und *Trixis* [2, 3]). In einer *Mutisia*-Art [4] kommt allerdings eine phenolische Vorstufe vor, die evt. auf gewisse Beziehungen zwischen den Gattungen *Acourtia* und *Mutisia* hindeuten könnte. Auch das gleichzeitige Vorkommen von **1** und **2** ist bei einigen Vertretern der Subtribus Mutisiinae zu beobachten [2–4]. Es fehlen bei *Acourtia* die sonst für die Subtribus Nassauviinae charakteristischen Isocedren-Derivate [3]. Zweifellos müssen weitere Arten untersucht werden, bevor klare Schlußfolgerungen gezogen werden können.

EXPERIMENTELLES

IR: CCl_4; MS: 70 eV, Direkteinlaß. Die lufttrocken zerkleinerten Pflanzenteile (Herbar Nr. RMK 7723, bei Nogales, Arizona gesammelt) 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).

10 g Wurzeln ergaben *ca* je 1 mg **1** und **2**, 6 mg **3** (Ether–Petrol, 1:3) und 50 mg **4** und **5** (Ether–Petrol, 1:1), die jedoch noch mit geringen Mengen aus Chinonen verunreinigt waren. Mit Boranat in MeOH wird die erhaltene weinrote Lösung entfärbt. Das ^{1}H-NMR-Spektrum des Rohgemisches zeigte, daß die Hydrochinone **4** und **5** zu etwa gleichen Teilen vorlagen (vor und nach der Reduktion). Zur Trennung des Gemisches haben wir bei RT das Gemisch in $CHCl_3$ mit 0.1 ml Ac_2O und 30 mg 4-Pyrrolidinopyridin 12 hr stehen lassen. Nach zweifacher DC (Ether–Petrol, 1:3) erhält man *ca* 20 mg **6** und 10 mg **7**.

Perezonangelicat (**3**). Gelb gefärbtes Öl, IR cm^{-1}: PhOCOC= C— 1745; Chinon 1675, 1670, 1625. MS: M$^+$ *m/e* 330.188 (1%) (ber. für $C_{20}H_{26}O_4$ 330.188); $-O{=}C{=}C(Me)CH{=}CH_2$ 248 (8); $C_4H_7CO^+$ 83 (100).

2-Hydroxy-dihydroperezon-2-O- *bzw.* 5-O-*angelicat* (**4** *und* **5**). Nicht getrenntes, öliges Gemisch, das mit Ac_2O acetyliert wurde (s.o.). Die erhaltenen Triacetate wurden durch DC (s.o.) getrennt. **6**: Farbloses Öl, IR cm^{-1}: PhOAc 1785, 1775; PhOAng 1750, 1645. MS: M$^+$ *m/e* 474.225 (1%) (ber. für $C_{26}H_{34}O_8$ 474.225); $-2 \times$ Keten 309 (7); 390 – Keten 348 (5); 390 $-O{=}C{=}C(Me)CH{=}CH_2$ 308 (14); 308 – Keten 266 (15); $C_4H_7CO^+$ 83 (100); $MeCO^+$ 43 (41). **7**: Farbloses Öl, IR cm^{-1}: PhOAc 1775; PhOAng 1750, 1645. MS: M$^+$ *m/e* 474.225 (1%) (ber. für $C_{26}H_{34}O_8$ 474.225); $-2 \times$ Keten 390 (6); 390 – Keten 348 (5); 390 $-O{=}C{=}C(Me)CH{=}CH_2$ 308 (12); 308 – Keten 266 (13); $C_4H_7CO^+$ 83 (100); $MeCO^+$ 43 (35).

Danksagung— Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit.

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Phytochemistry, 1979, Vol. 18, pp. 1895–1897. © Pergamon Press Ltd. Printed in England. 0031-9422/79/1101-1895 $02.00/0

DICTYOXIDE, A NEW DITERPENE FROM THE BROWN ALGA *DILOPHUS LIGULATUS**

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(*Received* 6 *April* 1979)

Key Word Index—*Dilophus ligulatus*; Dictyotaceae; diterpenes; dictyoxide.

INTRODUCTION

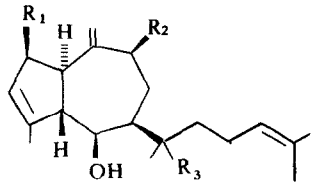
Following the isolation of pachydictyol A (**1**) from the Pacific brown alga *Pachydictyon coriaceum* [1], a number of perhydroazulene diterpenes have been obtained from seaweeds of the family Dictyotaceae. The four dictyols A–D (**2**–**5**) have been isolated from the Mediterranean alga *Dictyota dichotoma* var. *implexa*, and dictyol E (**6**) from the allied species *Dilophus ligulatus* (Kütz.) Feldm. (syn. *spiralis* (Montagne) Hamel) [2, 3]. Dictyol B acetate (**7**) and dictyotadiol (**8**) have been found to occur in a sample of *D. dichotoma* from the British coasts [4] and pachydictyol A epoxide (**9**) in *Dictyota flabellata* from the Gulf of California [5].

