Photochemical Conversion of Xenicane into the Crenulatane Skeleton with Diterpenoids of the Brown Seaweed *Dictyota* sp. from the Coasts of Senegal

Graziano Guella and Francesco Pietra

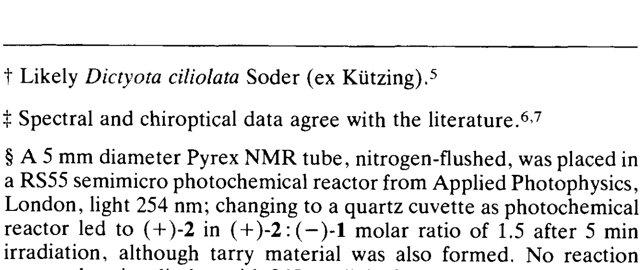
Istituto di Chimica, Università degli Studi di Trento, 38050 Povo-Trento, Italy

UV irradiation of 4-hydroxydictyolactone (−)-**1** in $CDCl_3$ under N_2 leads cleanly to 4-hydroxycrenulide (+)-**2**, reproducing what probably occurs under solar irradiation of the seaweed *Dictyota* sp. at low tide along the coasts of Senegal.

Photochemical conversion of marine secondary metabolites *in vivo* has been suggested in a few instances from laboratory irradiation experiments on isolated metabolites. Such instances comprise *E*/*Z* C=C isomerizations of indole alkaloids of scleractinian corals or sponges,[1] isomerization of cyclohexadiene into bicyclo[3.1.0]hexenepyrones of sacoglossans molluscs,[2] synfacial 1,3-acyl migration converting cembrene into cubitene diterpenes of gorgonians[3] and di-π-methane rearrangement converting briarane into erythrane diterpenes of gorgonians.[4] We report here on the novel photoisomerization of xenicane into the crenulatane skeleton, exemplified with compounds of a seaweed from Senegal.

A methanolic extract of the brown seaweed *Dictyota* sp.,† collected in September 1991 at low tide at the Pointe de Senti à Joal, south of Dakar, was evaporated and the residue extracted with hexane and subjected to extensive chromatography to give 4-hydroxydictyolactone (−)-**1**[6] and 4-hydroxycrenulide (+)-**2**,[7]‡ both already known as semisynthetic products. Irradiation of (−)-**1** *ca.* 0.01 mol dm^{-3} in either $CDCl_3$ or CD_3OD,§ led to (+)-**2** in (+)-**2**: (−)-**1** molar ratios of 0.2 or 1 after 1.5 or 7 h, respectively, the two compounds accounting for 100% of the materials, see Scheme 1.¶

By viewing the photoisomerization of (−)-**1** into (+)-**2** as a homo [1,5] hydrogen shift concertedly with 7,9 bond formation, antarafacial hydrogen shift would have been expected,[9] contrary to what has been observed. This suggests that either a photoinduced C(9)=C(1) to C(1)=C(2) shift followed by a [1,3] hydrogen shift, or a free radical route is followed. In either case, this may be viewed as an *in vivo* alternative to enzymatic, proton-catalysed isomerization of xenicanes[10] for the biogenesis of crenulatanes which co-occur with xenicanes in seaweeds of the order *Dictyotales* and opisthobranch molluscs that feed on them.[7,10,11] This is conceivable for a seaweed at low tide under the intense solar radiation of the tropics.||



(−)-**1** (+)-**2**

Scheme 1

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† Likely *Dictyota ciliolata* Soder (ex Kützing).[5]

‡ Spectral and chiroptical data agree with the literature.[6,7]

§ A 5 mm diameter Pyrex NMR tube, nitrogen-flushed, was placed in a RS55 semimicro photochemical reactor from Applied Photophysics, London, light 254 nm; changing to a quartz cuvette as photochemical reactor led to (+)-**2** in (+)-**2**:(−)-**1** molar ratio of 1.5 after 5 min irradiation, although tarry material was also formed. No reaction occurred on irradiation with 365 nm light for 2 h.

¶ In a similar UV irradiation of the (*Z*)-6,7-isomer of (−)-**1** only tars were observed. Also xeniolides failed to afford cyclopropane products on UV irradiation: coraxeniolide-B[8] merely gave *E*/*Z* photoisomerization at C(4)=C(12) and C(13)=C(14). Dictyolactone, while photoreactive, failed to give the corresponding crenulide. This shows that the photochemical conversion of xenicanes into crenulides is regulated by a fine balance of factors, perhaps involving also conformational dependence on steric effects. It may be relevant that the corresponding crenulide of dictyolactone has never been isolated.

|| Whether a similar—or sensitized and preceded by double bond shifts in the case of the absence of a suitable chromophore—photochemical route may account for the production of other crenulides,[7,11a] as well as isocrenulides[11b] and crenulacetals[11c] isolated from seaweeds or opisthobranch molluscs is difficult to judge since scarce details have been reported about collections of these species.

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