prof. Dr. T. Mabry for a sample of glaucolide A.

REFERENCES

1. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 1755.
2. Bohlmann, F. and Czerson, H. (1978) *Phytochemistry* **17**, 568.
3. Padolina, W. G. Yoshioka, H., Nakatani, N., Mabry, T., Monti, S. A., Davies, R. E., Cox, P. J., Sim, G. A., Watson, W. H. and Beth Nu, I. (1974) *Tetrahedron* **30**, 1161.