We wish to describe here the isolation from *D. ligulatus* of a new diterpene having the perhydroazulene skeleton.

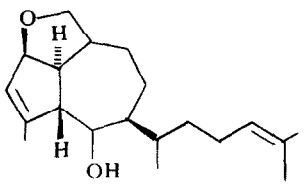
RESULTS AND DISCUSSION

The chloroform extract of *Dilophus ligulatus* was repeatedly column chromatographed on Si gel and selected fractions further purified by PLC to give dictyoxide (**10**) as an oil, $[\alpha]_D$ + 10.1°, molecular formula $C_{20}H_{32}O$ (high resolution MS). Since its IR spectrum discounted the presence of hydroxyl or carbonyl groups, the single oxygen atom in the molecule was assigned to an ether function, which was substantiated by the presence in the ^{13}C NMR spectrum of two signals for oxygen-bearing carbons at 76.62 (*d*) and 74.22 (*s*) ppm. The spectrum also contained

*Dedicated to Professor L. Panizzi on the occasion of his 70th birthday.



1 $R_1 = R_2 = R_3 = H$
3 $R_1 = R_3 = H$; $R_2 = OH$
5 $R_1 = OH$; $R_2 = R_3 = H$
6 $R_1 = R_2 = H$; $R_3 = OH$
7 $R_1 = R_3 = H$; $R_2 = OAc$



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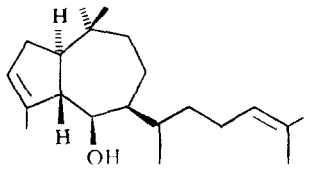

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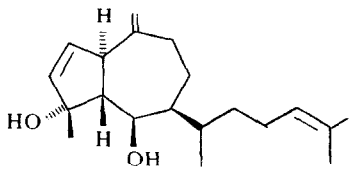

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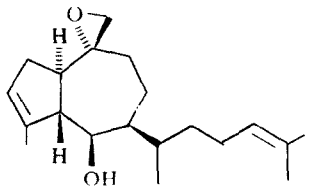

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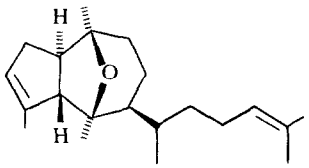

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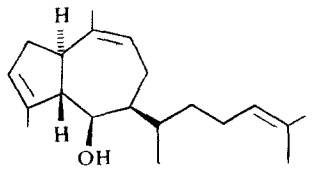

11

resonances for 14 sp^3 carbons at 15.99 (*q*), 16.46 (*q*), 17.66 (*q*), 20.44 (*t*), 22.29 (*q*), 25. 61 (*q*), 26. 32 (*t*), 29.81 (*t*), 34.49 (*t*), 37.37 (*d*), 38.36 (*d*), 38.80 (*t*), 61.31 (*d*), 63.11 (*d*), and 4 sp^2 carbons at 124.90 (*d*), 130.68 (*d*), 140.21 (*s*), 150.07 (*s*). Therefore, three out of the five degrees of unsaturation implied by the molecular formula of **10** were due to rings and two to double bonds.

Selenium aromatization of **10** afforded 1,4-dimethyl-7-(dimethylhex-5-enyl)-azulene, thus revealing the nature of the carbon skeleton.

Extensive double resonance experiments led to the following assignments of protons consistent with structure **10**: δ 5.50 (1H, *bs*, H-3), 5.08 (1H, *t*, $J = 6$ Hz, H-14), 3.98 (1H, *d*, $J = 2$ Hz, H-6), 2.62 (1H, *dd*, $J = 12$ and 2 Hz, H-5), 2.37 (1H, *dd*, $J = 12$ and 5.4 Hz, H-1), 1.74 (3H, *s*, Me-4), 1.64 (3H, *s*, *cis*-Me-15), 1.57 (3H, *s*, *trans*-Me-15), 1.22 (3H, *s*, Me-10), 0.87 (3H, *d*, $J = 6$ Hz, Me-11).

Unequivocal proof of the structure and stereochemistry of **10** was provided by acid treatment of dictyoxide which gave a mixture of pachydictyol A and the alcohol **11** (obtained previously [2] from dictyol B by reduction with sodium in liquid ammonia), both identified by comparison of their physical properties with those of authentic specimens. This result defined the stereochemistry of all the chiral centres apart from C-10, which must have the *S*-configuration since the closure of the ether bridge requires a *cis* relationship between H-6 and Me-10.

EXPERIMENTAL

General procedures. ^1H and ^{13}C NMR spectra were run at 270 and 67 MHz, respectively, with TMS as internal standard.

