(—CHO), 1730 (C=O) and 720 cm^{-1} (—CH=CH—, *cis*) but no band in the 960–970 cm^{-1} region (—CH=CH—, *trans*) indicating an aliphatic aldehyde with *cis* unsaturation. The MS and IR spectra were consistent with a C_{15} aldehyde containing one double bond. Ozonolysis of the compound yielded heptanal, as shown by GLC retention data, which established the position of the double bond at C-8. Collectively, the spectral and ozonolysis data led to the conclusion that the compound is *cis*-8-pentadecenal.

cis-8-Pentadecenal bears the same structural relationship to the naturally occurring fatty acid, palmitoleic acid (*cis*-8-hexadecenoic acid) as the other long chain (C_{17}–C_{10}) aldehydes isolated from cucumber [3] bear to the common fatty acids palmitic, oleic, linoleic and linolenic acids. That is, this series of aldehydes would result from the sequential removal of carbon from the carboxyl end of the fatty acid) Recently, Galliard and Matthew [5] partially purified and studied an enzyme system from cucumber which catalyzes the removal of carbon atoms from the carboxyl end of fatty acids to form aldehydes (α-oxidation). Using palmitic acid as a substrate they found that a homologous series of *n*-alkanals starting with pentadecanal was formed. In light of their research and structural considerations, it seems probable that this enzyme system gives rise to *cis*-8-pentadecenal and other long chain (C_{17}–C_{10}) aldehydes which we have isolated from volatile concentrates of cucumber fruit. *cis*-8-Pentadecenal has a weak odour which apparently does not contribute significantly to the flavour of the fruit.

EXPERIMENTAL

The concentrate of volatile compounds was prepared by red. press. steam distillation–extraction of macerated cucumber fruit (*Cucumis sativus* L.) in a H_2O recycling apparatus according to the procedure described previously [3]. *cis*-8-Pentadecenal was separated from the volatile concentrate by GLC using a 1.8 m × 6 mm O.D. stainless steel column packed with 20% SE-30 coated on 60–80 mesh, acid washed, silanized Chromosorb W. The column temp. was programmed from 100° to 180° at 1°/min. The peak which eluted from SE-30 immediately before pentadecanal was collected and rechromatographed on a 1.8 m × 6 mm O.D. stainless steel column packed with 10% diethylene glycol succinate (DEGS) coated on 60–80 mesh, acid washed, silanized Chromosorb W. A MS of the purified compound was recorded with an ionizing energy of 70 eV, *m/e* (rel. int.): 41 (100), 55 (98), 43 (63), 69 (57), 67 (47), 57 (42), 56 (37), 81 (35), 54 (33), 82 (32), 83 (32), 70 (31), 95 (21), 96 (20) and 84 (19). An IR spectrum was obtained with the aid of a NaCl microcell and a mirror beam condenser; spectral grade CS_2 was used as the solvent. Ozonolysis was carried out using a micro-ozonizer according to the procedure of Beroza and Bierl [6].

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NEUE GERMACROLIDE AUS *PLATYCARPHA GLOMERATA**

FERDINAND BOHLMANN und CHRISTA ZDERO

Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Deutschland

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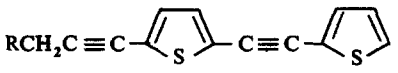
Key Word Index—*Platycarpha glomerata*; Compositae; new germacrolides; thiophenacetylenes.

Abstract—The roots of *Platycaroha glomerata* contain five thiophenes which have been isolated before only from *Berkheya* species. A new diol is also present. The aerial parts contain two new germacrolides, their structures being elucidated by spectroscopic methods. On the basis of the identification of these root constituents, this plant appears to be closely related to other genera in the tribe Arctotideae.

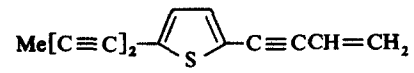
Die botanische Stellung der südafrikanischen Gattung *Platycarpha* ist teilweise unstritten. Wir haben daher *P. glomerata* näher untersucht. Die Wurzeln enthalten die bereits bekannten Thiophenacetylenverbindugen **1**–**5** [1], Isohumulen (**8**| [2] sowie eine weitere Thiophenverbindung, die bisher noch nicht isoliert wurde. Die Konstitution **6** folgt aus den spektroskopischen Daten und dem Ergebnis der Mangandioxid-Oxydation zum Keton **7**:

Die oberirdischen Teile liefern zwei schwer trennbare Lactone, ein Methylenlacton und offenbar die entsprechende Dihydroverbindung. Das ^{1}H-NMR-Spektrum des Methylenlactons in Deuteriobenzol ist weitgehend 1. Ordnung. interpretierbar. Systematische Entkopplungen fürhen zur Konstitution **9**, obwohl einige Signale

*110. Mitt. aus der Serie 'Natürlich vorkommende Terpen-Derivate', 109. Mitt Bohlmann, F. und Lonitz, M. (1977) *Chem. Ber.* im Druck.



