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DITERPENOIDS OF THE BROWN SEAWEED *GLOSSOPHORA GALAPAGENSIS*

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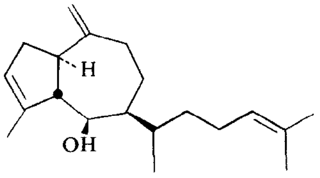
Key Word Index—*Glossophora galapagensis*; Dictyotaceae; Phaeophyta; marine diterpenoids; dolabelladienes.

It seems reasonably clear that the herbivorous sea hares (marine molluscs of the family Anaspidea) exercise specific feeding preferences for marine algae which produce large amounts of secondary metabolites. It further appears that the anaspideans concentrate the algal metabolites in their digestive glands, and that these noxious compounds provide for the sea hare a significant selective advantage against predation [1]. The algal sources of most digestive gland components have been encountered and consist of red seaweeds of the genera *Laurencia* [2] and *Plocamium* [2], brown seaweeds of the genus *Dictyota* [3] and blue-green algae of the genus *Lyngbya* [4]. A recent study of the digestive gland components of the Pacific sea hare *Dolabella californica* has resulted in the elucidation of a series of bicyclic diterpenoids of a unique structure type, the dolabelladienes [5, 6], the source of which remains to be described. We wish to report the isolation of several dolabelladienes from the brown alga *Glossophora galapagensis* and to suggest that *D. californica* feeds upon this or related algae of the family Dictyotaceae. *G. galapagensis* (Dictyotaceae) is closely related to the brown algae *Dictyota* which is known to be grazed upon by the sea hare *Aplysia depilans* [3].

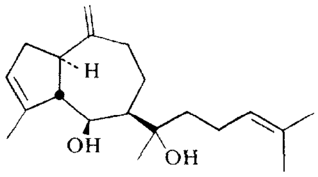
Glossophora galapagensis Taylor (Phaeophyta, Dictyotaceae) was collected near Isla Española (Galapagos Islands, Ecuador) in June 1977. Column chromatography followed by high pressure liquid chromatography resulted in the isolation of the five diterpenoids **1**–**5**. Pachydictyol A(**1**) had been isolated earlier from the brown alga *Pachydictyon coriaceum* [7], and dictyol E (**2**) was earlier described as a component of *Dictyota dichotoma* [8]. Both compounds were found to be identical to authentic material from other sources. The three dolabelladienes isolated, 10-acetoxy-18-hydroxy-2,7-dolabelladiene (**3**), 10,18-dihydroxy-2,7-dolabelladiene (**4**), and 18-hydroxy-2,7-dolabelladiene (**5**), were found to be identical with authentic samples of **3**–**5** isolated from *D. californica*.

EXPERIMENTAL

Glossophora galapagensis was collected in shallow water near Isla Española in June, 1977, and immediately preserved in MeOH. The wet plants were subsequently homogenized in $CHCl_3$/MeOH (2/1) and the extract was concd *in vacuo* to yield a green gum. The concentrate was chromatographed on Florisil using increasingly more polar solvents (isooctane–C_6H_6–Et_2O) to yield 25 fractions. Investigation of these fractions revealed



1



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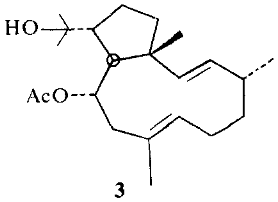

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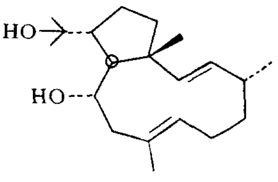

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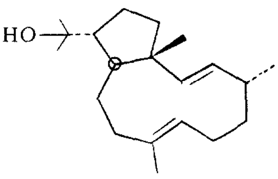

5

several pure compounds and several mixtures which were subsequently separated by HPLC on μ-porasil.

Pachydictyol A [**1**, 2.4% extract, $[\alpha]_D^{20} + 103°$ (c 1.22, hexanes)] was eluted with C_6H_6 as a mobile oil which showed spectral features identical with those from an authentic sample [7].