Plant material. Dilophus ligulatus was collected at Aci Castello, Sicily, Italy, during May 1978.

Isolation of dictyoxide (**10**). The freeze-dried and ground alga (200 g) was extracted 3× with $CHCl_3$ at room temp. Evapn of the $CHCl_3$ left a residue which was subjected to chromatography on a Si gel column (4.5 × 120 cm), using increasing concns of Et_2O in petrol as the eluent. All fractions containing **10**, which emerged from the column immediately before pachydictyol A, were combined and rechromatographed on a column (1.5 × 100 cm) of Si gel using the same solvent as above. PLC on Si gel (C_6H_6) gave pure dictoyoxide (**10**) as a viscous oil (0.04%), $[\alpha]_D$ +10.1° (c1 in $CHCl_3$). High resolution MS: $C_{20}H_{32}O$, M^+ *m/e* observed 288.2449, required 288.2453.

Selenium aromatization of **10**. A mixture of dictyoxide (30 mg) and selenium (60 mg) was heated at 280° for 20 min. After cooling, the reaction mixture was digested with petrol and the product extracted with 60% H_2SO_4. The acidic layer was diluted with H_2O and re-extracted with petrol. The organic phase, after washing with H_2O, was evapd to dryness to give 1,4-dimethyl-7-(1,5-dimethylhex-5-enyl)-azulene, identified by comparison of its physical properties (MS, UV, IR, NMR) with those of an authentic sample [6].

Acid treatment of **10**. A soln of dictyoxide (25 mg) and HCl (5 mg) in $CHCl_3$ (1 ml) was kept at room temp. (24 hr). The soln was evapd and the residue fractionated into constituents by

TLC ($AgNO_3$–Si gel; C_6H_6–Et_2O 7:3 as the eluent; band positions located by strip-spraying with 1% soln of $Ce(SO_4)_2$ in 2 N H_2SO_4 followed by heating) to give pachydictyol A (R_f 0.20; 5 mg) and the alcohol **11** (R_f 0.25; 8 mg), identified by comparison of their physical properties ($[\alpha]_D$, MS, NMR) with those of authentic specimens.

Acknowledgements—This work is a result of research sponsored by the Consiglio Nazionale delle Ricerche in the programme of the 'Progetto finalizzato per l'Oceanografia e i Fondi Marini.

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Phytochemistry, 1979, Vol. 18, pp. 1897–1898. © Pergamon Press Ltd. Printed in England. 0031-9422/79/1101–1897 $02.00/0

DIBENZOYLMETHANES AND FLAVONES OF *MALUS*

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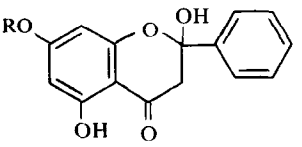
(*Revised received* 24 *April* 1979)

Key Word Index—*Malus*; Rosaceae; dibenzoylmethanes; flavones; dihydrochalcones; 2,4,6-trihydroxydibenzoylmethane 2-glucoside; toringin; chrysin biosynthesis.

The occurrence of an unusual glucoside in the leaf of a *Malus* cultivar (*Malus H*) has already been reported [1], together with details of its conversion to chrysin 7-glucoside both in the leaf and in extracts. The compound **1a** is known normally as a 2-hydroxyflavanone [2] but from its chemical reactions it can be regarded alternatively as a dibenzoylmethane (**2a**) or a β-hydroxychalcone (**3a**), when its 4′-glucosylation pattern then corresponds to that of the dihydrochalcone glucoside sieboldin (which also occurs in the leaf of *Malus H*) and not to the 2′-pattern of the common *Malus* dihydrochalcone phloridzin.

In an examination of the phenolics of *Malus* barks by PC, a substance was found in *M. fusca* bark with similar R_fs to that found in *Malus H* leaf. Sufficient of the new substance for examination was separated by chromatography on thick paper sheets. Acid hydrolysis gave only glucose and an aglucone indistinguishable in chromatographic and UV spectral properties from chrysin; this result is the same as was found on acid hydrolysis of the glucoside from *Malus H*, suggesting that the two substances might be isomeric glucosides. After storage a solution of the new compound gave a second slow-moving compound on PC in 2% acetic acid, which showed the distinctive fluorescence of the flavone glucoside toringin, chrysin 5-glucoside, already known as a bark constituent of *M. tschonoskii* [3]. Comparison of chromatographic and UV spectral properties with authentic toringin confirmed its identity.



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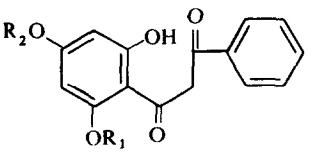
1b R = H



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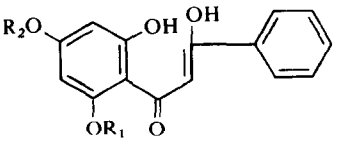
2b R_1 = Glc; R_2 = H



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