pound is only the second D:A-friedoursane type of triterpenoid to be isolated and the first triterpenoid with a 4(23) double bond.

The structural relationship between cymbopogonol and cymbopogone raises the possibility that cymbopogone is not a natural product but an artefact formed during the isolation of cymbopogonol. However, our attempts to demonstrate such a conversion have proved unsuccessful. Work is now in progress on the direct chemical correlation of cymbopogonol with α-amyrin.

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Phytochemistry, 1976, Vol. 15, pp. 1075–1076. Pergamon Press. Printed in England.

NEUE EUDESMAN-DERIVATE AUS *ISOCOMA WRIGHTII**

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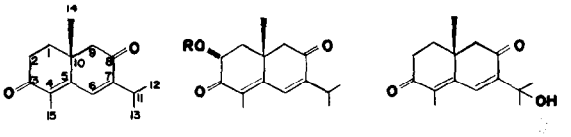
Key Word Index—*Isocoma* species; Compositae; new eudesmane type-sesquiterpenes.

Pflanze und Herkunft. Wurzeln von *Isocoma wrightii*, Prof. B. Turner, Department of Botany, University of Texas at Austin, Herbar 75–11.

Die zur Tribus Astereae gehörende Gattung *Isocoma* ist bisher noch nicht auf ihre Inhaltsstoffe untersucht worden. Der Extrakt der Wurzeln von *I. wrightii* liefert keine Acetylenverbindungen, dafür jedoch drei neue Sesquiterpene, deren Strukturen geklärt werden. Der Hauptinhaltsstoff ist das 8-Oxo-β-cyperon (**1**), während den beiden nicht trennbaren Alkoholen die Konstitutionen **2** und **4** zukommen dürften. Erst nach Acetylierung von **2** ist eine Trennung durch PLC möglich. Die absolute Konfiguration entspricht wahrscheinlich der des ß-Cyperons [1].



(1) (2) R = H (3) R = Ac (4)

In der Gattung *Haplopappus*, die der Gattung *Isocoma* nahe steht, sind derartige Sesquiterpene bisher nicht beobachtet worden. Dort findet man jedoch die für die Tribus Astereae typischen C_{10}-Acetylenderivate [2].

* 68 Mitt. in der Serie "Natürlich vorkommende Terpen-Derivate". 67 Mitt.: Bohlmann, F. und Zdero, C., vorstehend.

Table 1.

^{1}H-NMR-Daten für 1–4 (TMS als innerer Standard, δ-Werte)

	1			2	3	4
	C_6D_6	+Eu(fod)$_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
1α–H 1β–H	*m* 1.30	*ddd* 1.57	*ddd* 1.81 *dd* 2.04	2.0	2.10	*ddd* 1.85
2α–H	*dd* 2.17	*dd* 2.74	} *m* 2.60	—	—	} *m* 2.60
2β–H	*ddd* 2.26	*ddd* 2.85		*dd* 4.39	*dd* 5.58	
6 –H	*s*(*br*) 6.84	7.04	7.17	*s*(*br*) 7.14	*s*(*br*) 7.15	*s*(*br*) 7.43
9α–H	*d* 2.11	2.35	2.43	*d* 2.47	*d* 2.47	*d* 2.44
9β–H	*d*(*br*) 1.94	2.20	2.52	*d*(*br*) 2.55	*d*(*br*) 2.56	*d*(*br*) 2.57
11 –H	*qq*(*br*) 3.07	3.26	3.03	*qq*(*br*) 3.02	*qq*(*br*) 3.04	—
12 –H	*d* 1.05	1.13	1.12	*d* 1.15	*d* 1.16	1.52
13 –H	*d* 1.01	1.09	1.08	*d* 1.11	*d* 1.12	
14 –H	*s* 1.86	2.23	1.96	*s* 1.98	*s* 1.99	*s* 1.98
15 –H	*s* 0.79	0.97	1.23	*s* 1.51	*s* 1.40	*s* 1.29

* 0.1 mol bezogen auf **1**. Kopplungen in Hz: **1**: $J_{1\alpha,1\beta} = 14$; $J_{1\alpha,2\alpha} = J_{1\alpha,2\beta} = 6$; $J_{1\beta,2\beta} = 3$; $J_{2\alpha,2\beta} = J_{9\alpha,9\beta} = 15$; $J_{11,12} = J_{11,13} = 7$; Einstrahlung auf 11–H → 12–H und 13–H s; 6–H scharf. **2** und **3**: $1\alpha,2\alpha = 6.5$; $1\beta,2\alpha = 12$; $J_{9\alpha,9\beta} = 15$; $J_{11,12} = J_{11,13} = 7$. **4**: $J_{1\alpha,1\beta} = 14$; $J_{1\alpha,2\alpha} = 6$; $J_{1\beta,2\beta} = 3$; $J_{9\alpha,9\beta} = 15$.