Dictyol E [**2**, 3.0% extract, $[\alpha]_D^{20} + 27°$ (c 1.35, $CHCl_3$)] was eluted with 10% Et_2O in C_6H_6 as a viscous oil which showed spectral properties identical to those reported [8].

10-*Acetoxy*-18-*hydroxy*-2,7-*dolabelladiene* [**3**, 1.3% extract, $[\alpha]_D^{20} - 98.6°$ (c 0.78, $CHCl_3$)] was eluted, as a mixture, with 10% Et_2O in C_6H_6. HPLC separation (μ-porasil, 30% Et_2O in hexanes) afforded **3** as a viscous oil which failed to crystallize (lit. [5] mp 78°). The spectral properties of **3** were identical to those obtained from an authentic sample [5].

10,18-*Dihydroxy*-2,7-*dollabelladiene* [**4**, 1.5% extract, $[\alpha]_D^{20} - 73.1°$ (c 1.02, $CHCl_3$)] was eluted, as a mixture, with 20% Et_2O in C_6H_6. Subsequent HPLC isolation (μ-porasil, 30% Et_2O in hexanes) yielded the diol which crystallized from Et_2O, mp 152° (lit. [6] 152–3°). Diol **4** showed spectral properties identical to those obtained from an authentic sample [6].

18-*Hydroxy*-2,7-*dolabelladiene* [**5**, 1.4% extract, $[\alpha]_D^{20} - 73.1°$ (c 1.0, $CHCl_3$)] was eluted as a pure compound (an oil) upon elution with 5% Et_2O in C_6H_6. The alcohol showed spectral characteristics identical to those obtained from an authentic [6].

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ÜBER DIMERE TERPENKETONE AUS *TAGETES GRACILIS*[*]

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Key Word Index—*Tagetes* spp.; *Dyssodia decipiens*; *Hymenatherum tenuifolium*; *Thymophylla tenuiloba*; *Porophyllum lanceolatum*; *P. ruderale*; Compositae; Tageteae; new dimeric terpene ketones.

Über die Chemie der Tribus Tageteae, ehemals Subtribus in der Tribus Helenieae, ist noch nicht sehr viel bekannt [1]. Wir haben daher einige weitere Vertreter auf ihre Inhaltsstoffe untersucht.

Tagetes terniflora HBK enthält, wie alle bisher untersuchten *Tagetes*-Arten [2] **1**, **4**, **6** and **7** sowie die Terpenketone **12** und **14**.

Auch *T. zypaquirensis* H. et B. enthält **4**, **12** und **14**. Eine erneute Untersuchung der oberirdischen Teile von *T. patula* L. liefert **1**, **4**, **6**, **7** und **9**–**19**.

Die Wurzeln von *T. gracilis* DC. enthalten ebenfalls **1**, **4**, **6** und **7**, während die oberirdischen Teile neben **1**, **2**, **4** und **7** Germacren D (**20**) sowie die Ketone **12** und **14** enthalten. Daneben isoliert man zwei Diketone, bei denen es sich aufgrund der spektroskopischen Daten um die Verbindugen **21** und **22** handelt (s. Tabelle 1).

Tabelle 1. ^{1}H-NMR-Daten von **21** und **22**

	21	**22**
1-H	*d* 1.88	*d* 1.85
3-H	*qq* 6.01	*qq* 6.03
5-H	*dq* 5.90	*dq* 5.91
7-H	*dd(br)* 2.45	*dd(br)* 2.44
8-H	*m* 2.0	*m* 2.0
9-H	*m* 2.2	*m* 2.2
10-H	*d(br)* 5.67	*d(br)* 5.66
12-H	*d(br)* 3.33	*d(br)* 3.32
14-H	*qq* 6.05	*d* 2.24
15-H	—	*m* 2.1
16-H	*d* 1.83	*d* 0.89
17-H	*d* 2.01	
18-H	*s(br)* 1.63	*s(br)* 1.62
19-H	*d* 2.23	*d* 2.21
20-H	*d* 2.14	*d* 2.04

J(Hz): 1,3 = 3,20 = 5,19 = 14,16 = 14,17 = 1; 7,12 = 6; 7,8′ = 12; 7,8 = 1.5; 9,10 = 3.5.

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