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A dolabellane diterpene from the Brazilian brown alga *Dictyota pfaffii*☆

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1. Subject and source

In order to continue our chemosystematic and ecological studies of the genus *Dictyota* Lamouroux, Dictyotales, Phaeophyta (Teixeira et al., 2001, and references cited therein), we examined *Dictyota pfaffii* Schnetter collected during June 2000 at Atol das Rocas reef, Rio Grande do Norte State (latitude 03°51′03″ S, longitude 33°40′29″ W), Brazil. Atol das Rocas reef is a marine biological reserve in the northeast Brazil, and is the only atoll in the South Atlantic. The present study is the first reference for *D. pfaffii* from the Brazilian coast. Voucher specimens (HRJ 9117) are deposited in the Herbarium Bradeanum of the Universidade do Estado do Rio de Janeiro.

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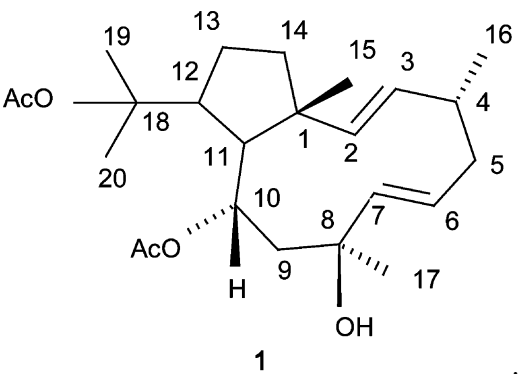
2. Previous study

Dolabellane diterpenes are the main secondary metabolites of *Dictyota bartayresiana* (e.g. Trimurtulu et al., 1992), *D. dichotoma* (e.g. Bheemasankara Rao et al., 1986), *D. pardalis* f. *pseudohamata* (e.g. König et al., 1994), all collected from the Indo-west tropical region, and *D. dichotoma* (e.g. Durán et al., 1997) and *Dilophus fasciola* (e.g. Tringali et al., 1986), both from the warm temperate Mediterranean–Atlantic region. In addition, many dolabellane diterpenes have been isolated from the digestive glands of opistobranch mollusks, as the result of dietary intake and further metabolism (Ireland and Faulkner, 1977).

3. Present study

Air-dried specimens (61 g) were successively extracted with CH_2Cl_2/MeOH (7:3) and MeOH. Evaporation of the crude extract yielded 4.1 g of brownish residue (about 6.7%—dry mass) of which 2 g was subjected to purification by silica gel-column chromatography (elution with *n*-hexane, CH_2Cl_2, EtOAc, and MeOH). The fractions eluted with CH_2Cl_2 and CH_2Cl_2/EtOAc (9:1) contained crude **1** (212 and 500 mg, respectively), a crystalline solid, which after re-crystallization with *n*-hexane, gave pure **1** (550 mg). The identification of **1** as 10,18-diacetoxy-8-hydroxy-2,6-dolabelladiene (dolabellane-1) was based on comparison of physical and spectroscopic data with literature data (Ireland and Faulkner, 1977).



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4. Chemotaxonomic significance

Dictyota pfaffii Schnetter are small and iridescent brown algae, with creeping thalli, forming flat cushions or turfs; rhizoids arise from the base and from the lower thallus surface. Thalli dichotomously to alternately branched, up to 3 cm high; bluish green iridescent under water (brown when dried); sinuses with an angle of about 60–120°; internodia 3–5 mm long and 2–4 mm broad (Littler and Littler, 2000). As

discussed by other phycologists (e.g. Wynne, 1998), *D. pfaffii* is conspecific with *D. humifusa* Hörnig, Schnetter et Coppejans; they are so similar, that there is no reason to consider these two taxa as distinct species. *D. pfaffii* (=*D. humifusa*) is known from the northern tropical to subtropical Atlantic region and from the East African coast (Wynne, 1998; Littler and Littler, 2000). *D. pfaffii* is recorded for the first time from the Brazilian coast. In addition, the presence of this dolabellane diterpene (**1**) is recorded for the first time, both in seaweed and in the Tropical Atlantic American region and suggest that this species is related to the collections of *D. bartayresiana*, *D. dichotoma*, *D. pardalis* f. *pseudohamata* (from Indo-west tropical region) and *D. dichotoma* and *Dilophus fasciola* (from warm temperate Mediterranean–Atlantic region).

5. Ecological significance

Previous assays demonstrated that *D. pfaffii* is chemically defended against sea-urchins (*Lytechinus variegatus*), and fishes (several species in the field) (Barbosa et al., 2003). This defensive property is due to compound **1**, found as the major secondary metabolite in this brown alga. This is the first time that a dolabellane diterpene from *Dictyota* species has been reported as an active chemical defense against herbivores.

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