1: R = H 2: R = OAc 3: R = H



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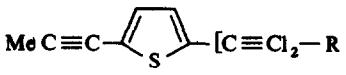
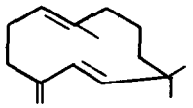
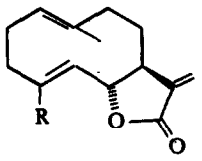


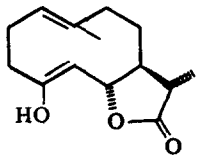
5: R = CH = CH$_2$ 6: R = CH(OH)CH$_2$OH
7: R = COCH$_2$OH



8

überlagert sind (2-H, 3α-H, 7-H und 8-H). Die relative Stellung der okfinischen Methylgruppen und der CH_2OH-Gruppe folgt aus der Lage des Methylsignals, das, wie in ähnlichen Germacroliden, mit *trans,trans*-Konfiguration durch den Shielding-Effekt der 4.5-Doppelbindung zu hohen Feldern verschoben wird. Sie wird bestätigt durch das Ergebnis der Mangandioxid-Oxydation. Das NMR-Spektrum des so erhaltenen Aldehyds **10** zeigt klar, daß die Aldehydgruppe an C-4 steht. Dem zweiten Lacton kommt die Konstitution und Konfiguration **11** zu. Dies folgt eindeutig aus den Ergebnissen von Entkopplungsexperimenten. Die unterschiedliche Lage der Signale für 15-H bestätigt noch einmal die Stellung der CH_2OH—Gruppe bei **9** und **11**.





9: R = CH_2OH 10: R = CHO 11

Tabelle 1. ^{1}H-NMR-Signale von **9–11** (δ-Werte in ppm, TMS als innerer Standard, 270 MHz)

	9 (C_6D_6)	**10** ($CDCl_3$)	**11** (C_6D_6)	+Eu(fod)$_3$
1-H	*dd(br)* 4.54	*d(br)* 5.05	*dd(br)* 4.58	*dd(br)* 4.82
2-H }	*m* 1.92	*m* 2.14	*m* 1.96	
3α-H }		*m* 2.62		
3β-H	*ddd* 2.41	*ddd* 3.07	*ddd* 2.50	*ddd* 3.17
5-H	*d(br)* 4.38	*d* 5.88	*m* 4.42	*d* 4.98
6-H	*dd* 4.25	*dd* 5.07		*dd* 5.13
7-H	*m* 1.92	*m* 2.62	*m* 1.96	*m* 2.16
8-H	*m* 1.43, 1.06	*m* 1.77	*m* 1.25, 1.11	*m* 1.53, 1.35
9α-H	*dd(br)* 1.65	*m* 2.21	*dd(br)* 1.68	*dd(br)* 1.84
9β-H	*dd(br)* 2.04	d(*br*) 2.50	*dd(br)* 2.04	*m* 2.16
11-H	—	—	*dq* 1.81	
13-H	*d* 6.21	*d* 6.37	*d* 0.96	*d* 1.31
13-H	*d* 4.93	*d* 5.63		
14-H	*s(br)* 1.03	*s(br)* 1.16	*s(br)* 1.09	*s(br)* 1.27
15-H	*d(br)* 3.86	*s(br)* 9.98	*d(br)* 4.08	*d(br)* 5.47
	d(br) 3.66		*d(br)* 3.77	*d(br)* 5.03

J (Hz): 1,2 = 8 und 6; 2,3 = 3.5; 3,3 = 11; 5,6 = 10; 6,7 = 9; 7,13 = 3.8 und 3.4; 15,15 = 13; **11**: 7,11 = 11; 11,13 = 7. Die Zuordnungen wurden durch systematische Entkopplungen überprüft.