EXPERIMENTELLES

NMR. Bruker WH 270, TMS als innerer Standard; IR: Beckman IR 9, in CCl_4; MS: Varian MAT 711 mit Datenverarbeitung, 70 eV. 95g zerkleinerte Wurzeln (lufttrocken) extrahierte man mit Et_2O–Petroläther (=PÄ) (1 : 2) und trennte den erhaltenen Extrakt durch mehrfache PLC (Si gel. GF 254, 1mm), Et_2O/PÄ 1 : 3 bzw. 1 : 1. Man erhielt 4 mg **1** und 3 mg **2** und **4**, die 1 hr mit Acetanhydrid auf 70° erwärmt wurden. Nach Eindampfen i. Vak. erhielt man nach PLC (Et_2O–PÄ 1 : 1) *ca* 1mg **3** und 1 mg **4**.

8-Oxo-β-cyperon (**1**). Nach Destillation i. Vak. (Sp. 90–100° 0.1 Torr) erhielt man farblose Kristalle aus Petroläther, Schmp. 85°. IR: 1687, 1670, 1600 cm^{-1} (C=C C=O). UV: λ_{max} = 304 nm (ϵ = 17000). MS: M^+ *m/e* 232.146 (100%) (ber für $C_{15}H_{20}O_2$ 232.146); –Me 217 (31).

$$\begin{array}{cccccc} \lambda & 589 & 578 & 546 & 436\text{nm} & \\ [\alpha]_{24} & +404 & +429 & +525 & +1645 & (c = 0.27) \end{array}$$

2β-Acetoxy-8-oxo-β-cyperon (**3**): Farbloses Öl, IR: 1750, 1230 (OAc); 1680, 1600 (C=C CO)cm^{-1}. MS: M^+ *m/e* 290.152 (12%) (ber. für $C_{17}H_{22}O_4$ 290.152); $-H_2C{=}C{=}O$ 248 (24); –AcOH 230 (9) 248 –Me 233 (11); 230 –CO 202 (100).

11-Hydroxy-8-oxo-β-cyperon (**4**). Farbloses Öl, IR: 3620 (OH); 1670, 1600 (C=C–CO)cm^{-1}. MS: M^+ *m/e* 248.141 (4%) (ber. für $C_{15}H_{20}O_3$ 248.141); –Me 233 (100); 233 $-H_2O$ 205 (57).

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ISOLATION OF FREE *CIS* AND *TRANS*-PHYTOL FROM THE RED ALGA *GRACILARIA ANDERSONIANA*

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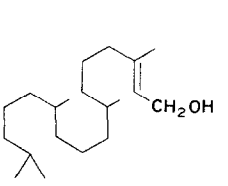
Key Word Index—*Gracilaria andersoniana*; Gracilariaceae; alga; free phytols.

The diterpene alcohol phytol is unusual among terpenes in that it has a definite role in plants as part of the chlorophyll molecule. Perhaps because of this important function in photosynthesis, there apparently never has been a report of free phytol and only one report of an isomer [1] existing in a plant. In fact there is evidence that phytol is not accumulated in etiolated leaves [2] and that phytol is involved in control of chlorophyll biosynthesis [3] in *Phaseolus vulgaris*.

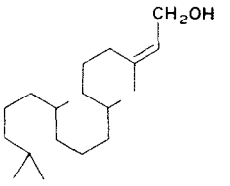
We have been investigating the secondary metabolites of a number of marine algae and note here our results on the red alga *Gracilaria andersoniana*. Hot hexane extraction of the air dried, ground alga gave a green oil which was chromatographed on silica gel. The phytols were eluted in several fractions which were pooled and rechromatographed by high pressure liquid chromatography to yield pure *trans*-phytol **1** and *cis*-phytol **2**. Three other compounds isolated from the extract were cholesterol, oleic and linoleic acids.

Extraction of the plant material remaining after hexane extraction with CH_2Cl_2 in a Soxhlet yielded a dark green oil. Saponification of this extract according to the "normal" phytol isolation procedure [4] yielded only the natural *trans*-phytol. Both **1** and **2** were also found in a cold MeOH–$CHCl_3$ extract of the fresh, wet alga, and a cold hexane extract of the air dried alga.

The identification of **1** and **2** was based on the work of Burrell *et al.* [5], who synthesized both phytols, and comparison of the published [6] NMR spectrum of **1**. The significant spectroscopic differences between **1** and **2** are found in their NMR spectra. The 3-methyl groups in 1 and 2 absorb as singlets at 1.64 and 1.71 compared to the reported values of 1.62 and 1.73 respectively [5]. The 1-methylene groups are found as doublets at δ 4.05 and δ 4.48 in **1** and **2** respectively, while the position of the olefinic proton in both compounds is δ 5.33. The downfield position of the 1-methylene in **2** with respect to **1** can be explained in terms of intramolecular van



(**1**)



(**2**)

der Waals deshielding between the 1-methylene group and the moderately bulky C_{16}-group which are *cis*-substituted at the double bond.

This is the first isolation of *cis*-phytol from a natural source. It is only present in the free form. The phytol isolated from saponification of chlorophyll is the usual *trans* isomer. The presence of phytol in Chlorophyta [7], Phaeophyta [4] and Cyanophyta [4] has been reported. Now a representative of the Rhodophyta can be included in this group.

EXPERIMENTAL

Isolation. Graciliaria andersoniana collected intertidally at Laguna Niguel, California was air dried. The finely ground material (2.64 kg) was Soxhlet extracted with hexane for 48 hr. Removal of the hexane *in vacuo* yielded 5.33 g of a green oil (0.21%). This extract was chromatographed on an open Si gel