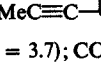
Demnach handelt es sich bei den beiden neuen Germacroliden um 8-Desoxyderivate des Salonitenolids [3], das wie einige seiner Ester in Vertretern der Tribus Cynareae vorkommt [4].

Die aufgefundenen Inhaltsstoffe zeigen, daß die Gattung Platycarpha wahrscheinlich eng verwandt ist mit *Berkheya*. Nur in dieser Gattung sind Verbindungen vom Typ **1–3** isoliert worden. Die Germacrolide **9** und **11** lassen jedoch eine gewisse Verwandtschaft zu der Tribus Cynareae vermuten, jedoch sind Germacrolide bei den Compositen sehr verbreitet. Beziehungen zu der Tribus Mutisieae sind nicht erkennbar, obwohl die anatomischen Merkmale zu dieser Annahme geführt haben [5].

EXPERIMENTELLES

IR: Beckman IR 9 in CCl_4; ^{1}H-NMR: Bruker WH 270, δ-Werte in ppm, TMS als innerer Standard; MS: Varian MAT 711 mit Datenverarbeitung, 70 eV, Direkteinlaß; Optische Rotation: Perkin-Elmer-Polarimeter, $CHCl_3$. Die lufttrockenen, im Februar in Natal gesammelten Pflanzenteile (Herbar Nr. 77/202) extrahierte man mit Ether–Petrol (1:2) und trennte die erhaltenen Extrakte zunächst grob durch SC (Si gel, Akt.-St. II) und weiter durch DC (Si gel GF 254). Als Laufmittel dienten Ether–Petrol-Gemische. 1 kg Wurzeln lieferten 15 mg **8**, 15 mg **1**, 4 mg **4**, 1 mg **5**, 25 mg **2**, 5 mg **3** und 2 mg **6** (Ether–Petrol 1:1). 640 g oberirdische Teile ergaben je 25 mg **9** (Ether–Petrol 2:1) und **11** (Ether–Petrol 2:1).

2-Prop-1-inyl-5-[5.6-dihydroxyhexa-1.3-diinyl]-thiophen (**6**). Nicht völlig rein erhaltenes zähes, farbloses Öl, IR: OH 3600; C≡C 2210 cm^{-1}; UV (Et_2O) λ_{max} 335 nm. 2 mg **6** rührte man 1 hr in 3 ml Et_2O mit 30 mg MnO_2. Nach DC (Ether–Petrol 1:1) erhielt man 1.5 mg **7**, gelbliches Öl, UV (Et_2O) λ_{max} 358 nm.

^{1}H-NMR: MeC≡C–  –C≡C: *s* 2.10 (3), *d* 7.15 (1) (*J* = 3.7), *d* 7.63 (1) (*J* = 3.7); $COCH_2OH$ *s* 5.19 (2). MS: M^+ *m/e* 228.024 (100%) (ber. für $C_{13}H_8O_2$ 228.025).

8-Desoxysalonitenolid (**9**). Farblose Kristalle aus Ether–Petrol, Schmp. 102°, IR: OH 3600; Methylenlacton 1760, 1665 cm^{-1}. MS: M^+ *m/e* 248.141 (3%) (ber. für $C_{15}H_{20}O_3$ 248.141); —H_2O 230 (21); —·CH_2OH 217 (39); $C_3H_7^+$ 43 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{+93 \quad +96 \quad +112 \quad +220 \quad +411°} (c = 0.22).$$

10 mg **9** in 3 ml Et_2O rühre man 1 hr mit 100 mg MnO_2. Nach Umkristallisieren aus Ether–Petrol erhielt man 7 mg **10**, farblose Kristalle, Schmp. 155°C. IR: CHO 1682; Methylenlacton 1775 cm^{-1}. MS: M^+ *m/e* 246.126 (9%) (ber. für $C_{15}H_{18}O_3$ 246.126); —·CH_3 231 (1); —CHO 217 (5); $C_3H_7^+$ 43 (100).

β-11.13-Dihydro-8-desoxysalonitenolid (**11**). Farblose Kristalle aus Ether–Petrol, Schmp. 146°. IR: OH 3600; γ-Lacton 1765 cm^{-1}. MS: M^+ *m/e* 250.157 (1%) (ber. für

250.157); —H_2O 232 (7); —CH_2OH 219 (17); $C_6H_9^+$ 81 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{+84 \quad +87 \quad +103 \quad +211 \quad +426°}$$

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit, Frau Dr. O. Hilliard, Dept. of Botany, University of Natal, für die Bestimmung der Pflanze.

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ERIOFERTOPIN AND 2-*O*-ACETYLERIOFERTOPIN, NEW TUMOR INHIBITORY GERMACRADIENOLIDES FROM *ERIOPHYLLUM CONFERTIFLORUM**

S. MORRIS KUPCHAN✠, JOHN W. ASHMORE and ALBERT T. SNEDEN†
Department of Chemistry, University of Virginia, Charlottesville, VA 22901, U.S.A.

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Key Word Index—*Eriophyllum confertiflorum*; Asteraceae; new germacranolides; eriofertopin and 2-*O*-acetyleriofertopin; confertiphyllide.

During the course of our continuing search for tumor inhibitors, we have isolated two new significantly active tumor inhibitory germacradienolides, eriofertopin, **1a**, and 2-*O*-acetyleriofertopin, **1b**, from *Eriophyllum confertiflorum* Gray (Asteraceae).

Activity guided fractionation (KB) [1] of a 95% EtOH (Soxhlet) extract of the twigs, leaves and flowers showed the activity to be successively concentrated in the $CHCl_3$ phase of a $CHCl_3$–H_2O partition, 10% aq. MeOH phase of a 10% aq. MeOH–Skellysolve B partition, 20% aq. MeOH phase of a 20% aq. MeOH–CCl_4 partiton and finally in the $CHCl_3$ phase of a $CHCl_3$–40% aq. MeOH partition. The final $CHCl_3$ phase was chromatographed on Si gel. Elution with 2% MeOH–$CHCl_3$ yielded 2-*O*-acetyleriofertopin, **1b**, as a colorless, air sensitive foam. Elution with 5% MeOH–$CHCl_3$ afforded eriofertopin (**1a**) as a highly air sensitive colorless foam. The structures of **1a** and **1b** were assigned on the basis of their spectral data (Table 1). The stereochemistry at C-2 and C-8 was determined by comparison

*Tumor Inhibitors, Part 123. For previous paper in this series see; Kupchan, S. M., Komoda, Y., Branfman, A. R., Sneden, A. T., Court, W. A., Thomas, G. J., Hintz, H. P. J., Smith, R. M., Karim, A., Howie, G. A., Verma, A. K., Nagao, Y., Dailey, Jr., R. G., Zimmerly, V. A. and Sumner, Jr., W. C., *J. Org. Chem.* in Press.

†To whom correspondence should be addressed.

Table 1. PMR data for eriofertopin (**1a**), 2-*O*-acetyleriofertopin (**1b**) and eriofertopin diacetate (**1c**) Chemical shifts are given as δ-values, coupling constants (Hz) are quoted in parenthesis

	1a	**1b**	**1c**
H-1	5.06 *m*	5.10 *obsc*	5.09 *obsc*
H-2	4.84 *dt* (5.9, 10)	5.81 *obsc*	5.78 *obsc*
H-5	5.05 *m*	5.10 *obsc*	5.09 *obsc*
H-6	5.05 *m*	5.10 *obsc*	5. 24 *d* (10)
H-7	2.98 *m*	2.95 *m*	2.98 *m*
H-8	5.82 *brd* (5)	5.81 *obsc*	5.78 *obsc*
H-9	3.37 *dd* (5.3, 14.5)	3.18 *dd* (5.6, 14.2)	3.33 *dd* (5.6, 14.6)
	2.16 *obsc*	2.39 *obsc*	2.23 *obsc*
H-13A, B	5.63 *obsc*	5.65 *obsc*	5.62 *obsc*
	6.32 *d* (3.5)	6.33 *d* (3.4)	6.33 *d* (3.4)
H-14	3.74 *d*	3.74 *d*	4.21 *d*
	4.28 *d* (AB *q* 12.7)	4.41 *d* (AB *q* 13.8)	4.82 *d* (AB *q* 12.7)
H-15	1.72 *brs*	1.78 *brs*	1.81 *brs*
H-3′	6.02 *brs*	6.03 *brs*	6.03 *brs*
	5.62 *brs*	5.68 *obsc*	5.62 *obsc*
H-4′	1.94 *brs*	1.94 *brs*	1.91 *brs*
-COMe		2.08	1.96
			2.07